ELSEVIER
PERGAMON

Comprehensive Coordination Chemistry II

FROM BIOLOGY TO NANOTECHNOLOGY

EDITORS-IN-CHIEF
Jon A McCleverty
Thomas J Meyer

Edited by
E.C. Constable
J.R. Dilworth

Volume 5
Transition Metal Groups 7 and 8

Introduction to Volume 5

This volume presents a survey of significant developments in the chemistry of Groups 7 and 8 of the transition metals since the publication of *Comprehensive Coordination Chemistry* (CCC) in 1987. The material for each element is organized by oxidation state of the metal and also by the nature of the ligands involved, with additional sections covering special features of the coordination chemistry and applications of the complexes.

Manganese, Technetium, and Rhenium

The coverage for manganese and rhenium is from 1982, whereas for technetium the earlier literature is included, as technetium did not feature in CCC (1987). The biological role of manganese has been a significant driving force for recent studies of its coordination chemistry and this area is treated in some detail, as are the uses of manganese complexes for selective oxidations. For technetium much of the literature is closely linked to the applications of 99m–Tc complexes in diagnostic nuclear medicine and the development of first- and second-generation agents is placed in the context of the reported coordination chemistry. The potential role of radioactive rhenium complexes for therapy is a comparatively recent theme, and is again placed against the backdrop of a systematic account of the fundamental coordination chemistry of the element.

Iron, Ruthenium, and Osmium

The coverage for iron commences in 1984–1985 and aims to provide a broad-based introduction to important advances in the chemistry of this element over the past 20 years. A comprehensive coverage of the chemistry of iron over this period would be impossible and the authors have done an admirable job in selecting the most important papers in the primary literature and have made extensive reference to the review literature to give as broad an overview as possible. Similar constraints apply to the coverage of ruthenium and osmium in both high and low oxidation states. However, the coverage in these two chapters gives an excellent overview of the primary literature since 1982 and leads the reader naturally to the important review literature for these elements.

It would be invidious to pick any particular area of activity in the chemistry of these elements for particular attention, but very significant advances have been made in many aspects of the coordination chemistry of iron, ruthenium, and osmium. Our understanding of the roles which iron can play in biological systems and the subtle chemical control over iron metabolism has increased enormously since 1987 and they represent beautiful aspects of applied coordination chemistry. Much iron coordination chemistry is designed to further understand biomimetic aspects. In low-oxidation-state ruthenium chemistry, renewed interest in photovoltaic cells is generating a resurgence in $\{Ru(bpy)_3\}$ chemistry. In high-oxidation-state ruthenium and osmium chemistry, the utilization of complexes as increasingly selective catalytic or stoichiometric oxidizing agents shows no sign of abating.

Finally, we would like to thank the authors involved with these elements for their fortitude in approaching such a potentially enormous task with good humor and a positive attitude.

E C Constable
Basel, Switzerland
April 2003

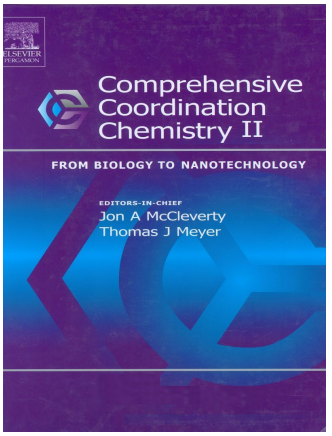
J R Dilworth
Oxford, UK
April 2003

COMPREHENSIVE COORDINATION CHEMISTRY II

From Biology to Nanotechnology

Second Edition

Edited by
J.A. McCleverty, University of Bristol, UK
T.J. Meyer, Los Alamos National Laboratory, Los Alamos, USA



Description

This is the sequel of what has become a classic in the field, Comprehensive Coordination Chemistry. The first edition, CCC-I, appeared in 1987 under the editorship of Sir Geoffrey Wilkinson (Editor-in-Chief), Robert D. Gillard and Jon A. McCleverty (Executive Editors). It was intended to give a contemporary overview of the field, providing both a convenient first source of information and a vehicle to stimulate further advances in the field. The second edition, CCC-II, builds on the first and will survey developments since 1980 authoritatively and critically with a greater emphasis on current trends in biology, materials science and other areas of contemporary scientific interest. Since the 1980s, an astonishing growth and specialisation of knowledge within coordination chemistry, including the rapid development of interdisciplinary fields has made it impossible to provide a totally comprehensive review. CCC-II provides its readers with reliable and informative background information in particular areas based on key primary and secondary references. It gives a clear overview of the state-of-the-art research findings in those areas that the International Advisory Board, the Volume Editors, and the Editors-in-Chief believed to be especially important to the field. CCC-II will provide researchers at all levels of sophistication, from academia, industry and national labs, with an unparalleled depth of coverage.

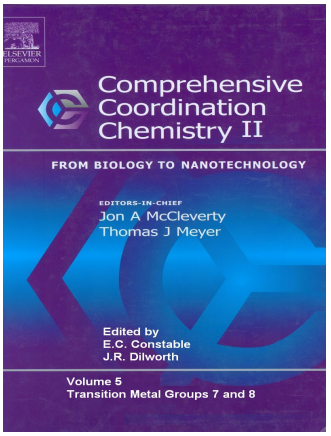
Bibliographic Information

10-Volume Set - Comprehensive Coordination Chemistry II
Hardbound, ISBN: 0-08-043748-6, 9500 pages
Imprint: ELSEVIER
Price:
USD 5,975
EUR 6,274 Books and electronic products are priced in US dollars (USD) and euro (EUR). USD prices apply world-wide except in Europe and Japan.EUR prices apply in Europe and Japan. See also information about conditions of sale & ordering procedures -http://www.elsevier.com/wps/find/bookconditionsofsale.cws_home/622954/conditionsofsale, and links to our regional sales officeshttp://www.elsevier.com/wps/find/contact.cws_home/regional
GBP 4,182.50
030/301
Last update: 10 Sep 2005

Volumes

Volume 1: Fundamentals: Ligands, Complexes, Synthesis, Purification, and Structure
Volume 2: Fundamentals: Physical Methods, Theoretical Analysis, and Case Studies
Volume 3: Coordination Chemistry of the s, p, and f Metals
Volume 4: Transition Metal Groups 3 - 6
Volume 5: Transition Metal Groups 7 and 8
Volume 6: Transition Metal Groups 9 - 12
Volume 7: From the Molecular to the Nanoscale: Synthesis, Structure, and Properties
Volume 8: Bio-coordination Chemistry
Volume 9: Applications of Coordination Chemistry
Volume 10: Cumulative Subject Index

10-Volume Set: Comprehensive Coordination Chemistry II



COMPREHENSIVE COORDINATION CHEMISTRY II

Volume 5:
Transition Metal Groups 7 and 8

Edited by
E.C. Constable
J.R. Dilworth

Contents

5.1
Manganese

D. C. WEATHERBURN
Victoria University of Wellington, New Zealand
S. MANDAL
Dow Corning Corporation, Midland, MI, USA
S. MUKHOPADHYAY
Massachusetts Institute of Technology, Cambridge, USA
S. BHADURI
Harvard University, Cambridge, USA
and
L. F. LINDOY
University of Sydney, NSW, Australia

5.1.1 INTRODUCTION

The manganese section of the *Comprehensive Coordination Chemistry* (*CCC*, 1987) opened with an excellent overview of the basic coordination chemistry of the element and much of this is still relevant to the chemistry that has appeared since. One of the major areas of expansion since the last review has been in the field of cluster complexes where the driving force has been the development of materials with novel magnetic properties and attempts to model the structures

and functions of manganese metalloenzymes. The discovery of the selective epoxidation catalysts based on the Mn^{III} salen system has also prompted much coordination chemistry in the search for higher selectivities and enantiospecific catalysis.

Due to circumstances beyond the control of the Editors it has not been possible to complete a truly comprehensive account of the coordination chemistry of manganese. Nevertheless, what follows provides complete coverage of oxidation states Mn^{VII}, Mn^{VI}, Mn^{V}, and Mn^{III}, and clusters involving Mn^{III} and those with mixed Mn^{III}/Mn^{IV} oxidation states. Macrocyclic chemistry has played a significant role in manganese coordination chemistry in all oxidation states and this is treated in a separate section (Section 5.1.7).

Significant advances have been made in our knowledge of the chemistry of the higher oxidation state complexes (Mn^{VII}, Mn^{VI}, and Mn^{V}) and now the chemistry is not dominated to the same extent by the tetraoxomanganate ions.

5.1.2 OXIDATION STATE VII

5.1.2.1 Oxo and Halide Ligands

$KMnO_4$ is the most familiar compound of manganese in this oxidation state and it continues to be widely used as an oxidant in preparative chemistry and in analysis. Kinetic studies of the oxidation, by permanganate, of both organic and inorganic species are active areas of research but those studies are beyond the scope of this review. Thermal decomposition of $KMnO_4$ has been reviewed[1] and its X-ray photoelectron spectrum has been reported.[2] Other permanganate salts are proving useful in certain circumstances. The use of barium permanganate as an oxidant in nonaqueous and aprotic solvents has been reviewed.[3] Quaternary ammonium, phosphonium, and arsonium permangantes have been used as oxidants in nonpolar and slightly polar solvents,[4] as analytical reagents,[5] and as synthetic reagents for the preparation of high-valent Mn complexes.[6–9] Solutions of quaternary ammonium permanganates in dichloromethane are unstable and the kinetics of their decomposition has been measured.[4] **CARE!** Some quaternary ammonium permanganates have been reported to explode violently under certain conditions.[10–12] Complexation of MnO_4^- by dicyclohexano[18]crown-6 and other crown ethers is another method of solubilizing the MnO_4^- ion in organic solvents and these complexes can be used as oxidants.[13] Rare earth permanganates $M(MnO_4)_3 \cdot nH_2O$ (M = La, Pr, Nd, Sm, Gd, Dy, Er, Yb, Y; $n = 4$–9) have been prepared by adding Mn_2O_7 to rare earth oxides in CCl_4.[14]

Mn_2O_7 has been characterized both experimentally and theoretically. Its crystal structure has been determined and the structure consists of isolated Mn_2O_7 molecules formed by corner sharing between a pair of MnO_4 tetrahedrons. The Mn—O(bridge) lengths are 1.770(3) Å and the Mn—O(terminal) lengths are 1.595(8) Å. The Mn—O—Mn bond angle is 120.7°.[15,16] The force constants of the bonds have been calculated from reported IR data.[17] *Ab initio* calculations of the molecular structure and vibrational frequencies of Mn_2O_7 have been performed using effective core potentials at the Harktree–Fock and density functional theory (DFT) levels. The results indicate that Mn_2O_7 prefers an eclipsed configuration with a calculated Mn—O—Mn bond angle of 125°.[18]

An improved preparation of MnO_3F from MnO_4^- has been described.[19] IR spectroscopy shows that MnO_3F is monomeric in the solid state. Manganese K-edge EXAFS data from the solid at 10 K give Mn—O distances of 1.59 Å, and Mn—F = 1.72 Å.[20] MnO_3F in inert gas matrixes at low temperatures has been studied by IR and UV–visible spectroscopy. The principal charge transfer bands and the fundamental infrared vibrational bands have been assigned.[21,22] DFT predicts the structure, vibrational wavenumbers, and harmonic as well the anharmonic spectroscopic constants of MnO_3F that are in good agreement with the available experimental data.[22] Resonance Raman spectra of MnO_3F and MnO_3Cl have also been measured.[23,24]

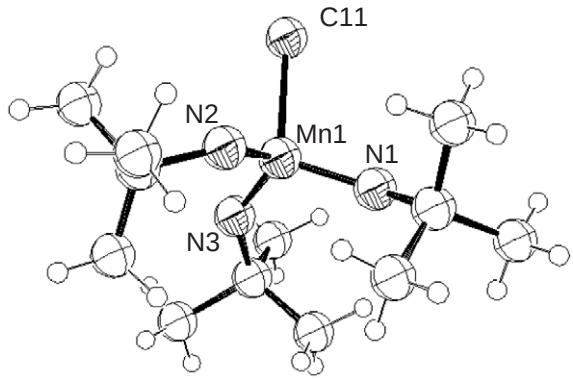
Bond distances and excited state energy levels in MnO_3Cl have been calculated, using *ab initio* methods, and compared with the absorption spectra.[25] A study of the reaction of MnO_3Cl with tetramethylethylene using matrix isolation techniques, and in solution, showed that the epoxidation product $[ClO_2Mn[O(C(CH_3)_2)_2]]$ was formed. DFT calculations predict that the [2+3] addition of tetramethylethylene to the MnO_2 moiety of MnO_3Cl is thermodynamically favored over [2+1] addition (epoxidation). The experimental result was rationalized in terms of the much broader reaction channel leading to epoxidation as opposed to the much more narrow approach path for formation of the glycolate.[26]

The Robin and Day class 1[27] mixed-valent double salt $KMnO_4 \cdot K_2MnO_4$ has been structurally characterized and electron transfer between the MnO_4^- and MnO_4^{2-} ions measured.[28,29] Discrete MnO_4^- and MnO_4^{2-} anions are identifiable in the solid on the basis of the Mn—O bond lengths (1.60–1.61 Å and 1.65–1.66 Å, respectively) and this has been confirmed by a polarized neutron diffraction study.[30] The high rate of electron transfer, together with the ability to distinguish crystallographically between anionic centers, implies a rapidly reversible electron transfer in the solid.[29] Muon spin relaxation experiments have identified the likely sites for the incorporation of muons within the unit cell and the magnetic coupling between the metal centers in this compound has been studied using muon spin relaxation measurements.[31]

A mixed Mn^{VII}/P^V salt $Na_4Mn_{0.5}P_{0.5}O_5$ (formulated as $[Na_4O]^{2+}[Mn_{0.5}P_{0.5}O_4]^{2-}$) has been synthesized and characterized crystallographically. The MnO_4^- and PO_4^{3-} tetrahedrons share one site in the unit cell.[32]

5.1.2.2 Nitrogen Donor Ligands

Complexes of Mn^{VII} with nitrogen and other donor atoms ($[Mn(NR)_3X]$, $R = Bu^t$ or $MeCH_2CMe_2$, $X = Cl^-$, Br^-, $OC(O)Me^-$, $OC(O)CF_3^-$, $OC_6F_5^-$, $OC_6Cl_5^-$, $OCH(CF_3)_2^-$, $SC_6F_5^-$, $C_6F_5^-$, or $NHBu^{t-}$) have been prepared and characterized. A review of the chemistry of these imido ligands with high oxidation state Mn^{VII}, Mn^{VI}, and Mn^V has appeared.[33] The reaction of $MnCl_3$ with $NHR(SiMe_3)$ ($R = Bu^t$ or $MeCH_2CMe_2$) in MeCN yields the neutral complex $[Mn^{VII}(NR)_3Cl]$ as a thermally and air-stable green crystalline solid. The Cl^- in $Mn(NBu^t)_3Cl$ can be substituted by Br^-, —$OC(O)R^-$ ($R = Me$ or CF_3), —$OC_6X_5^-$ ($X = F$ or Cl), —$OCH(CF_3)_2^-$, —$SC_6F_5^-$, —$C_6F_5^-$, or —$NHBu^{t-}$. The chloride (**1**), acetate (**2**), —OC_6F_5, and —SC_6F_5 (**3**) complexes have been structurally characterized.[34] All these complexes have a distorted tetrahedral geometry; Mn—N(imido) bond lengths are in the range 1.64–1.67 Å and the Mn—N—C angles are 139.9(2)–144.6(3)°, indicating partial multiple-bond character. The Mn—X distances indicate single bonds. $Mn(NBu^t)_3Cl$ also reacts with $Li(NHBu^t)$ to give a Mn^{VI} dimer discussed below and salts of the anion $[Mn(N)(NBu^t)_3]^{2-}$ that contain the N^{3-} ligand.[35]



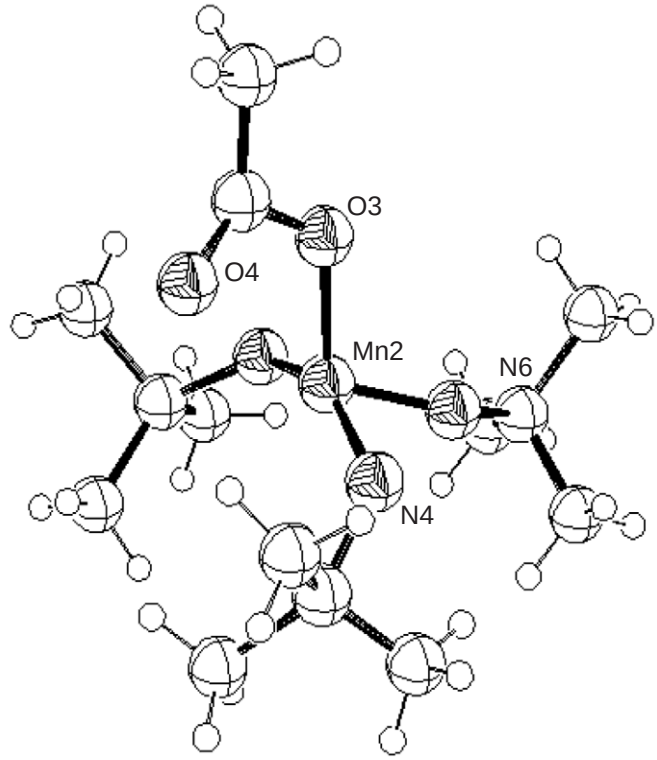
(**1**)

5.1.3 OXIDATION STATE VI

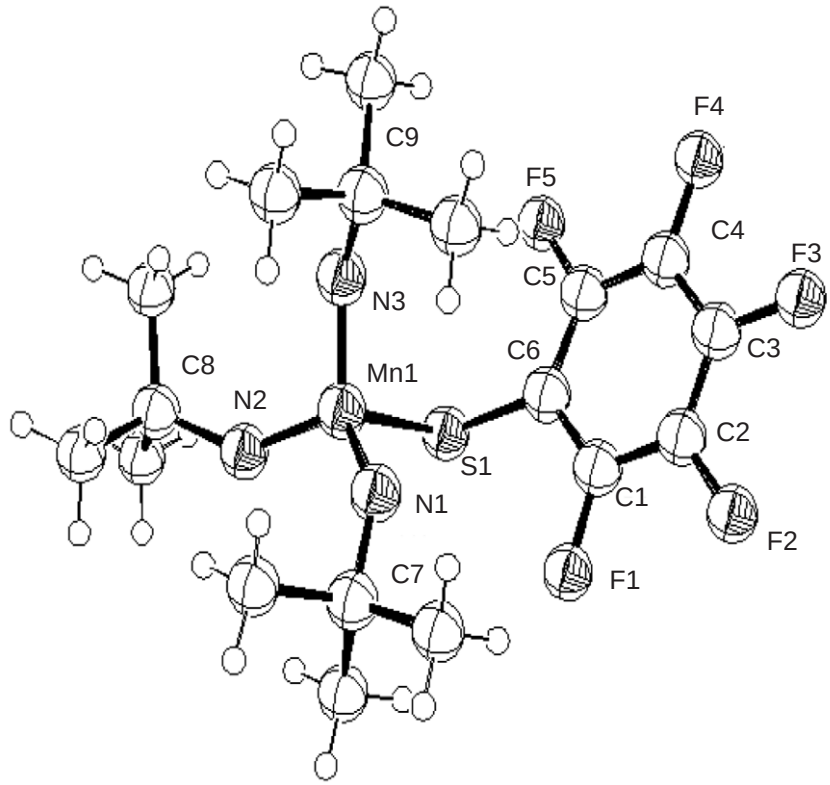
5.1.3.1 Oxo Ligands

The preparation of manganates and their structural characterization has been the subject of two studies.[36,37] Cs_2MnO_4 and K_2MnO_4 are isostructural, having the same orthorhombic structure as β-K_2SO_4, whereas Na_2MnO_4 is hexagonal. Potassium and barium manganates have attracted some interest as oxidizing agents, particularly of alcohols and aldehydes.[38,39] The X-ray photoelectron spectra of K_2MnO_4 have been reported.[2]

Reduction by pulse radiolysis of MnO_4^{2-} under acidic conditions has allowed a study of the UV–visible spectra of the unstable ion $O_3Mn^{VI}(OH)^-$ and the determination of the pK_a of this ion, 7.4 ± 0.1.[40] Abrasive stripping voltammetry has been used to characterize solid barium and


O3
O4
Mn2
N6
N4

(**2**)


C9
F4
F5
C4
F3
C5
N3
C6
C3
C8
Mn1
N2
C2
S1
N1
C1
F2
C7
F1

(**3**)

strontium manganates and hypomanganates. Multiple three- or four-electron, irreversible processes were observed. Voltammetric reduction peak potentials are linearly related to the average Mn—O distances in the anions.[41]

5.1.3.2 Spectra

There has been considerable interest in the electronic spectral behavior of the green MnO_4^{2-} ion. This interest arises because this ion may be useful in the development of near-IR lasers.[42] The absorption spectrum, which is usually studied with samples of MnO_4^{2-} doped into a host lattice, shows an intense band in the ultraviolet at 316 nm, a broad band at ca. 671 nm, together with a weak band at 847 nm. The host lattices used in these studies include orthorhombic Cs_2CrO_4,[43,44] orthorhombic Cs_2SO_4 and orthorhombic $BaXO_4$ (X = Cr, S, Se, Mo),[45–47] monoclinic $SrCrO_4$,[44] orthorhombic K_2XO_4 (X = S, Cr, Se), cubic CsBr,[44] and cubic CsI.[44]

Below 625 nm the reported absorption spectra consist of a series of intense LMCT excitations and their marked polarization dependence allows an unambiguous band assignment. In the red and near-IR region of the spectrum the highly structured *d–d* transitions are of low intensity. The vibrational progressions that are observed in the $^2E \leftrightarrow {}^2T_2$ absorption and in the luminescence spectra are dominated by O—Mn—O bending modes. The symmetry of the host lattice can result in splitting of these *d–d* transitions.[43] A study of the Raman excitation profile of the totally symmetric ν_1 stretching mode at 786 cm^{-1} suggests that the 671 nm band is not purely a *d–d* transition but contains a charge transfer component.[48] A broadband spontaneous emission between 900 nm and 1,430 nm is observed in all doped crystals upon visible or near-IR excitation. In $BaSO_4$ as host lattice, at temperatures below 100 K the quantum yield for this emission is unity, at 300 K the quantum yield is still 20%.[46] Local density approximation (LDA) and DFT calculations have been used for theoretical investigations of the MnO_4^{2-} ion.[49–51]

Oxygen-deficient perovskites that contain Mn have been shown to have Mn^{IV}, Mn^{V}, and Mn^{VI}. The Mn^{IV} is octahedrally coordinated, Mn^{VI} is tetrahedrally coordinated, and Mn^{V} apparently exists in both O_h and T_d symmetries.[52–54]

5.1.3.3 Nitrogen Donor Ligands

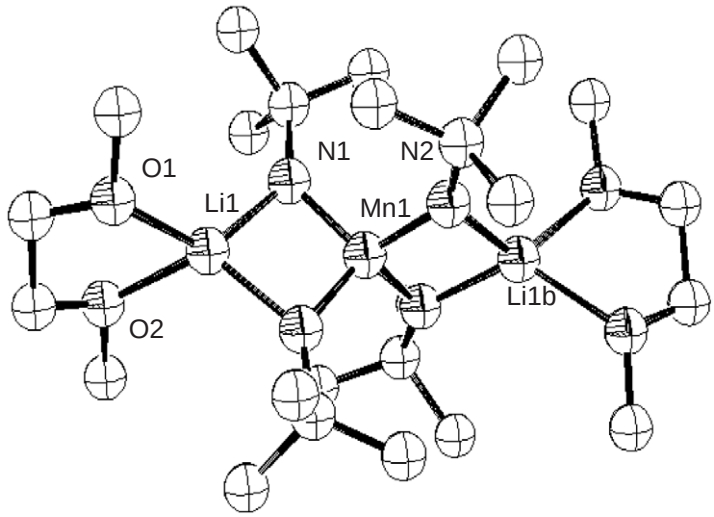
Reaction of $Mn^{VII}(NBu^t)_3Cl$ with $Li(NHBu^t)$ gives the nitrogen donor Mn^{VI} analogue of the manganate(VI) anion, $[Mn(NBu^t)_4]^{2-}$, that has been crystallographically characterized as $(Li(dme))_2(Mn(NBu^t)_4)$ (**4**) (dme = 1,2-dimethoxyethane). This anion reacts with HCl yielding an unstable five-coordinate complex $Mn(NMe_3)_2(NHBu^t)Cl_2$ characterized by NMR. The reaction is reversed by the addition of pyridine. Reaction of $Mn^{VII}(NBu^t)_3Cl$ with Ag^+ in CH_2Cl_2 solution in the presence of Bu^tNH_2 gave green $[Mn(NBu^t)_3(NH_2Bu^t)]Y$ (Y = $CF_3SO_3^-$ or PF_6^-) salts (**5**). In all the compounds the Mn atom has distorted tetrahedral geometry.[34]

Reaction of $Mn(NBu^t)_3Cl$ with $Li(NHBu^t)$ using different conditions to those used above results in the isolation of a Mn^{VI} dimer, $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}]_2$ (**6**), together with Li^+ salts of the Mn^{VII} anion $[Mn(N)(NBu^t)_3]^{2-}$ containing N^{3-}. $Mn(NBu^t)_3Cl$ reacts with MeLi or $ZnMe_2$ yielding a dimeric compound $[MnMe(NBu^t)(\mu\text{-}NBu^t)]_2$ containing a Mn^{VI}—C bond, while interaction with ZnR_2 (R = —CH_2CH_3, —CH_2Bu^t, —CH_2CMe_2Ph, —CH_2SiMe_3, or —CH_2Ph) gives similar alkyls. $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}]_2$ reacts with ZnR_2 (R = Me or -CH_2Bu^t) to give a dimeric, mixed-valent (valence-localized) Mn^V/Mn^{VI} species $Mn_2(NBu^t)_2(\mu\text{-}NBu^t)_4ZnR$. The R = Me compound (**7**) has been crystallographically characterized. A similar mixed-valent dimer, $Mn_2(NBu^t)_2(\mu\text{-}NBu^t)_4AlMe_2]$, is obtained by reaction with Al_2Me_6. Reaction of $[Li(dme)]_2[Mn(NBu^t)_4]$ and Al_2Me_6 gives $Mn[(\mu\text{-}NBu^t)_2AlMe_2]_2$ characterized by mass spectrometry.[35]

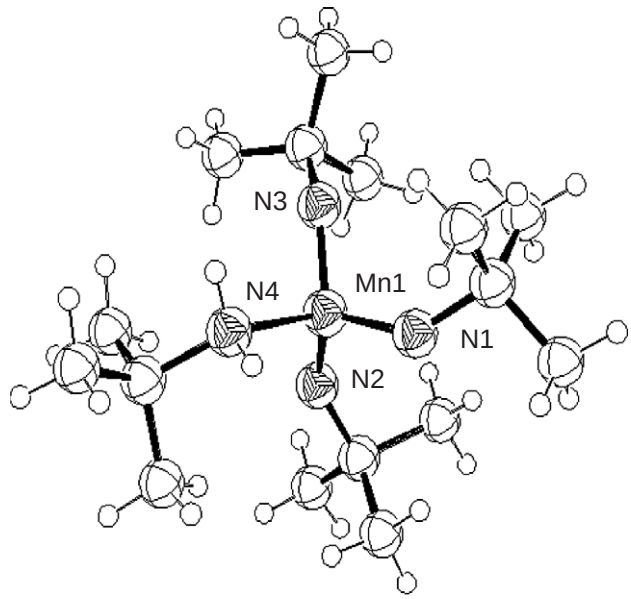
Reaction of $[Mn_2(NBu^t)_4(\mu\text{-}NBu^t)_2]^+$ with $HgCl_2$ gives the Mn^{VI} cations $[[Mn_2(NBu^t)_2(\mu\text{-}NBu^t)_2]_2]^+$, isolated and structurally characterized as the $[Hg_2Cl_6]^{2-}$ salt, and $[(NBu^t)_2Mn(\mu\text{-}NBu^t)_2Mn(NHBu^t)(NBu^t)]^+$, isolated and structurally characterized as the $[Hg_3Cl_8]^{2-}$ salt.[55]

5.1.3.4 Other Complexes

There are a number of reports of the electrochemical oxidation of Mn^{IV} and Mn^{V} to higher oxidation state species that have some stability in solution but no complexes have been isolated.



(**4**)



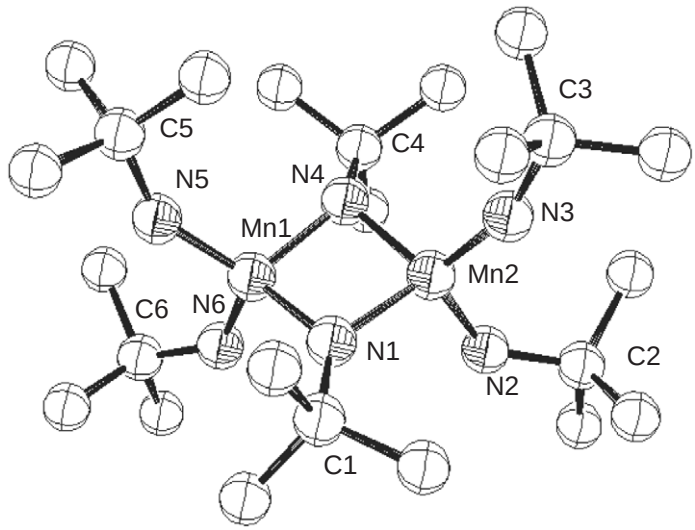
(**5**)

For example, the complexes $[Mn^{V}(N)(CN)_4]^{2-}$ and $[Mn^{IV}(L)_3]^{2-}$ (L = benzohydroxamic acid) in CH_3CN solutions show irreversible anodic responses in their cyclic voltammograms suggesting Mn^{V} and Mn^{VI} complexes are formed.[56,57]

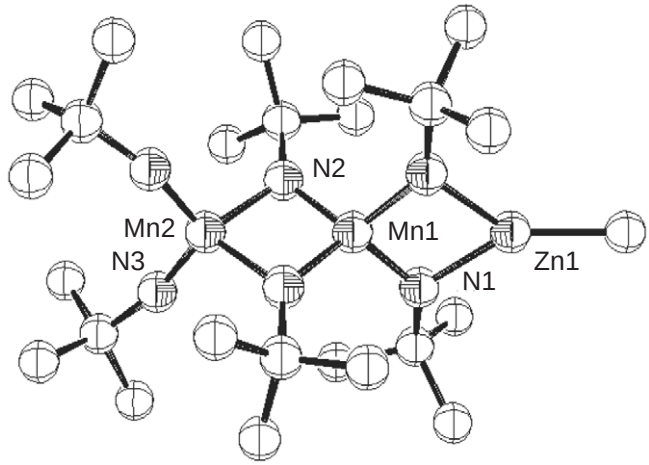
5.1.4 OXIDATION STATE V

5.1.4.1 Oxo Ligands

Green $Ba_3(MnO_4)_2$ is prepared by the reaction of $BaCO_3$ and Mn_2O_3 or $MnCO_3$ in air at 900 °C. It has been structurally characterized using neutron powder diffraction.[58] The Mn—O bond distances are 1.67 Å and 1.71 Å. Magnetic susceptibility has been measured in polycrystalline $Ba_3(MnO_4)_2$; the ground state is a spin singlet indicating a coupled antiferromagnetic interaction



(6)



(7)

between two MnO_4^{3-} ions in the solid.[59] $Ba_3(MnO_4)_2$ continues to attract attention as an oxidant and deprotecting reagent in organic chemistry.[60,61] It shows a reactivity pattern toward some organic substrates that is distinctly different from that of MnO_4^-.[39,62] The UV–visible spectra of the unstable ion $O_3Mn(OH)^{2-}$ has been measured, the pK_a (13.7 ± 0.2) of this ion determined, and rate constants for the reduction MnO_4^{3-} by alcohol radicals; CO_2^-, O_2^-, and e_{aq}^- have been reported.[40]

5.1.4.2 Spectra

There has been considerable interest in the electronic spectral properties of the MnO_4^{3-} ion. This interest arises from a proposal that this ion as a dopant in other solids may be useful in the development of near-IR lasers. This topic has been the subject of a number of reviews.[63–65] MnO_4^{3-} may be doped into tetrahedral sites of oxidic solids such as apatites, $M_5(PO_4)_3X$, e.g., M = Ba; X = Cl;[66–68] M = Sr; X = F;[69–72] M = Sr; X = Cl;[73–77] M = Ca; X = F;[69,78] $Ba_5(MnO_4)_3Cl$;[79] $Sr_5(VO_4)_3F$;[80] spodiosites, e.g., M_2VO_4Cl, M = Ca;[66,68,70] M = Sr;[76,81] Sr_2VO_4F;[82] fluoroapatites, $M_5(XO_4)_6F_2$ (M = Ca, Sr, Ba; X = P, V);[83,84] garnet $Y_3Ga_5O_{12}$ or $Y_3Al_5O_{12}$;[78] melilite $SrGdGa_3O_7$;[78] $Ca_2(XO_4)Cl$ (X = P, V, As);[67,68,76,77,85,86] Li_3PO_4;[87] $Ba_3(VO_4)_2$;[69,74,88–94] $Sr_3(VO_4)_2$;[69] $LaGaO_3$;[95] K_2XO_4 (X = S, Cr, Se);[96] $BaXO_4$ (X = S, Cr, Se, Mo);[96] $YAlO_3$;[97] $Bi_{12}SiO_{20}$;[98–101] $Bi_{12}GeO_{20}$,[99] $Bi_{12}TiO_{20}$;[99] and Y_2SiO_5.[69,102,103] The absorption and photoluminescence

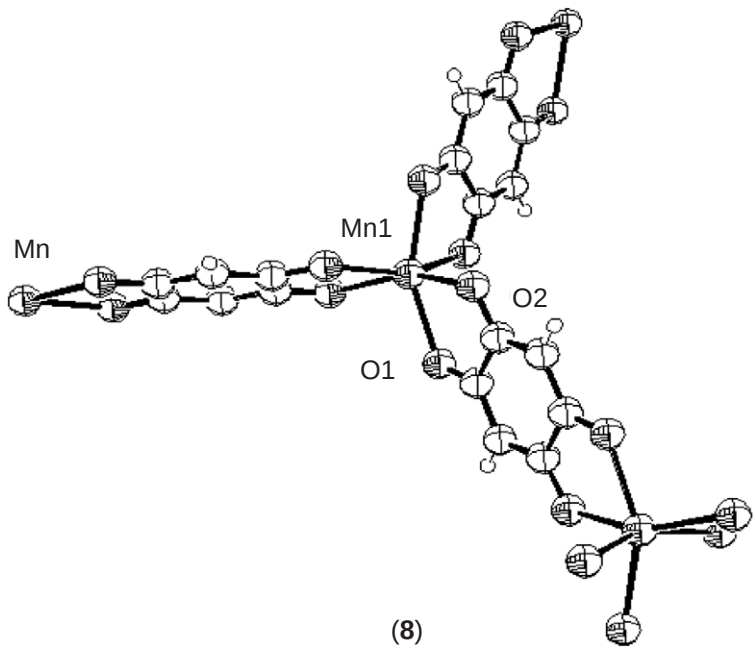
spectra of a Mn^{V}-doped calcium aluminosilicate glass and oxygen-deficient perovskites have also been reported.[54,104,105] Manganese blue, an industrial pigment, has been shown to contain Mn^{V} as the color center.[96]

The absorption spectrum of MnO_4^{3-} shows an intense band in the UV at 316 nm, a broad band at ~671 nm, and a weak band at 847 nm. Theoretical studies at various levels of theory have been performed on the MnO_4^{3-} ion.[68,103,106–108] The color of the doped solids varies from blue to green depending on the level of doping. In the case of the phosphates the size difference between the MnO_4^{3-} ion (Mn^{V}—O distance 1.70–1.73 Å) and the PO_4^{3-} (P—O distance ~1.60 Å) may cause a distortion of the solid, and a color change, that is dependant on the level of doping.[68,79,84]

Isolation of the MnO_3^{-} anion has been claimed in a dark blue $KH_3(SeO_3)_2$ host crystal.[109] The reactivity of this anion in the gas phase has also been studied.[110,111]

5.1.4.3 Oxygen Donor Ligands

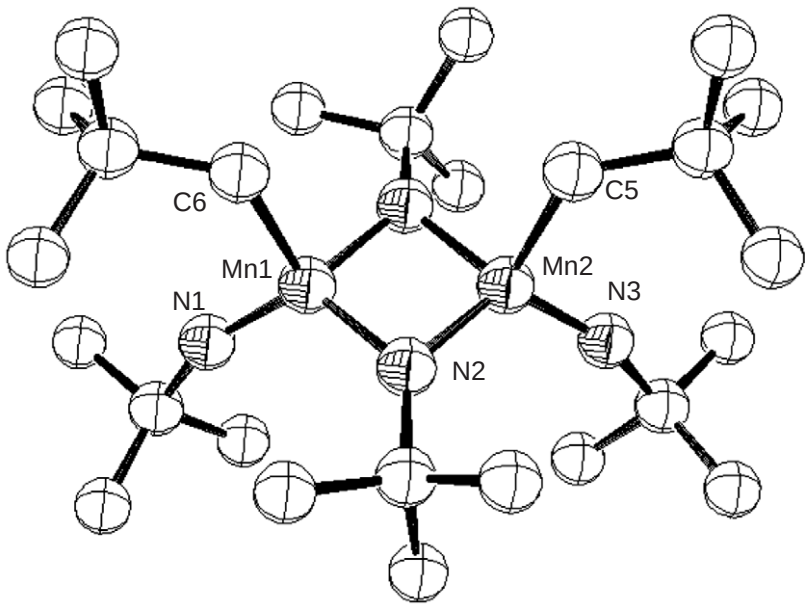
A complex of Mn^{V}, catena-tris(μ-2,5-dihydroxy-1,4-benzoquinonato)-dimanganese(V)$^{4+}$ (**8**), has been structurally characterized but the evidence for the Mn^{V} formulation is scanty.[112]



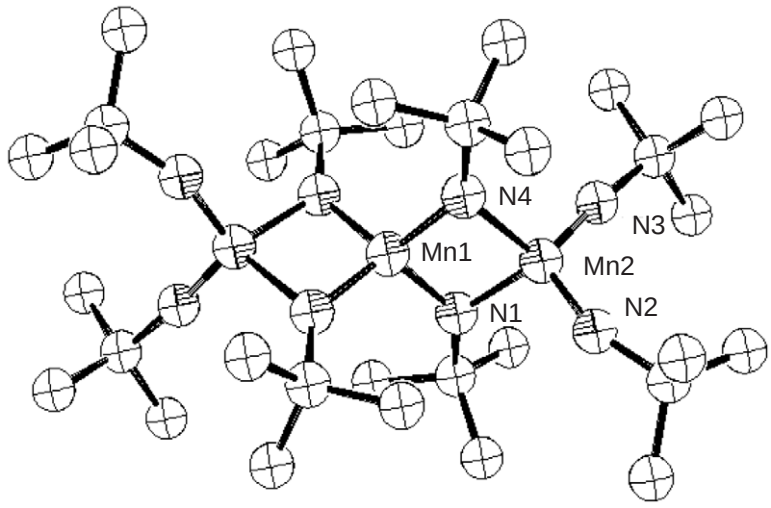
(**8**)

5.1.4.4 Nitrogen Donor Ligands

Reduction of the Mn^{VI} dimer $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ with Li gives the green air-sensitive Mn^{V} anion $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}]_2^{2-}$.[55] Reduction of the $[Mn^{VII}(NBu^t)_3Cl]$ complex with sodium amalgam gives a mixed-valent orange-brown Mn^{VI}–Mn^{V} dimeric anion $[\{Mn(NBu^t)_2(\mu\text{-}NBu^t)\}]_2^{-}$ that has been structurally characterized as its sodium salt (**9**). The manganese ions in this structure are almost crystallographically equivalent. Treatment of the Mn^{VI} dimer $[Mn(NBu^t)_2(\mu\text{-}NBu^t)]_2$ with iodine yielded the red trimeric cation $[Mn_3(NBu^t)_4(\mu\text{-}NBu^t)_4]^{+}$ (**10**), structurally characterized as the triiodide salt which probably has the $2Mn^{VI}/Mn^{V}$ oxidation formulation. This compound unexpectedly gives no EPR signal and has a sharp ^{1}H NMR spectrum. Manganese(V) alkyl compounds $[Mn_2R_2(NBu^t)_2(\mu\text{-}NBu^t)]$ were prepared by the reaction of $[Mn^{VII}(NBu^t)_3Cl]$ with ZnR_2 (R = —CH_3, —CH_2SiMe_3, —CH_2CMe_2Ph, —CH_2CMe_3, and —$CH_2C_6H_5$). Two of these compounds were characterized crystallographically and the benzyl derivative is shown as (**11**).[35]



(**9**)



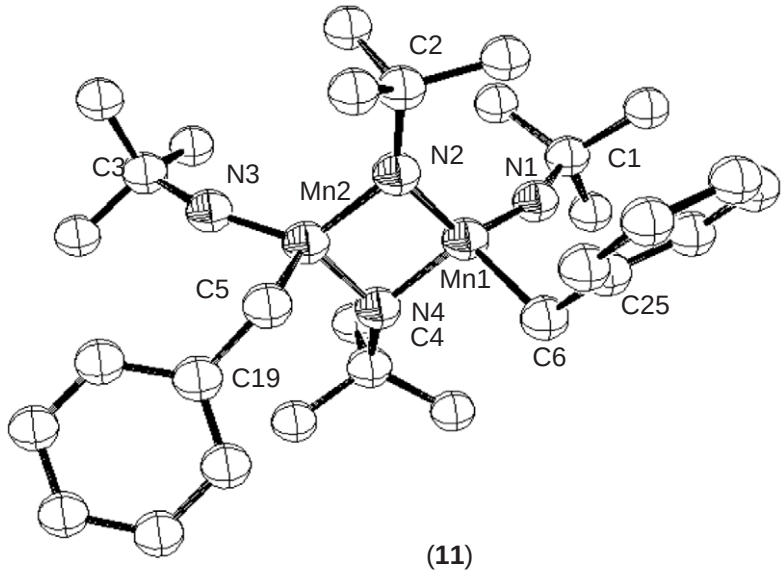
(**10**)

5.1.4.5 Nitrogen and Oxygen Donor Ligands

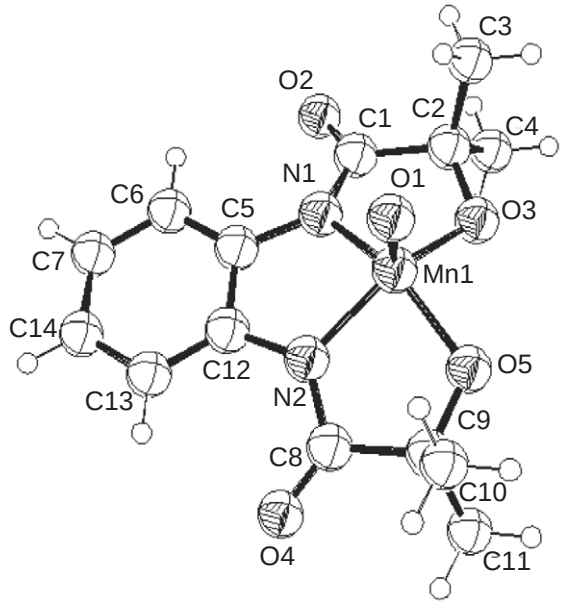
Two five-coordinate $Mn^{V}{=}O$ complexes with N_2O_2 tetradentate ligands $Ph_4P[MnOL]$ (L = 1,2-bis(2-methyl-2-oxypropanamido)benzene and 1,2-bis(2,2-diphenyl-2-hydroxyethanamido)benzene) have been prepared and structurally characterized: (**12**) and (**13**), respectively.[113,114] These complexes and the oxo complexes discussed in the next section may have utility in oxo-transfer reactions to organic substrates such as olefins and ethers.

5.1.4.6 Schiff Base Ligands

Manganese(V) complexes of the Schiff base ligand salen and its derivatives have been the focus of intense study. These complexes have one additional ligand, either an oxo, O^{2-}, or a nitrido, N^{3-}, group and much of the interest arises because these oxygen or nitrogen atoms are readily

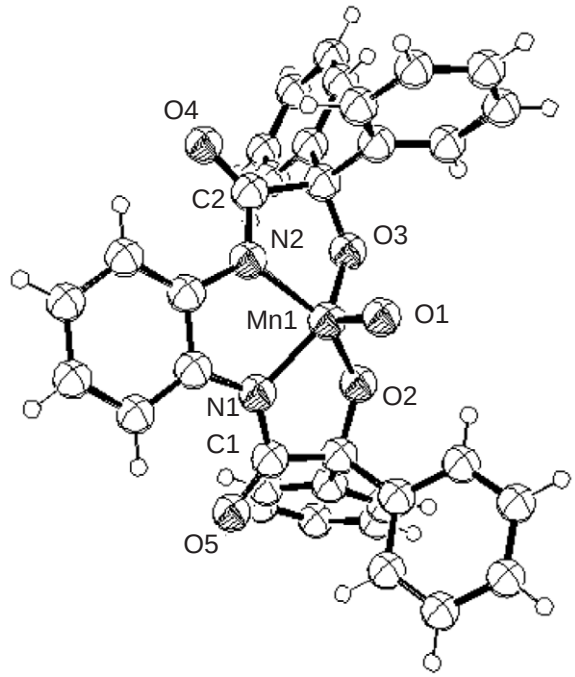


(**11**)



(**12**)

transferred to other substrates. Du Bois *et al.* have reviewed the earlier work on these complexes.[115] The production of optically active epoxides by oxygen transfer to unfunctionalized conjugated olefins is an important industrial process and represents a very elegant example of carbon–oxygen bond formation in asymmetric synthesis.[116,117] This chemistry has been the subject of a number of reviews.[118,119] These oxo complexes can also oxidize aliphatic[120] and aromatic alcohols,[121] aromatic aldehydes,[122] and organic sulfur compounds.[123–126] The catalysts for these reactions, developed by Jacobsen and co-workers,[127–130] are derivatives of Mn^{III}–salen complexes, but the catalytically active species are almost certainly the Mn^{V}–oxo–salen complexes.[131] The Mn^{V}–oxo–salen species have been identified in solution using electrospray mass spectrometry.[131–133] A dinuclear, μ-oxo-bridged $[L(salen)Mn\text{-}O\text{-}Mn\text{-}(salen)L]^{2+}$ (L = iodosobenzene or an amine oxide), also present in these solutions, acts as a reservoir species. Electron-withdrawing substituents on the salen ligand and additional axial ligands decrease the



(**13**)

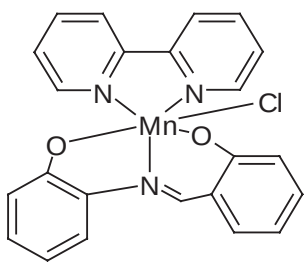
stability and hence enhance the reactivity of the Mn=O moiety, while electron-donating salen substituents have a strong stabilizing effect.[133]

The geometries and spin multiplicities of models of the Mn^{III}–salen catalyst and the Mn^{V}–oxo intermediate have been studied using DFT. The Mn^{III} complexes have quintet ground states, while the nature of the salen ligand influences whether quintet, triplet, or singlet ground states are lowest in energy for the Mn^{V}–oxo intermediates.

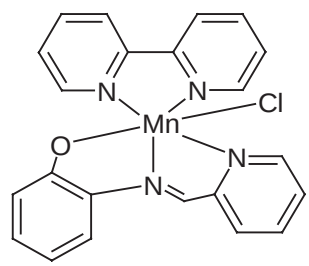
Up until the end of 2002 no structurally characterized examples of the oxo complexes Mn^{V} with salen ligands had been reported, but examples with macrocyclic ligands (Section 5.1.7) and the two quadridentate N_2O_2 donor ligands discussed above are known. *Ab initio* calculations of the structure of the complexes with salen ligands have been performed and the Mn=O bond distance was calculated to be 1.546 Å, similar to that reported in the above examples. The Mn=O bond order is calculated to be 2.3 and the LUMO is 6.3 eV lower in energy than in the corresponding Mn≡N complex which may account for the greater reactivity of the Mn=O complexes.[134] Reduction potentials of Mn^{V}–oxo complexes (range 0.739–0.798 V) have been estimated by applying Marcus theory to the observed rate constants for oxidation of organic sulfides.[123]

Most complexes with catalytic properties are tetradentate derivatives of salen but other ligands, e.g., *N*-(hydroxyphenyl)salicyldimine and *N*-(hydroxyphenyl)pyridine-2-carboxaldimine, form ternary complexes with bipy and Cl^- ((**14**) and (**15**), respectively) that are catalytically competent.[135]

Nitrido complexes of Mn^{V} with porphyrin ligands were first prepared by Hill and Hollander[136] and independantly by Buchler *et al.* in 1982[137,138]. These are described in Section 5.1.7.1.1. Nitrido Mn^{V} complexes with Schiff base ligands were first reported in 1996.[139] The nitrido ligand



(**14**)



(**15**)

is prepared either photolytically from an azide complex or by oxidation of a lower-valent complex with either NaOCl or *N*-bromosuccinimide in the presence of NH_3. Transfer of the N^{3-} group bound to Mn^{V} Schiff base complexes to aromatic silyl enol ethers,[139–141] olefins,[142,143] sugars,[144] Mn^{III} Schiff base complexes,[145] and rhenium(III) complexes[146] has been reported. Similar reactions are observed with the Mn^{V}(N)porphyrin complexes. The reaction products are dependant on the nature of the Schiff base ligand, both the yield and the enantiomeric excess being affected.[140] Salen nitridomanganese(V) complexes have been incorporated into Zeolite Y.[147]

Most Mn^{V} nitrido complexes are five-coordinate with very short Mn≡N bonds (typically 1.54 Å), the Mn atom lies ~0.5 Å above the plane defined by the Schiff base donor atoms. The Mn—N stretching frequencies at ~1050 cm^{-1} are good evidence for a metal–nitrogen triple bond. Some cyano complexes[57] and the 1,4,8,11-tetraazacyclotetradecane-1-acetate complex[148] are six-coordinate and the Mn—N stretching frequency in these complexes varies from 980 cm^{-1} to 1045 cm^{-1} depending on the donor strength of the group *trans* to the nitrido ligand.

Structural studies of the nitrido complexes are listed in Table 1.

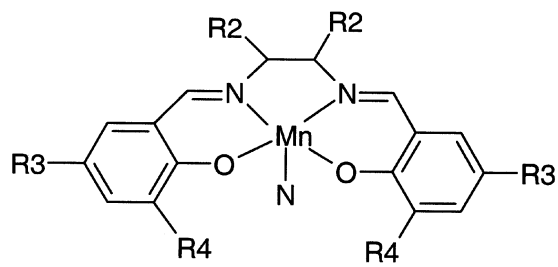
Complexes of Schiff bases formed from salicylaldehyde and primary amines also form Mn^{V}≡N complexes, one of which has been structurally characterized.[142]

DFT calculations of the structures of the nitrido complexes reproduce the observed structures well. The calculations give a Mn≡N bond order of 2.8.[134] The electronic structure and the magnetic properties of the nitridomanganese(V) complexes are readily described by a model developed to account for the absorption spectrum of $VO(H_2O)_5^{2+}$.[149] Nonequivalent π-interactions between the Mn≡N and the salen ligands removes the degeneracy of the d_{xz} and d_{yz} orbitals and this results in the ligand field diagram shown in Figure 1. The magnetic behavior of these nitrido complexes (d^2) indicates a low-spin diamagnetic electron configuration and NMR spectra are typical of diamagnetic complexes.[148] The ground state has the two electrons in the $a'(x^2 - y^2)$ orbital, and the LUMO orbitals are the $a'(yz)$ and $a''(xz)$ orbitals which have Mn≡N π-antibonding character. The visible absorption spectrum is composed of a weak ($\varepsilon = 150\ M^{-1}\ cm^{-1}$), broad asymmetric band with a maximum at ~600 nm assigned to a spin-allowed $a'(x^2 - y^2) \rightarrow d\pi^*$ transition.

5.1.4.7 Cyano Ligands

$[Mn^{V}(N)(salen)]$ reacts with NaCN at elevated temperatures to afford salts of the pink-violet anion $[Mn^{V}(N)(CN)_5]^{3-}$ characterized crystallographically as the $[Rh(en)_3]^{3+}$ salt. The cyano

Table 1 Crystal structure determinations of the nitrido Schiff base Mn^{V} complexes. Ligand substituents are shown in the structure below.



Substituent				
R2	*R3*	*R4*	*CCDC references*	*References*
Cyclohexyl	Bu^t	Bu^t	CAQCUS	143
Cyclohexyl	Bu^t	Bu^t	GORYER	140
Cyclohexyl	Bu^t	Br	GORYIV	140
Ph	H	H	KOQCIC	141
Ph	CH_3	Bu^t	PIKROQ	134,140
Ph	H	H	PUSZUY	149
H	H	H	QETJOO	150
H	H	H	QETJUU	150
H	H	H	ZOPNOH	139

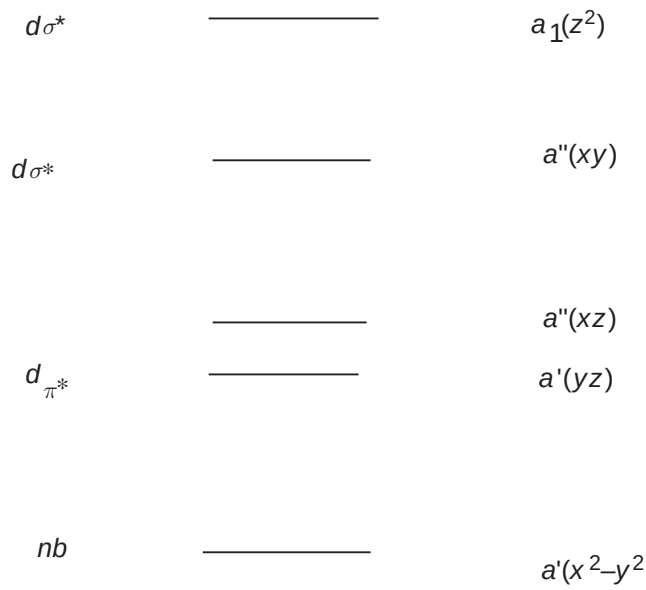


Figure 1 Simplified ligand field splitting diagram for $Mn^{V}(N)(salen)$ complexes.

group *trans* to the N^{3-} is labile. Recrystallization from H_2O yields a distorted square pyramidal five-coordinate species $[Mn^{V}(N)(CN)_4]^{2-}$ whereas recrystallization from pyridine solutions gives the $[Mn^{V}(N)(CN)_4py]^{2-}$ anion with the pyridine ligand *trans* to the N^{3-}. Electrochemical oxidation of $[Mn^{V}(N)(CN)_4]^{2-}$ in acetonitrile solution yields the relatively stable $[Mn^{VI}(N)(CN)_4]^{-}$ complex.[57]

Three salts of a mixed-valent (μ-nitrido)dimanganese complex anion $[(CN)_5Mn(\mu\text{-}N)Mn(CN)_5]^{6-}$, $K_5H[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 2H_2O$, $Na_2Rb_4[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 6H_2O$, and $[Rh(tn)_3]_2[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 10H_2O$ (tn = propane-1,3-diamine), have been prepared and characterized spectroscopically, by magnetic moment measurements and in the case of $Na_2Rb_4[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 6H_2O$ structurally. This very unusual anion contains a mixed-valent Mn^{V} and Mn^{II} center. The X-ray structure, the ESR spectra, and the magnetic data strongly suggest that $[Mn_2(\mu\text{-}N)(CN)_{10}]^{6-}$ is a class II (Robin and Day)[27] valence-localized Mn^{V}–Mn^{II} system.[151] In the $Na_2Rb_4[Mn_2(\mu\text{-}N)(CN)_{10}]\cdot 6H_2O$ salt the anion resides on an inversion center but is clearly disordered. Modeling the disorder shows that the anion is asymmetric with a short Mn—N bond (1.58(1) Å) and a long Mn—N bond (1.84(1) Å). The Mn—C bonds *trans* to the (μ-nitrido) group are 2.19(2) Å and 1.95(2) Å, respectively. The UV–visible spectrum has a very intense band at 345 nm, tentatively assigned to an intervalence band and a less intense *d–d* band at 543 nm of the Mn^{V} center.[151]

5.1.5 MIXED OXIDATION STATES Mn^{IV}/Mn^{III}

5.1.5.1 Introduction

The high-valent manganese clusters contain manganese ions in +3 (d^4) and +4 (d^3) oxidation states, which are primarily stabilized with the help of bridging oxide (O^{2-}) ligands. N-donor chelating ligands also play important roles forming multinuclear manganese complexes containing Mn^{III} and Mn^{IV} ions, where the harder oxide ions help to bridge between the metal centers. Halide ions are also found to be coordinated to the metal centers in a monodentate or bridging modes. Generally the spontaneous self-assembly approach has been employed in forming these high-valent oxomanganese complexes. They have been synthesized frequently from Mn^{II} starting materials, the most abundant source of manganese, by oxidizing with suitable oxidants, such as bromine water, iodine, Ce^{IV}, iodosobenzene, peroxides, and bromate.[152–156] Being a rich source of dioxygen, air often helps in forming oxomanganese complexes as well. A few cases also have employed Mn^{III} starting materials to prepare mixed-valent Mn^{III}–Mn^{IV} clusters.[157,158] The permanganate salts, which contain the Mn^{7+} ion, have also been used extensively in delivering oxidizing equivalents. Permanganate can act as both an oxidant and a source of

manganese. A very common reaction pathway to form high-valent manganese clusters involves the comproportionation reaction between stoichiometric amounts of Mn^{II} and Mn^{VII} sources. Potassium or sodium salts of permanganate are used for the reactions in aqueous media, whereas the tetraalkyl ammonium salts are used for the reactions conducted in organic solvents.[159–162]

The ancillary N-donor and O-donor ligands are also important in the formation and stabilization of oxomanganese clusters. N-donor ligands are especially common ranging and range from bidentate to predesigned polydentate and include aliphatic, cyclic, Schiff base, and polypyridyl systems (Figures 2 and 3).

Based on the donor sites of the ligands, as well as on the nuclearity and geometry, the high-valent complexes containing Mn^{3+} and Mn^{4+} ions have been categorized into the ligand-based

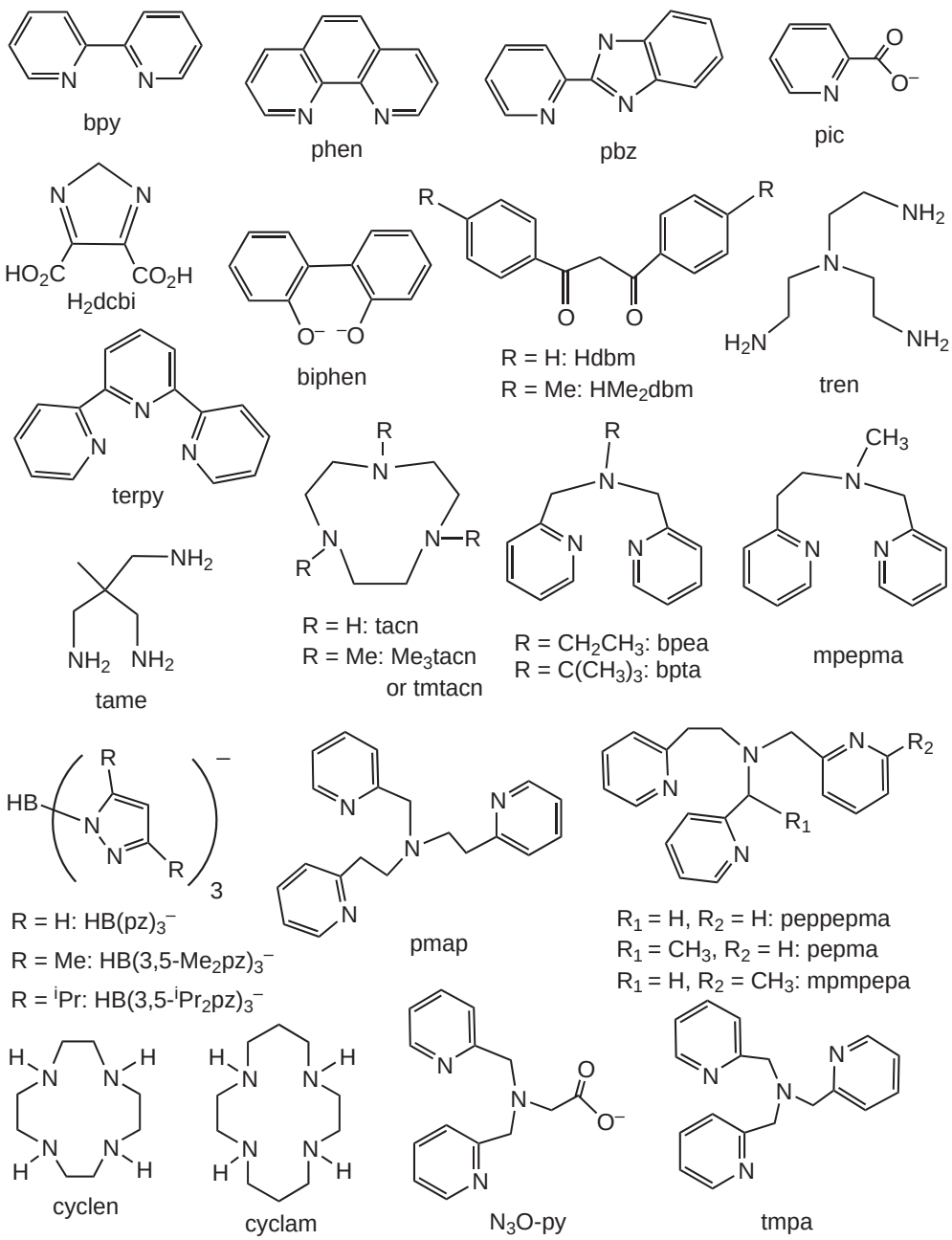
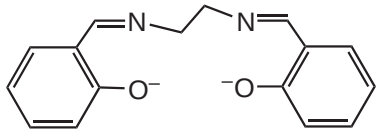
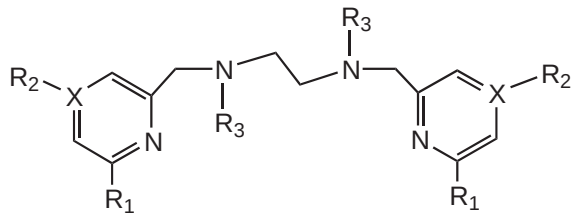


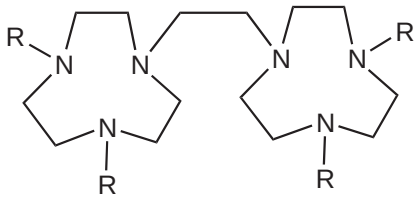
Figure 2 Ligands and their abbreviations.



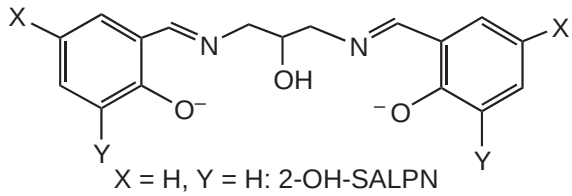
salen



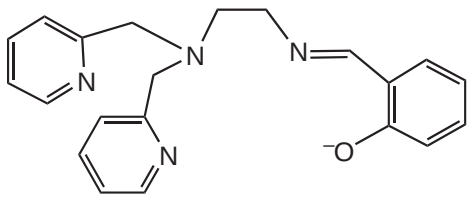
$R_1 = CH_3$; $R_2 = H$; X = C, $R_3 = H$: bpen
$R_1 = H$; $R_2 = H$; X = N, $R_3 = H$: bped
$R_1 = H$; $R_2 = H$; X = C, $R_3 = H$: bispicen
$R_1 = H$; $R_2 = H$; X = C, $R_3 = CH_3$: bispicMe$_2$en



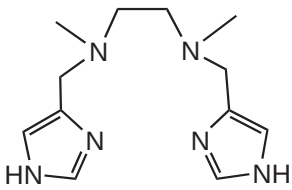
R = H: dtne
R= Me: Me$_4$dtne



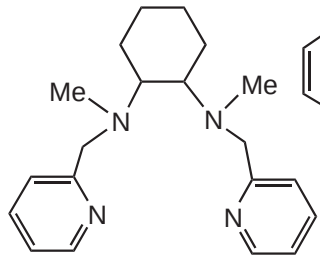
X = H, Y = H: 2-OH-SALPN
X = H, Y = Cl: 2-OH-5-Cl-SALPN
X = Y = Cl: 2-OH-3,5-Cl$_2$-SALPN
X = H, Y = NO_2: 2-OH-3-NO_2-SALPN
X = NO_2, Y = H: 2-OH-5-NO_2-SALPN



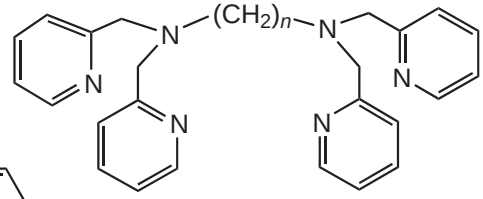
bpmsed



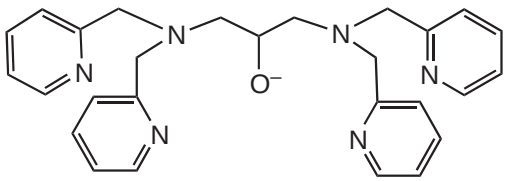
bisimMe$_2$en



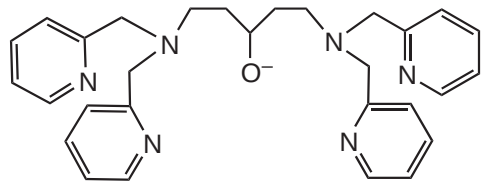
bispicMe$_2$(–)chxn



n = 2: tpen; *n* = 3: tppn



tphpn



tmdp

Figure 3 Ligands and their abbreviations.

groups and subgroups as described below. The structures and abbreviations of the ligands referred to in the text and tables are shown in Figures 2 and 3.

5.1.5.2 Nitrogen and Oxygen Donor Ligands

These complexes have been divided into classes and subclasses based on their nuclearity and their structure, respectively.

5.1.5.2.1 Dinuclear complexes

Many dinuclear manganese(III,IV) complexes have been synthesized and structurally characterized, mainly in the effort towards modeling of the active sites of metalloenzymes.[179] The biological relevance of these complexes is explained elsewhere. These complexes have been found to contain a varying number of bridging oxygen donor ligands. Based on the nature and number of the bridging groups, these complexes have been divided into six major categories: (i) mono-μ-oxo, (ii) bis-μ-oxo, (iii) bis-μ-oxo, mono-μ-carboxylato, (iv) mono-μ-oxo, bis-μ-carboxylato, (v) alkoxide and aryloxide bridged, and (vi) imidazole bridged. The structures of these units are shown in Figure 4 and the Mn···Mn separations are given in Table 2.

(i) Mono-μ-oxo bridging

There has been only one report of a structurally characterized mono-oxo-bridged dinuclear Mn(III,IV) complex, $[Mn_2O(bpmsed)_2]^{3+}$ (**16**) by Girerd and co-workers.[163] The supporting chelating ligand is a Schiff base, *N*,*N*-bis(2-pyridylmethyl)-*N*′-salicylidene-ethane-1,2-diamine, a monoanionic pentadentate ligand (bpmsed). The Mn—O—Mn unit is approximately linear (the Mn—O—Mn angle is 178.7(2)°). The Mn^{IV}—O_{oxo} distance of 1.727(2) Å is shorter than the Mn^{III}—O_{oxo} distance of 1.797(2) Å. The manganese centers are strongly antiferromagnetically coupled ($J = -176.5\,cm^{-1}$) to give rise to a $S = 1/2$ ground state. This complex gives an 18-line EPR signal at $g \approx 2$, which shows rhombic symmetry of ligands around the Mn^{III} center.

(ii) Bis-μ-oxo bridging

The di-μ-oxo Mn(III,IV) complex in presence of 2,2′-bipyridine (bpy) chelating ligand was first reported in 1960 by Nyholm and Turco.[164] and structurally characterized in 1972 by Plaksin *et al.*[165] Since then, several complexes containing the $[Mn_2(\mu\text{-}O)_2]^{3+}$ core with diverse ligand systems have been synthesized. These complexes (**17**–**33**) along with their Mn···Mn distances are summarized in Table 2. Generally, bidentate and tetradentate ligands help to support the so formed "diamond" cores. The Mn···Mn separations in these complexes range between ~2.6 and 2.7 Å. The metal centers are found to be antiferromagnetically coupled and display a characteristic 16–19-line EPR signal centered at $g \approx 2$ below 77 K. This signal arises from the antiferromagnetically coupled valence-trapped Mn(III,IV) ions. These complexes generally possess Jahn–Teller elongated Mn^{III}–ligand axial bonds. A dinuclear bis-μ-oxo Mn(III,IV) complex with tridentate terpyridine ligand, $[Mn_2(\mu\text{-}O)_2(terpy)_2(H_2O)_2]^{3+}$ (**26**) where terminal water molecules

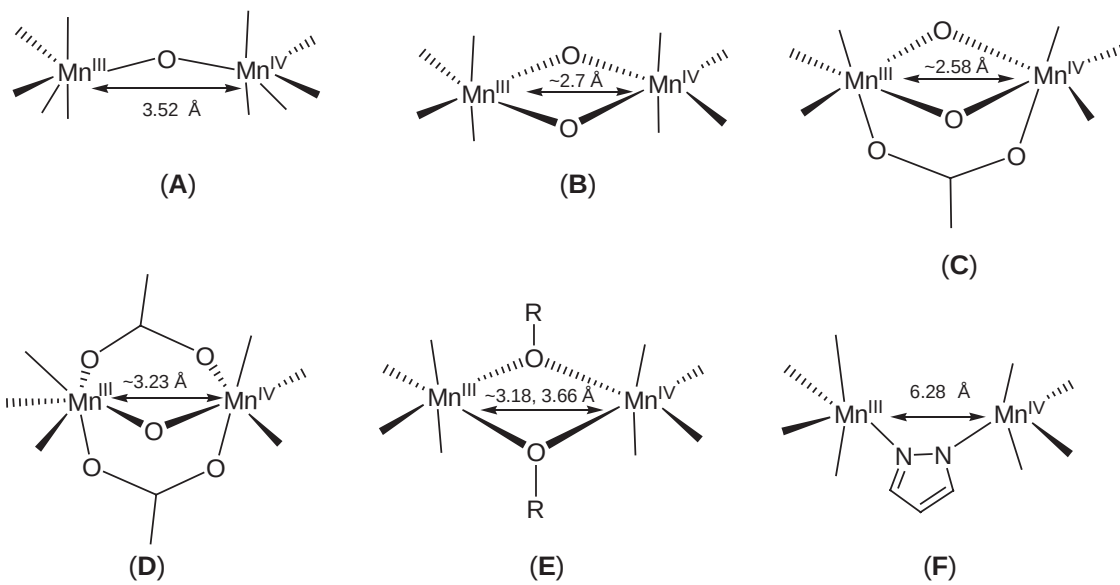


Figure 4 Dinuclear Mn(III/IV) cores (**16**–**47**) and (**58**) along with associated Mn···Mn distances.

Table 2 Dinuclear manganese(III,IV) complexes.

Complex	*Mn···Mn distance*(Å)	*References*
Mono-μ-oxo		
(**16**) $[Mn_2O_2(bpmsed)_2]^{3+}$	3.524	411
Di-μ-oxo		
(**17**) $[Mn_2(\mu\text{-}O)_2(bpy)_4]^{3+}$	2.716	413
(**18**) $[Mn_2(\mu\text{-}O)_2(bispicen)_2]^{3+}$	2.659	482
(**19**) $[Mn_2(\mu\text{-}O)_2(cyclam)_2]^{3+}$	2.741	483
(**20**) $[Mn_2(\mu\text{-}O)_2(pepma)_2]^{3+}$	2.693	484
(**21**) $[Mn_2(\mu\text{-}O)_2(peppepma)_2]^{3+}$	2.682, 2.702	484
(**22**) $[Mn_2(\mu\text{-}O)_2(N_3O\text{-}py)_2]^{3+}$	2.656	485
(**23**) $[Mn_2(\mu\text{-}O)_2(phen)_4]^{3+}$	2.700	486
(**24**) $[Mn_2(\mu\text{-}O)_2(tmpa)_4]^{3+}$	2.643	487
(**25**) $[Mn_2(\mu\text{-}O)_2(tren)_4]^{3+}$	2.679	400
(**26**) $[Mn_2(\mu\text{-}O)_2(terpy)_2(H_2O)_2]^{3+}$	2.73	414,415
(**27**) $[Mn_2(\mu\text{-}O)_2(terpy)_2(CF_3CO_2)_2]^{+}$	2.727	416
(**28**) $[Mn_2(\mu\text{-}O)_2(bispicMe_2en)_2]^{3+}$	2.679	488
(**29**) $[Mn_2(\mu\text{-}O)_2(bispicMe_2(\text{-})chxn)_2]^{3+}$	2.692	488
(**30**) $[Mn_2(\mu\text{-}O)_2(pmap)_2]^{3+}$	2.738	489
(**31**) $[Mn_2(\mu\text{-}O)_2(cyclen)_2]^{3+}$	2.675	490
(**32**) $[Mn_2(\mu\text{-}O)_2(bisimMe_2en)_2]^{3+}$	2.677	491
(**33**) $[Mn_2(\mu\text{-}O)_2(pbz)_2]^{3+}$	2.669	492
Di-μ-oxo μ-carboxylato		
(**34**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(tacn)_2]^{2+}$	2.588	493
(**35**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(tmtacn)_2]^{2+}$		494
(**36**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(bpea)_2]^{2+}$	2.580	408
(**37**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(tpen)]^{2+}$	2.591	417
(**38**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(HB(3,5\text{-}Pr^i{}_2pz)_3)_2]^{0}$		495
(**39**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(dtne)]^{2+}$	2.553	418
(**40**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(Me_4dtne)]^{2+}$	2.573	418
(**41**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(mpepma)_2]^{2+}$	2.622	496
(**42**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(tmtacn)(CH_3CO_2)_2]$	2.665	419
(**43**) $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(tmtacn)(MeOH)(bpy)]^{2+}$	2.628	419
μ-Oxo di-μ-carboxylato		
(**44**) $[Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2(tmtacn)_2]^{3+}$	3.229	420
Other classes		
(**45**) $[Mn_2(\mu\text{-phenolato})_2(bpy)_2(phenolato)]^{2+}$	3.181	421
(**46**) $[Mn_2(2\text{-OH-}3,5Cl_2\text{-SALPN})_2(THF)]^{+}$	3.661	422
(**47**) $[Mn_2(dtsalpn)_2(DCBI)]$	6.28	423
(**58**) $[Mn_2(b\text{-D-}ManfH_{-5})_2]^{-}$	3.245	445

coordinate to both the metal centers, has been reported independantly by Brudvig and Pecaut and their co-workers.[166,167] A similar complex, $[Mn_2(\mu\text{-}O)_2(terpy)_2(CF_3CO_2)_2]^{+}$ (**27**), where the water molecules are replaced by monodentate trifluoroacetate groups, has also been synthesized.[168] In all these complexes, the terminal ligands are *trans* to each other and lie in the plane of the di-μ-oxo groups.

(iii) Bis-μ-oxo, mono-μ-carboxylato bridging

Tridentate ligands (tacv, tritacv, bpea) have often been utilized in synthesizing mono-carboxylato-bridged $[Mn^{III,IV}{}_2\text{-}O_2]$ dinuclear complexes. Acetic acid or acetate buffer generally serve as the source of the bridging acetate group. A polypyridyl hexadentate ligand (tpen) was also employed to synthesize a similar core, $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(tpen)]^{2+}$ (**37**), by Pal and Armstrong.[169] Wieghardt and co-workers have utilized aliphatic hexadentate ligands (dtne and Me_4dtne) to synthesize complexes (**39**) and (**40**).[170] Two asymmetric di-μ-oxo, mono-μ-carboxylato Mn(III,IV) complexes were isolated and structurally characterized.[171] One of them, $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(tmtacn)(MeOH)(bpy)]^{2+}$ (**43**), possesses two different chelating ligands. The Mn^{III} center is chelated by a bpy ligand, whereas the Mn^{IV} center is coordinated to a tridentate tmtacn (also abbreviated as Me_3tacn) ligand. A methanol solvent occupies the sixth position of the Mn^{III}

ion and lies along the Jahn–Teller distortion axis. In the second compound, $[Mn_2(\mu\text{-}O)_2(\mu\text{-}CH_3CO_2)(tmtacn)(CH_3CO_2)_2]$ (**42**), one tmtacn ligand binds to the Mn^{IV} center facially, whereas the Mn^{III} center is only bound to two monodentate acetate groups and possesses a square-planar geometry. The additional bridging group in this class of complexes results in a shortening of the Mn···Mn distance to about 2.6 Å (complexes (**34**)–(**43**), summarized in Table 2). The metal centers are found to be strongly antiferromagnetically coupled with each other as observed in the previous group of complexes. They also display characteristic 16-line EPR signal below 77 K.

(iv) Mono-μ-oxo, bis-μ-carboxylato bridging

To date only one Mn(III,IV) species, $[Mn_2(\mu\text{-}O)(\mu\text{-}CH_3CO_2)_2(tmtacn)_2]^{3+}$ (**44**), possessing a mono-oxo, bis-carboxylato-bridged core has been reported by Wieghardt *et al.* with the tmtacn chelating ligand.[172] Generally, this is a common core for a dinuclear $Mn^{III}{}_2$ complex (see Section 5.1.6). The Mn—O—Mn angle in this complex is much larger (~125°) compared to bis-oxo-bridged complexes (generally <100°). The manganese centers are weakly antiferromagnetically coupled and have a J value of $-40\,cm^{-1}$.

(v) Alkoxide and aryloxide bridging

A bis-μ-phenolato asymmetric Mn(III,IV) complex with diphenolate and bpy ligands, $[Mn_2(\mu\text{-phenolato})_2(bpy)_2(phenolato)]^{2+}$ (**45**), was reported by Christou and co-workers[173] where the Mn···Mn separation and average Mn—O—Mn angles are 3.18 Å and ~100°, respectively. This complex was prepared by reacting $(Et_3NH)_2[Mn(biphen)_2(biphenH)]$ ($biphenH_2$ = biphenol) in CH_2Cl_2 with solid bpy to give $[Mn_2(biphen)_2(biphenH)(bpy)_2]\cdot 3CH_2Cl_2$. Another highly asymmetric alkoxide-bridged dinuclear complex, $[Mn_2(2\text{-}OH\text{-}3,5Cl_2\text{-}SALPN)_2(THF)]^+$ (**46**), supported by a Schiff base ligand, 2-OH-3,5Cl_2-SALPN, has been reported by Pecoraro and co-workers.[174] This complex was synthesized by bulk electrolysis of $[Mn^{III}{}_2(2\text{-}OH\text{-}3,5Cl_2\text{-}SALPN)_2(MeOH)]$ at 600 mV vs. SCE. The valence-trapped Mn centers are weakly antiferromagnetically coupled ($J = -10\,cm^{-1}$) owing to the long Mn···Mn distance (~3.66 Å) and large Mn—O—Mn angle (126.7°). The X-band EPR spectrum at 20 K displays a 12-line signal centered at $g \approx 2$. When the temperature is raised to 43 K and 110 K a broad signal at $g \approx 5$ appeared. This low-field signal was assigned as arising from low-lying $S = 3/2$ excited state which becomes populated at higher temperatures.

(vi) Imidazole bridging

An imidazole-bridged mixed-valent dinuclear complex sustained by Schiff base chelating ligands (dtsalpn) has been reported by Pecoraro and co-workers.[175] This complex, $[Mn_2(dtsalpn)_2(DCBI)]$ (**47**) (DCBI = dicarboxyimidazole), is an example of a Mn(III,IV) dinuclear species where the Mn centers are weakly ferromagnetically coupled with a J value of $+1.4\,cm^{-1}$ to give rise to a $S = 7/2$ ground sate. The Mn···Mn distance in this complex is found to be 6.28 Å. The variable-temperature EPR study exhibits a multiline signal originating from an excited $S = 1/2$ state.

5.1.5.2.2 Tetranuclear clusters

Synthesis of high-valent oxo-bridged tetranuclear manganese clusters focuses on the structural and functional modeling of the Photosystem II (PSII) oxygen-evolving complex (OEC), which is responsible for the photoinduced oxidation of water to produce oxygen, a process responsible for the sustenance of life on earth.[176–181] A tetranuclear oxo-bridged manganese (Mn_4) cluster is believed to play a key role in this light-driven catalytic process that goes through five redox intermediate states (denoted S_0 to S_4). Precise structural information regarding the actual geometry and the ligand environment of this Mn_4 cluster is still unclear. However, site-directed mutagenesis and EPR studies have suggested that several amino acids possessing carboxylate and imidazole side chains coordinate to the manganese centers.[182–184] In addition, X-ray absorption studies have provided two different types of Mn···Mn separations of 2.7 Å and 3.3 Å in the S_2 state of the OEC Mn_4 cluster.[185] Based on these data, Klein and co-workers proposed an open

"dimer-of-dimers" model for the PSII active site where the 2.7 Å distance was assigned as the separation between the Mn ions within each dimer and the 3.3 Å distance as the shorter interdimer distance between the Mn ions at the closed end of the Mn_4 structure (Figure 5A). Crystal structures of the enzyme have shown a different metal ion topology, although the exact ligand coordination environment is still lacking.[186,187] In an effort to obtain a model for the OEC active site several structurally distinct tetranuclear complexes containing Mn^{3+} and Mn^{4+} ions supported by oxygen and nitrogen donor ligands have been synthesized.

Chan and Armstrong have employed a heptadentate polypyridyl ligand, htphpn, in synthesizing desired tetramanganese complexes. An open-chain Mn_4 complex, $[Mn_4O_2(tphpn)_2(OTf)_2(H_2O)_2]^{3+}$ (**48**), with the oxidation state assignment of $[Mn^{II}Mn^{III}Mn^{IV}\ Mn^{II}]$ was isolated (Scheme 1).[188] The outer manganese atoms were assigned as in the +2 oxidation state, whereas the inner core contains a $[Mn^{III,IV}{}_2(\mu\text{-}O)_2]$ moiety with a Mn···Mn separation of 2.72 Å. A water molecule and a triflate counterion are ligated to the Mn^{II} centers. The water molecules are hydrogen bonded to the bridging oxide groups. The manganese ions in this complex are found to be overall antiferromagnetically coupled as depicted by magnetic susceptibility studies. It should be mentioned that a similar compound has been also reported by Suzuki *et al.*[189]

Aerial oxidation of the above-mentioned complex (**48**) yielded a mixed-valent tetranuclear species, $[Mn_4O_4(tphpn)_2]^{4+}$ (**49**) (Scheme 1) where two $[Mn^{III,IV}{}_2(\mu\text{-}O)_2]^{3+}$ units are connected to each other by the alkoxide bridges, a closed analogue to the proposed "dimer-of-dimers" model (Figure 5B).[190] The Mn···Mn separations in the dimeric unit and within two units are 2.65 Å and 3.97 Å, respectively. The valence-trapped manganese centers are antiferromagnetically coupled with each other to give a $S = 1/2$ state in each dinuclear unit and two dinuclear units interact with each other ferromagnetically to give an overall $S = 1$ ground state. This complex gives a broad EPR signal, centered at $g \approx 6$ that resembles that of one of the intermediate states (S_1) in the water oxidation catalytic cycle.

Another "dimer-of-dimers" complex, $[Mn_4O_4(tmdp)_2(H_2O)_2]^{4+}$ (**50**), was reported by Uehara and co-workers, where they used a similar polydentate pyridyl-based ligand, tmdp.[191] This

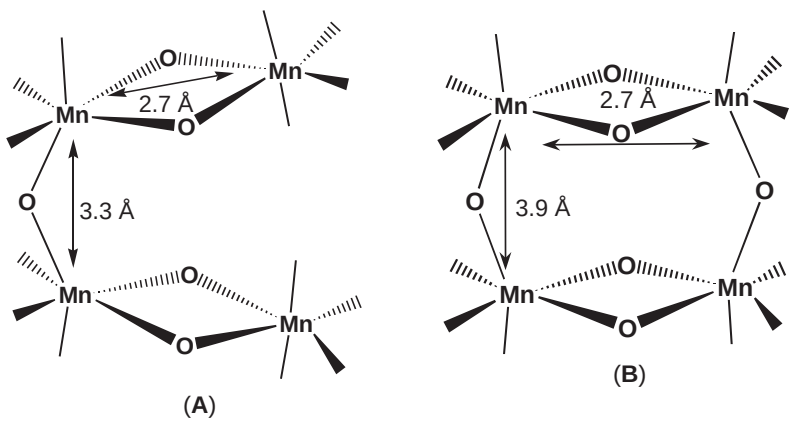
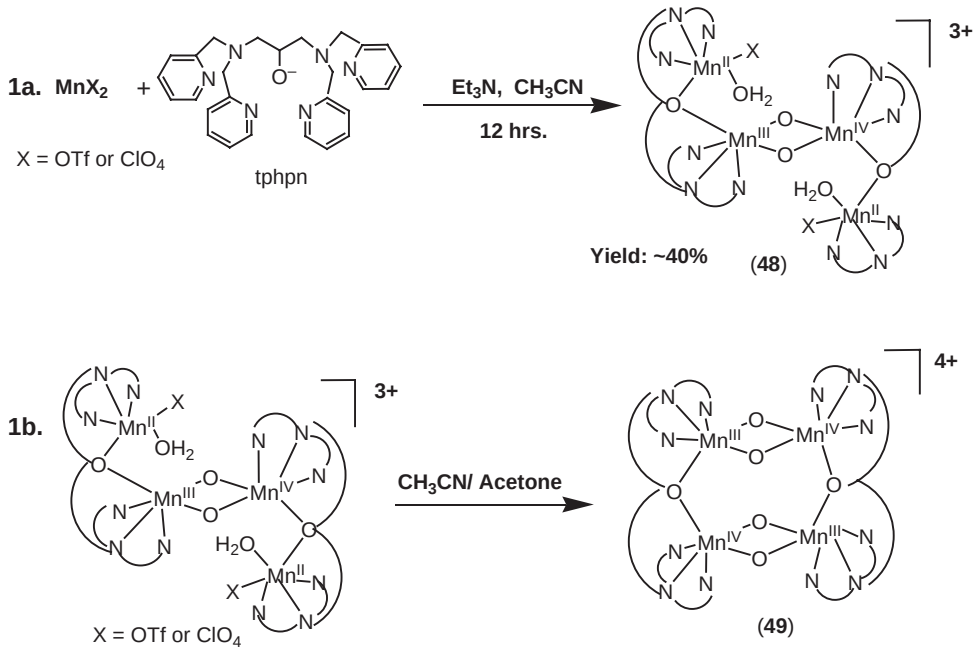


Figure 5 Tetranuclear manganese cluster core structures.



Scheme 1

complex contains two dimeric units, each containing two valence-trapped Mn^{III} and Mn^{IV} ions. In this complex, the alkoxide groups bind to the dimers alternately as opposed to the previous complex where the alkoxide groups are coordinated to both the dimers simultaneously. As a result, the Mn···Mn separation between the dimers is 5.9 Å. The Mn···Mn distance within the dimer is ~2.65 Å. Water molecules occupy the sixth coordination sites of the Mn^{III} centers. The intradimer interaction is strongly antiferromagnetic in nature with $J = -145\,cm^{-1}$, whereas the interdimer interaction is weakly ferromagnetic ($J = 0.2\,cm^{-1}$) giving rise to a triplet ground state. Hydrogen bonding is believed to be responsible for the observed interdimer exchange interactions. A broad EPR signal centered at $g \approx 4.5$ was obtained in the frozen solution. Quasireversible redox responses were observed for this complex. The one-electron oxidized $[Mn^{III}Mn^{IV}{}_3]$ species, which was generated electrochemically by bulk electrolysis at +1.0 V, showed a 16-line EPR signal centered at $g \approx 2$, supporting the retention of the "dimer-of-dimers" core.

A different class of tetranuclear manganese cluster with a distorted cubane geometry containing a $[Mn^{IV}Mn^{III}{}_3O_3X]$ (where X is a heteroatom) core has been reported by Christou and co-workers (Figure 5C). Two complexes with oxygen and nitrogen donor ligands, where $X = N_3^-$ (**51**) and NCO^- (**52**), have been synthesized.[157] Both the complexes have a $S = 9/2$ ground state, which has been described as the result of "spin frustration," a phenomenon where an intermediate spin ground state results due to the competition between similar magnetic exchange interactions in complexes with certain topologies, e.g., triangular and butterfly-like geometries. In the above complexes the $Mn^{IV}\cdots Mn^{III}$ antiferromagnetic exchange interaction dominates "frustrates" the spins of three Mn^{III} ions that are aligned parallel. The $S = 9/2$ ground state is well isolated, being $\sim 180\,cm^{-1}$ below the first excited state. Precise structural and magnetic properties of the cubane complexes are described in Sections 5.1.5.3 and 5.1.5.4.

An adamantane-shaped complex with a $[Mn^{III}Mn^{IV}{}_3(\mu\text{-}O)_6(bpea)_4]^{3+}$ (**53**) core supported by a tridentate bpea ligand was reported by Armstrong and co-workers (Figure 5D).[161] This one-electron reduced product of the $[Mn^{IV}{}_4(\mu\text{-}O)_6(bpea)_4]^{4+}$ complex resulted when a ligand substitution reaction was attempted with a tmtacn ligand. Other tertiary amines and reducing agents, such as $Fe(Cp^*)_2$, were also able to perform the reduction. Controlled potential electrolysis of $[Mn^{IV}{}_4(\mu\text{-}O)_6(bpea)_4]^{4+}$ at −0.1 V in acetonitrile formed the reduced adamantane shaped species as well in a very high yield. This contains a crystallographically distinguishable Mn^{III} center that has Jahn–Teller elongated Mn—N_{alkyl} bonds. The Mn···Mn distances range between 3.22 Å and 3.25 Å, whereas the Mn—O—Mn angles are between ~126 and 130°. Interestingly, the solution magnetic susceptibility of an acetonitrile solution of this mixed-valent adamantane shaped complex prepared by bulk coulometry (μ_{eff}/Mn of 3.19 μ_B at 295 K) indicated that the reduction of $[Mn_4O_6]^{4+}$ to $[Mn_4O_6]^{3+}$ is attened by a change from net ferromagnetic coupling to overall moderately antiferromagentic coupling within the

manganese-oxo core. Magnetic susceptibility studies and EPR analysis show that this complex has an $S = 5/2$ ground state and displays a broad signal centered at $g \approx 4$ analogous to one of the EPR signals of the PSII S_2 state.[192] Consequently, this complex has been proposed as the first spin-topological model for the $g = 5.1$ S_2 state of the PSII water oxidase Mn_4 cluster.

5.1.5.2.3 Hexanuclear cluster

Christou and co-workers reported a structurally characterized hexanuclear manganese cluster, $[Mn_6O_7(mpdp)_3(bpy)_3]^+$ (**54**) consisting of a $[Mn^{III}{}_3Mn^{IV}{}_3O_7]^{7+}$ core, with the aid of a dicarboxylate-based ligand, *m*-phenylenedipropionate (mpdp).[193] This high-valent Mn_6 complex was obtained by oxidizing a dinuclear $Mn^{III}{}_2$ complex, $[Mn_2(\mu\text{-O})(\mu\text{-mpdp})(bpy)_2(H_2O)(MeCN)]^{2+}$, with $[Bu^n{}_4N]MnO_4$. The structure of the complex has been described as the superposition of two triangular units with a noncrystallographic C_3, one of them consisting of three Mn^{III}, whereas the other one has three Mn^{IV} centers (Figure 6). All the Mn atoms have highly distorted octahedral arrangements. The $[Mn^{IV}{}_3(\mu\text{-O})_3]^{6+}$ triangular unit has each Mn^{IV} atom connected through two μ-oxides to the adjacent Mn^{IV} atoms and through a μ_3-oxide to two Mn^{III} atoms from the other trinuclear segment. The three remaining coordination positions of the Mn^{IV} centers are occupied by two N atoms from a chelating bpy and by an O atom from the bridging carboxylate that also binds to an Mn^{III} ion in the other triangle. The other $[Mn^{III}{}_3(\mu_3\text{-O})_4]^+$ triangular fragment has an oxide-centered basic carboxylate core. Each Mn^{III} is coordinated to three μ_3-O ligands, one being in the center of the triangle and the other two in the edges, bridging this unit with the $Mn^{IV}{}_3$ fragment. The other three coordination positions are occupied by bridging carboxylates: two of them link the Mn^{III} with the other two Mn^{III} atoms in the same triangle, whereas the third one connects the Mn^{III} center with an Mn^{IV} from the other triangle. The three Mn^{III} (high-spin d^4 systems) ions possess Jahn–Teller elongated axes. These axes pass through one of the edge μ_3-oxide ions and the opposite carboxylate group, causing an apparent distortion in the $[Mn^{III}{}_3(\mu_3\text{-O})_4]^+$ unit. Magnetic susceptibility studies show that this complex has an $S = 3/2$ spin ground state, which results from a strong antiferromagnetic coupling present among the Mn ions.

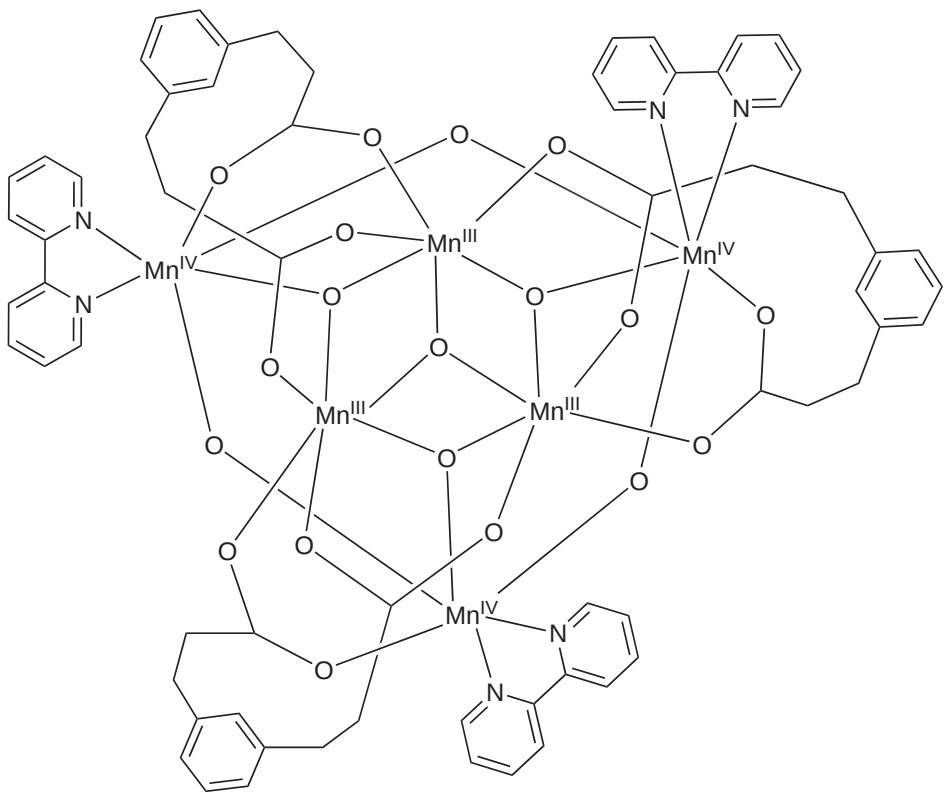


Figure 6 Schematic structure of $[Mn_6O_7(mpdp)_3(bpy)_3]^+$ (**54**).

5.1.5.2.4 Octanuclear cluster

A novel octanuclear manganese cluster, $[Mn_8O_{10}(O_2CMe)_6(H_2O)_2(bpy)_6]^{4+}$ (**55**) with an $[Mn^{III}{}_2Mn^{IV}{}_6O_{10}]^{10+}$ unit, described as a "serpentine-like" core, has been reported (Figure 7) by Christou and co-workers.[194] This compound is also the highest valent polynuclear Mn_n ($n > 4$) species discovered to date, with an average oxidation state of +3.75. This complex was synthesized by the comproportionation reaction between Mn^{II} and Mn^{VII} ion sources in a ratio of 3:2 in the presence of bpy ligand. The structure can be described as the aggregation of five $[Mn_2O_2]$ units in a winding manner to give the serpentine topology. All of the Mn^{4+} ions are ligated by six bpy ligands. The valence-trapped Mn^{3+} centers were distinguished by their Jahn–Teller elongated bond lengths and absence of coordinated N-donor ligands. There are six μ-acetate groups present in the complex. The terminal manganese centers are bonded to two water molecules. The distance between the Mn ions in the $[Mn_2O_2]$ units ranges between 2.67 Å and 2.79 Å, whereas the separation between the Mn^{3+} and Mn^{4+} ions within two adjacent $[Mn_2O_2]$ units that are connected through a μ_3-oxo group is 3.27 Å. The solid-state magnetic susceptibility studies indicate an $S = 0$ ground state, where the Mn centers are antiferromagnetically coupled as expected.

5.1.5.2.5 Nonanuclear cluster

Brechin *et al*. have recently reported a new class of single-molecule magnets with a nonanuclear manganese core. The reaction of a reduced basic carboxylate compound, $[Mn_3O(OAc)_6(py)_3]$, with 1,1,1-tris(hydroxymethyl)ethane (H_3thme) afforded the $Mn^{IV}{}_3Mn^{III}{}_4Mn^{II}{}_2$ complex

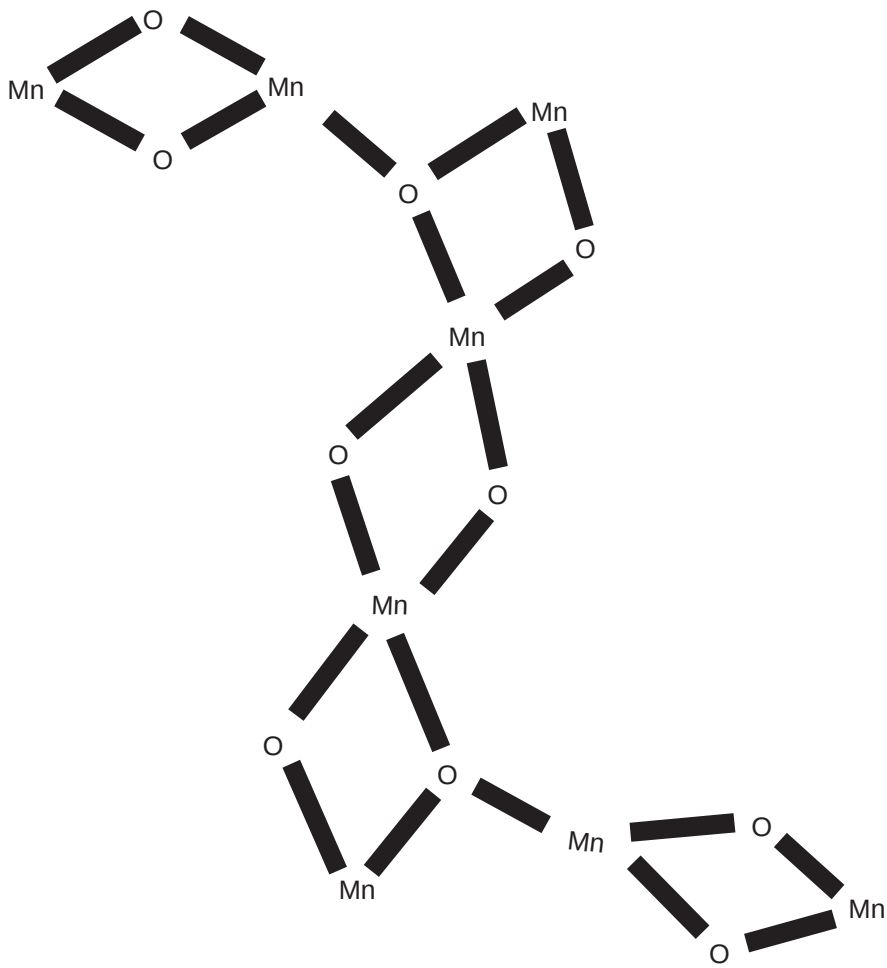


Figure 7 Core structure of $[Mn_8O_{10}(OAc)_6(bpy)_6(H_2O)_2]^{4+}$ (**55**).

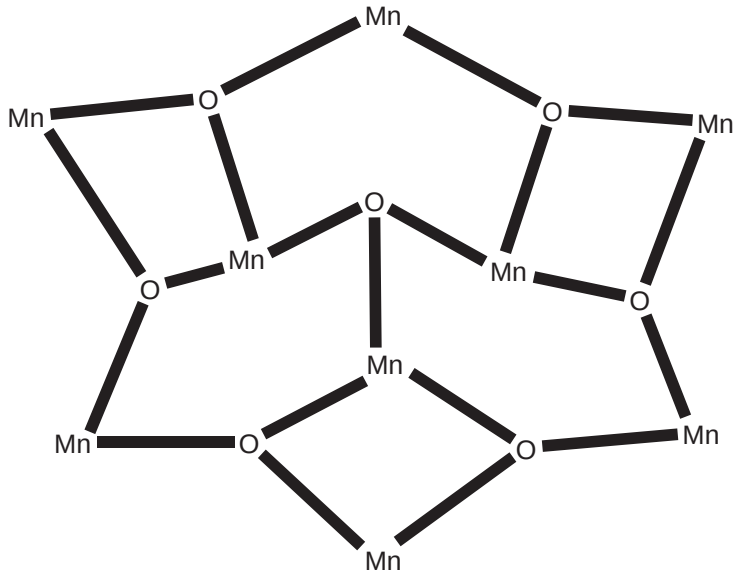


Figure 8 Core structure of $[Mn_9O_7(OAc)_{11}(thme)(py)_3(H_2O)_2]$ (**56**).

$[Mn_9O_7(OAc)_{11}(thme)(py)_3(H_2O)_2]$ (**56**).[195] The core of this complex consists of an $[Mn^{III}{}_4Mn^{II}{}_2O_6]^{4+}$ unit and a smaller $[Mn^{IV}{}_3O]^{10+}$ unit embedded in it. The $[Mn^{III}{}_4Mn^{II}{}_2O]^{4+}$ segment is trapped valence with the Mn^{II} ions being Mn4 and Mn8 in Figure 8. The $[Mn^{IV}{}_3O]^{10+}$ unit is connected to the $[Mn^{III}{}_4Mn^{II}{}_2O]^{4+}$ unit by six μ_3-oxides. All the Mn ions are in distorted octahedral geometries. The Jahn–Teller elongations of the Mn^{III} ions (Mn5, Mn6, Mn7, Mn9) are perpendicular to the plane of the $[Mn^{III}{}_4Mn^{II}{}_2O_6]^{4+}$ unit. The solid-state DC magnetic measurements show that this complex has a high-spin ground state of $S = 17/2$. It displays strong out-of-phase signals in AC susceptibility studies that establish it as a new class of single-molecule magnet (a brief discussion about the properties of single-molecule magnets (SMMs) is provided in Section 5.1.5.3).

5.1.5.2.6 Decanuclear cluster

A novel decanuclear complex, $[Mn^{III}{}_4Mn^{IV}{}_6]$ of the formula $[Mn_{10}O_{14}(tren)_6]^{8+}$ (**57**), was prepared by Armstrong and co-workers by prolonged air oxidation of $Mn(OTf)_2$ in the presence of the N-donor ligand tren.[196] As usual, the manganese oxidation states are assigned on the basis of charge consideration and the presence of Jahn–Teller distortion as expected for MnIII ions. As a result, the longest Mn^{III}–N distance of 2.29 Å is longer than the Mn^{IV}–N distance of 2.07 Å. There are three types of bridging oxo groups present in the molecule: six μ-oxos, four "T-shaped" μ_3-oxos, and four pyramidal μ_3-oxo groups. The inner core containing six Mn atoms can be portrayed as four partial Mn_3O_4 cuboidal fragments fused along common faces (Figure 9). This structural motif can be seen in layered CdI_2-like structures of lithiophorite and chalcophanite. Alternatively, the structure can be described as a layered one in an extended lattice of edge-sharing MX_6 octahedrons. Preliminary magnetic studies indicate a value of 3.3 μ_B/Mn as compared to calculated 4.3 μ_B/Mn that is consistent with an overall antiferromagnetic interaction within the cluster aggregate. A frozen solution of the complex is EPR silent at 4 K, and the cyclic voltammogram reveals no reversible responses in the range −1.5 to +1.5 V vs. Ag/Ag^+.

5.1.5.3 Oxygen Donor Ligands

5.1.5.3.1 Dinuclear complexes

A Mn(III,IV) dinuclear complex supported by the aldohexose D-mannose (D-Man), $Ba_2[Mn_2$-(b-D-Man*f*$H_{-5})_2]Cl$ (**58**) (where Man*f* = mannofuranose), was reported by Geisselmann *et al.*[197] This complex was formed *in situ* when $Ca(OH)_2$, $Mn(OAc)_3{\cdot}2H_2O$, and D-Man were mixed in a ratio of

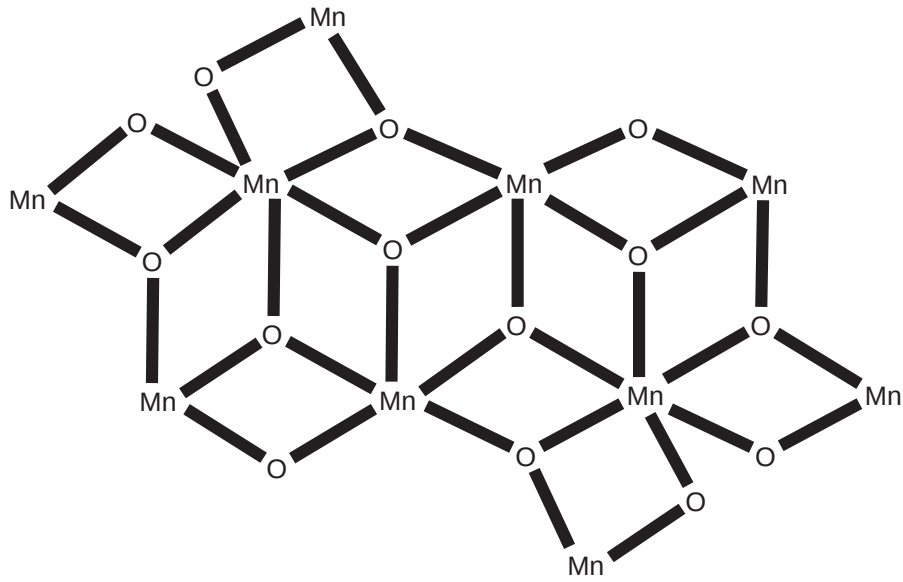


Figure 9 Core structure of $[Mn_{10}O_{14}(tren)_6]^{8+}$ (**57**).

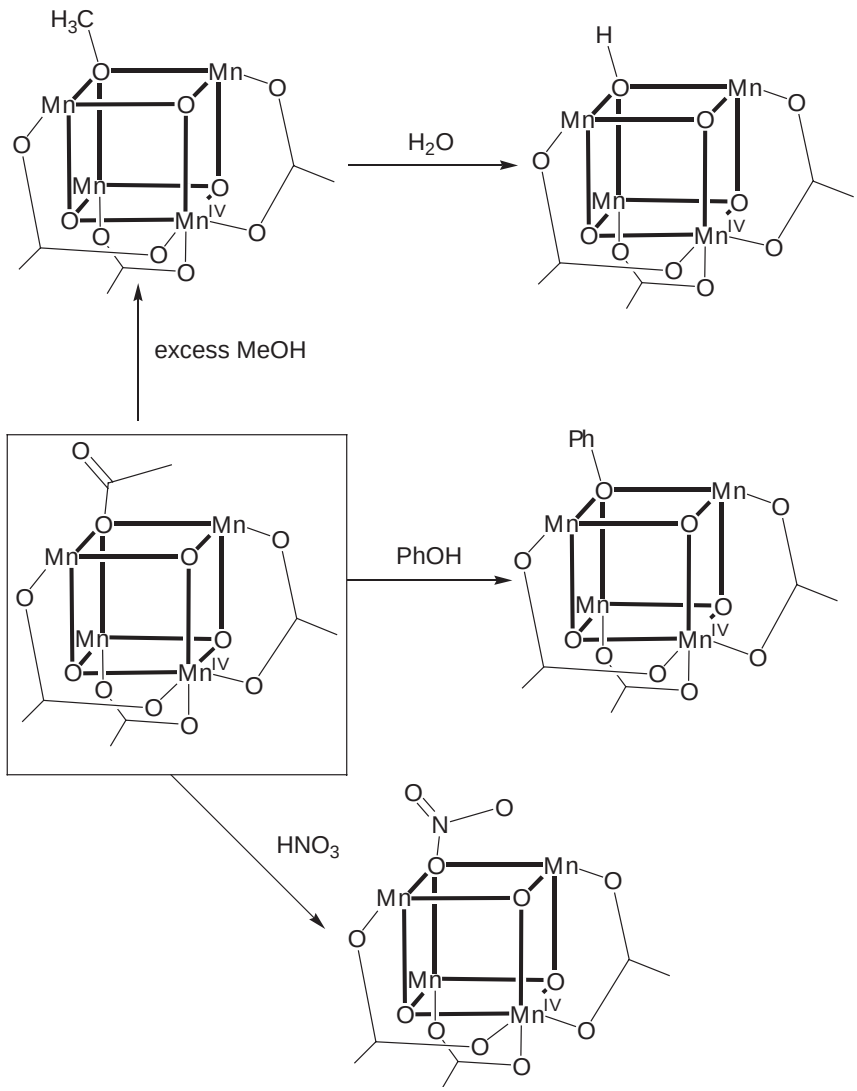
3.5:2:6 to obtain a pH of 9. Addition of $BaCl_2$ precipitated the complex as a red-brown solid. The Mn···Mn separation is 3.245 Å and Mn—O—Mn angle is ~104°. A ferromagnetic interaction was observed between the metal centers with a coupling constant of $+19\,cm^{-1}$.

5.1.5.3.2 Tetranuclear clusters

A large family of complexes is now known possessing a mixed-valent $[Mn^{III}{}_3Mn^{IV}O_3X]$ ($X = {}^{-}O_2CMe$,[198] ${}^{-}O_2CPh$,[199] ${}^{-}OH$,[200] ${}^{-}OMe$,[200] ${}^{-}OPh$, $NO_3{}^{-}$[201]) (**59**–**64**) core supported by the chelating ligand dibenzoylmethane (dbm^{-}) reported by Christou and co-workers (see Figure 10). The Mn ions in all these complexes can best be described to be trapped-valent in nature with a distorted cubane-like topology with Mn^{III} ions at the base of a tetrahedron and the Mn^{IV} ion at the apex. The Mn^{III} ions are characterized by longer bonds (average distance ~2.1 Å) compared to those surrounding the Mn^{IV} ion (average distance = 1.9 Å). The Mn^{IV} distances to the harder oxide ions are slightly shorter (~1.86 Å) than those bound to the carboxylate (~1.94 Å). The $Mn^{III}\cdots Mn^{III}$ separations range from ~3.1 Å to 3.2 Å while those between $Mn^{III}\cdots Mn^{IV}$ are ~2.7 Å to 2.8 Å. These distances closely resemble those found by EXAFS measurements of the S_2 state of the PSII active site[185] making it a potential structural model. In these complexes, Jahn–Teller elongation causes the axial bonds at the Mn^{III} ions to be significantly lengthened (average axial bonds = 2.2 Å, average nonaxial bonds = 1.9 Å) over the equatorial counterparts. There are three μ-carboxylates (Me, Ph, *p*-OMe-Ph, *p*-Me-Ph) that bridge adjacent Mn^{III}–Mn^{IV} pairs along with three chelating dbm^{-} that coordinate each Mn^{III} ion. The unique μ_3 site is occupied by variety of oxygen donor ligands like acetate, benzoate, methoxide, phenoxide, hydroxide, and nitrate. Typical Mn^{III}—O bond distances range between 2.1 Å and 2.3 Å. All of the complexes possess an effective C_{3v} symmetry in solution and display characteristic ^1H NMR spectra that enable their characterization and complete spectral assignment despite their expected broadness and wide range of chemical shifts. These clusters also possess a well-defined spin ground state $S = 9/2$ derived from ferromagnetic coupling between the Mn^{III} ions ($J = \sim 4$–$14\,cm^{-1}$) and antiferromagnetic interaction between adjacent Mn^{III} and Mn^{IV} pairs ($J = \sim -20$ to $-35\,cm^{-1}$). Furthermore, the near-parallel alignment of the three Jahn–Teller axes results in a high magnetic anisotropy ($D \sim -0.30$ to $-0.62\,cm^{-1}$) for these complexes. The relatively high spin, coupled with the high anisotropy, causes the distorted cubane complexes to display SMM behavior at low temperatures.[202] This observation has resulted in a tremendous interest in the study of magnetic properties for these complexes. Characteristic features of magnets such as appearance of hysteresis loops have been reported for these complexes at low temperatures ($T \sim 2.0$ K). The appearance of tunneling in this half-integer system that should not display quantum tunneling of magnetization (QTM) has been explained due

to higher-order anisotropic terms (rhombic parameter, E, and quartic term, B_4^o). Anisotropic energy barriers $U_{eff} \sim 20\,K$ have been reported. The all oxygen ligands containing $[Mn_3^{III}Mn^{IV}]$ cubanes have been prepared by alcoholysis, hydrolysis, and acidolysis reactions that are summarized in Scheme 2. Also, controlled potential electrolysis has also permitted the conversion of $[Mn_4O_2]^{8+}$ with a butterfly core to a distorted cubane-like complex with $[Mn_4O_3(O_2CR)]^{7+}$.[199] This has been suggested to mimic one of the basic features of S state catalytic water oxidation cycle, i.e., one-electron oxidation of tetranuclear Mn-oxo clusters. A comproportionation reaction involving Mn^{II} and Mn^{VII} (NBu_4MnO_4) sources has provided an easy route to the acetate-bridged $[Mn_4O_3(OAc)_4(dbm)_3]$ cluster.[203] The acetate at the μ_3 site is bridged in a $[\eta^1{:}\mu^3]$ manner while the benzoate binds $[\eta^2{:}\mu_3]$ that have been rationalized due to the steric interactions caused between the phenyl ring of dbm ligand and the carboxylate. Consequently, the $[Mn_4O_3(O_2CPh)]^{6+}$ core has an effective C_s symmetry. This is the lowest symmetry cluster reported in this family, which has a pronounced effect on the magnetic properties of the complex.[204] Magnetochemical studies reveal admixing of quantized states due to the greater rhombic E term enhancing quantum tunneling.

The synthesis of a $[Mn^{III}{}_2Mn^{IV}{}_2O_4]$ cubane-like complex, $[Mn_4O_4(O_2PPh_2)_6]$ (**65**), by Dismutes and co-workers has also been reported by adopting a "dimerization" strategy of two preformed $[Mn_2O_2]^{3+}$ units.[205] The addition of diphenylphosphinate salts to a solution of $[Mn_2O_2(bpy)_4](ClO_4)_3$ results in the formation of the cluster. No appreciable Jahn–Teller distortions are observed



Scheme 2

in the Mn—O bond lengths, and this absence appears not to be due to a superposition of nonequivalent Mn valences. Further support comes from the absence of appreciable differences in the anisotropic displacement factors for different O atoms, unlike the mixed-valence complex $[Mn_2O_2(phen)_4]^{3+}$, where these are 5–8 times larger for the axial metal ligand bonds. These features suggest that the valence electrons may be delocalized, yielding a rare example of a class III (delocalized) mixed-valence $Mn^{III}Mn^{IV}$ compound. This conclusion is supported by variable-temperature ^1H NMR spectra showing that in solution only one set of three paramagnetically shifted resonances for all 12 phenyl rings is observed. The Mn···Mn distances in the complex vary between 2.90 Å and 2.95 Å that are considerably longer than observed for both the di-oxo-bridged dimers (2.6–2.7 Å), as well as the tri-oxo-bridged Mn^{IV} dimer (2.29 Å). The Mn···Mn distances are comparable to the $Mn^{IV}{}_4$ cubanes embedded within the larger clusters of $Mn_{12}O_{12}$ and $Mn_8Fe_4O_{12}$ (2.82–2.99 Å) and to the central pair in the Mn_4O_2 butterfly complexes (see Section 5.1.6.2) (2.85 Å) both of which contain exclusively triply bridging oxo groups. Reaction of the $Mn_4O_4{}^{6+}$ cubane core complex $Mn_4O_4L_6$ (L = diphenylphosphinate, $Ph_2PO_2^-$) with a hydrogen atom donor, phenothiazine (pzH), has been shown to form the dehydrated cluster

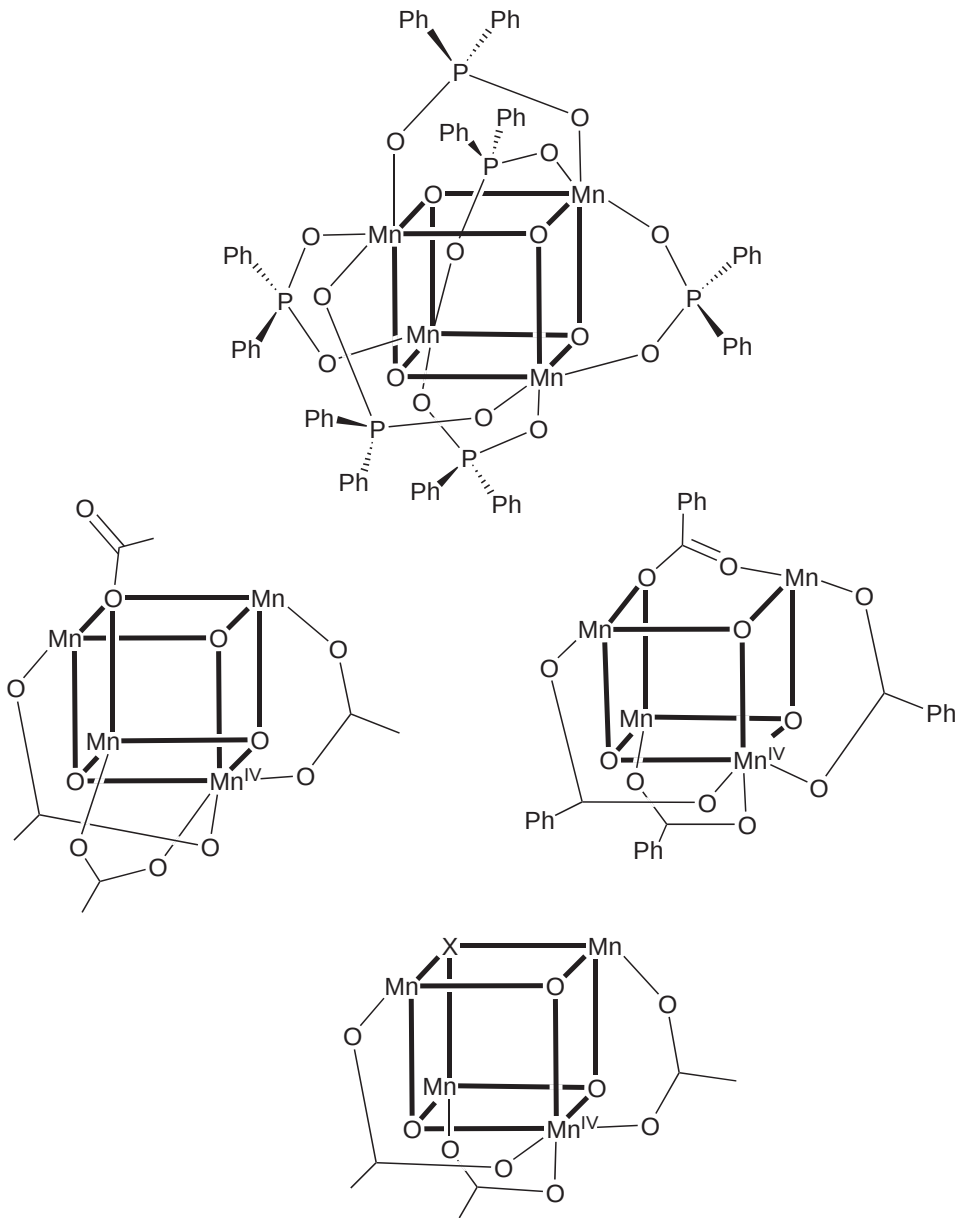


Figure 10 Cubane complexes with bridging phosphinato and carboxylato ligands.

$Mn_4O_2L_6$ which has lost two μ-oxo bridges by reduction to water (H_2O).[206] The formation of the latter was established by electrospray mass spectrometry, whereas FTIR spectroscopy confirmed the release of water molecules into solution during the reduction. UV–visible and EPR spectroscopies established the stoichiometry and chemical form of the pzH product by showing the production of four equivalents of the neutral pz· radical. By contrast, the irreversible decomposition of the cubane complex to individual Mn^{II} ions occurs if the reduction is performed using electrons provided by various proton-lacking reductants, such as cobaltocene, or when the reduction was performed electrochemically. Thus, the $Mn_4O_4^{6+}$ cubane complex undergoes coupled four-electron/four-proton reduction with the release of two water molecules, a reaction formally analogous to the reverse sequence of the steps that occur during photosynthetic water oxidation leading to O_2 evolution.[207]

5.1.5.3.3 Dodecanuclear clusters

The complex $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_n]$ (R = alkyl or aryl; $n = 3$ or 4), commonly referred to as Mn_{12}, represents a unique class of complexes possessing μ_3-oxo groups and bridging carboxylates as ligands. The first in this series of clusters, $[Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4]$ (**66**) (Mn_{12}ac), was prepared by Lis by treating $Mn(O_2CCH_3)_2{\cdot}4H_2O$ with $KMnO_4$ in a solvent consisting of acetic acid and water.[159] Subsequently, other Mn_{12} derivatives have been prepared by carboxylate exchange reactions.[208] These clusters have been extensively studied since the early 1990s primarily because of the ability of discrete molecules to exhibit superparamagnetic behavior at very low temperatures ($T < 4$ K) for which the term SMM has been coined.[209] These molecules possess the useful property of retaining their magnetization in the absence of an applied magnetic field, a classical property of a magnet. This slow relaxation has been attributed to their high-spin ground state (S) as well as high and negative magnetic anisotropy gauged by the parameter D (axial zero-field spitting).[210–212] This results in a significantly high barrier ($U_{eff} = S^2D$) for the relaxation of the magnetization that can be estimated from the Arrhenius relation. Consequently, this bistability may be useful as storage devices.[213] Moreover, these complexes are the first to display QTM, properties characteristic of mesoscopic magnetic particles.[214] The family of Mn_{12} complexes is now known to exist in three oxidation state levels. The neutral form of the complex $[Mn_4^{IV}Mn_8^{III}]$ (Mn_{12}) has a central $[Mn^{IV}{}_4O_4]$ cuboidal unit surrounded by a noncoplanar ring of eight Mn^{III} ions (Figure 11). There are 16 carboxylates that can be divided into two classes, eight of them are axial, and while the remaining eight are equatorial in nature. Monodentate water molecules bind to Mn^{III} ion in the outer ring complete the coordination environment. Several single-molecule magnets with the composition $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_x]$ ($x = 3$ or 4) exhibit two out-of-phase AC magnetic susceptibility signals, one in the 4–7 K region and the other in the 2–3 K region.[215] These correspond to slightly different anisotropic barriers. Jahn–Teller isomerism has been invoked to explain this effect. Ideally, the Jahn–Teller axes at Mn^{III} ions avoid the harder oxide ions and point themselves towards weakly bound carboxylate ligands. However, in certain cases the Jahn–Teller axes are directed oxide ions that may be due to crystal packing forces. In solution there is rapid ligand exchange and no evidence for the different isomeric forms of Mn_{12} complexes seen in the solid state.

It has been possible to substitute the axial carboxylates with a different carboxylate to form the mixed-carboxylate complexes $[Mn_{12}O_{12}(O_2CCHCl_2)_8(O_2CCH_2Bu^t)_8(H_2O)_3]$ (**67**) and $[Mn_{12}O_{12}(O_2CHCl_2)_8(O_2CEt)_8(H_2O)_3]$ (**68**).[216] Both the complexes contain a $[Mn_{12}O_{12}]$ core with the $CHCl_2CO_2^-$ ligands ordered in the axial positions and the RCO_2^- ligands (R = CH_2Bu^t or Et) in equatorial positions. There is a preference for the $CHCl_2CO_2^-$ ligands to occupy the sites lying on the Mn^{III} Jahn–Teller axes, and this is rationalized on the basis of the relative basicities of the carboxylate groups. ^{1}H NMR spectra show that although they are the main species present on dissolution, there is evidence for some ligand distribution between axial and equatorial sites, by intra- and/or intermolecular exchange processes. These complexes are synthesized by 1:1 reaction of carboxylate with the corresponding homocarboxylate species. All of the neutral Mn_{12} complexes possess a well-isolated spin ground state of $S = 10$ and $D = -0.40$ to $-0.50\,cm^{-1}$ and show characteristic SMM behavior, i.e., a frequency-dependant peak in out-of-phase AC susceptibility measurement studies as well as magnetic hysteresis loops. The energy barrier for magnetization reversal for the neutral derivatives is $\sim$42–50 cm^{-1} (60–72 K) and is the largest observed for any SMM so far. The cyclic voltammogram of the neutral species displays at least two

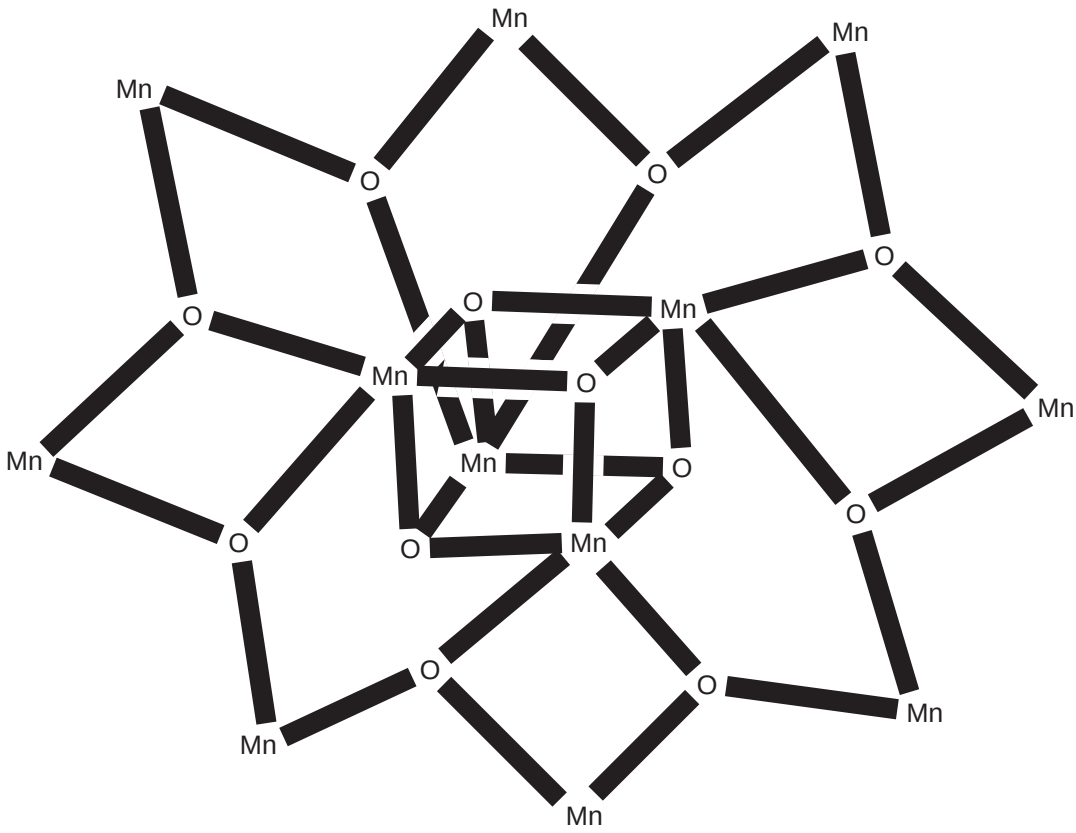


Figure 11 Core structure of Mn_{12} complex.

quasireversible reduction waves (one- and two-electron reduced). One-electron reduced forms of the cluster, $[Mn_{12}]^{1-}$, has since been crystallographically characterized.[217] These include $(PPh_4)[Mn_{12}O_{12}(O_2CEt)_{16}(H_2O)_4]$ (**69**) and $(PPh_4)[Mn_{12}O_{12}(O_2CPh)_{16}(H_2O)_4]\cdot 8CH_2Cl_2$ (**70**) complexes. Reduction is achieved by treating the neutral Mn_{12} derivatives with one equivalent of PPh_4I. The propionate-bridged one-electron reduced product possesses the mixed valence formulation $[Mn^{II}Mn_7^{III}Mn_4^{IV}]$. This was supported by the pronounced Jahn–Teller elongation of Mn^{III}—O bonds found for seven of the Mn atoms in the outer rings. In this case, the electron is trapped in the outer ring of the Mn_{12} molecule reducing one of the Mn^{III} to an Mn^{II} ion. The electron avoids the inner cuboidal core that possesses extremely strong Mn^{IV}—oxo bonds and a rigid $[Mn_4O_4]$ fragment. It has been argued that generation of Mn^{III} would then result in significant weakening of the strongest bonds due to the Jahn–Teller effect expected for an Mn^{III} ion. In contrast, for the benzoate system it was not clear whether a valence delocalized or trapped valence view is appropriate. This is because of disorder in both phenyl rings and solvate molecules, due to which it was difficult to use bond valence sum values to determine definitively the oxidation state of each Mn atom. The Mn_{12}^{1-} species possesses a spin ground state of $S = 19/2$ and is also an SMM with $D = -0.44\,cm^{-1}$ and an energy barrier of $\sim 58\,K$.[218] The two-electron version of the Mn_{12} cluster, Mn_{12}^{2-} $(PPh_4)_2[Mn_{12}O_{12}(O_2CCHCl_2)_{16}(H_2O)_4]$ (**71**) has also been reported by treating the neutral complex with two equivalents of PPh_4I.[219,220] Crystallization yields a mixture of two crystal forms, both of which have been structurally characterized as triclinic and monoclinic, respectively. They have also been characterized by a variety of physical techniques and their magnetic properties investigated. They possess a spin ground state $S = 10$, $D = -0.28\,cm^{-1}$, $g = 2.00$. In this case unperturbed molecular structures very similar to the neutral complex are also obtained with the added electrons being localized on two former Mn^{III} ions to give a trapped-valence $2Mn^{II}$, $6Mn^{III}$, $4Mn^{IV}$ oxidation state description. Magnetization vs. DC field sweeps on single crystals of the two forms gave hysteresis loops containing steps due to QTM. The step separations yielded D/g values of $0.087\,cm^{-1}$ and $0.14\,cm^{-1}$ for the forms, respectively, suggesting that the differences in U_{eff} are primarily caused by changes to D. Additionally, it has been noted that as gradual reduction of the Mn_{12} complex causes a reduction of the Jahn–Teller elongated Mn^{III} ions in the outer ring it results in a

concomitant lowering of the magnetoanisotropy along the series: $Mn_{12}{}^{0} < Mn_{12}{}^{1-} < Mn_{12}{}^{2-}$. The work demonstrates the sensitivity of the magnetic properties of these new $[Mn_{12}]^{2-}$ SMMs to subtle differences in their environment as determined by the precise packing, solvent molecules, and overall crystal symmetry space group.

It has been possible to incorporate Fe^{III} into the Mn_{12} complex to give a heterobimetallic cluster of the type $[Mn_8Fe_4O_{12}(O_2CMe)_{16}(H_2O)_4]$ (**72**).[221] This is obtained by treating $Fe(O_2CMe)_2$ with $KMnO_4$ (16.3:6.4 molar ratio). The molecule consists of a central $[Mn_4O_4]^{8+}$ cubane held within a nonplanar ring of eight alternating Mn^{III} and Fe^{III} ions by eight μ_3-O^{2-} ions. Peripheral ligation is provided by 16 μ-$MeCO_2^-$ and four terminal H_2O groups, the latter being ligated one each on the four Fe^{III} ions. The identification of the Fe^{III} ions was facilitated by the absence of a Jahn–Teller axial elongation as seen for the Mn^{III} ions. Cyclic voltammograms reveal quasireversible oxidation and quasireversible reduction processes that are observed at the same position as for the Mn_{12} species, implying the redox process to be occurring at the Mn centers. Magnetic studies indicate the spin ground state of $S = 2$ with $D = -1.8\,cm^{-1}$. The origin for such a drastic change in spin ground state of a complex by a simple metal ion substitution has been qualitatively explained on the basis of spin-frustration effects on butterfly complexes that are fused together in the dodecanuclear complex.

Although all of the Mn_{12} family of complexes described thus far have been observed with carboxylate as the bridging ligand, nitrate (NO_3^-) and the diphenylphosphinate group (Ph_2PO_2H) have been utilized to form $[Mn_{12}O_{12}(NO_3)_4(O_2CR)_{12}(H_2O)_4]$ and $[Mn_{12}O_{12}(O_2CMe)_8(O_2PPh_2)_8(H_2O)_4]$, respectively. This functionalization might prove very useful for a variety of further reactivity studies and applications, such as binding the complex to other species or surfaces without loss of the intrinsic Mn_{12} structure or magnetic properties. Site-selective carboxylate abstraction has been achieved from $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes by treatment with HNO_3 to form $[Mn_{12}O_{12}(NO_3)_4(O_2CR)_{12}(H_2O)_4]$ ($R = CH_2Bu^t$ (**73**) or Ph (**74**)) in excellent yield.[222] The replacement of the carboxylate group with nitrate causes insignificant perturbation of the magnetic properties, the complexes retaining their structural integrity along with their magnetic properties. The $[Mn_{12}O_{12}(O_2CMe)_8(O_2PPh_2)_8(H_2O)_4]$ (**75**) complex is derived by reacting Mn_{12}–acetate with eight equivalents of Ph_2PO_2H.[223] In this case, the acetate groups at the four axial Mn^{III}–Mn^{III} and four of the eight equatorial Mn^{III}–Mn^{III} carboxylate sites have been replaced by diphenylphosphinate groups, while the remaining equatorial sites and the four axial Mn^{IV}–Mn^{III} sites remain occupied by acetates. This results in a significant distortion of the $[Mn_{12}O_{12}]^{16+}$ core that is reflected in the bond angles and an increase of ~0.1 Å in all of the Mn^{III}–Mn^{III} distances, and is most apparent as a "bowing" in each of the linear Mn_4 units. Additionally, the complex has three distinct Jahn–Teller isomers, two of which cocrystallize in the same crystal emphasizing the small energy differences involved. In both cases, these "abnormally" oriented Jahn–Teller axes are located at the Mn^{III} centers with H_2O ligands, as has been observed for the previously reported examples of Jahn–Teller isomerism. Magnetically, it is similar to the all-carboxylate derivatized cluster with $S = 10$, $D = -0.41\,cm^{-1}$.

5.1.5.3.4 Hexadecanuclear cluster

The complex $[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3]\cdot 6H_2O$ $[Mn^{IV}{}_6Mn^{III}{}_{10}]$ (**76**) has been obtained upon the addition of $Bu^n{}_4NMnO_4$ to $Mn(NO_3)_2\cdot 4H_2O$.[224] The presence of alkoxide bridges here is rare in high-valent Mn clusters and probably responsible for the nuclearity obtained. The cluster contains 6 Mn^{IV} and 10 Mn^{III} ions held together by 14 μ_3-O^{2-}, 2 μ-O^{2-}, 4 μ-OMe^-, and 2 μ-OAc^- groups to give an approximately elliptical planar $[Mn_{16}O_{16}(OMe)_4(OAc)_2]^{18+}$ core (Figure 12). Peripheral ligation is completed by the remaining 14 μ-OAc^-, 2 μ-OMe^-, and 3 axial water and methanol molecules. Preliminary studies indicate presence of overall antiferromagnetic coupling and SMM behavior is observed at low temperatures. Frequency-dependant out-of-phase AC peaks or hysteresis data have not yet been reported for this cluster.

5.1.5.3.5 Higher nuclearity clusters

An aesthetically pleasing high-nuclearity mixed-valence complex of formula $[Mn_{21}O_{24}(OMe)_8(O_2CCH_2Bu^t)_{16}(H_2O)_{10}]$ (**77**) $[Mn^{IV}{}_9Mn^{III}{}_{12}]$ has also been reported.[225] The structure consists of an Mn core that is approximately planar and is ligated on the periphery by 16 μ-$O_2CCH_2Bu^t$ groups

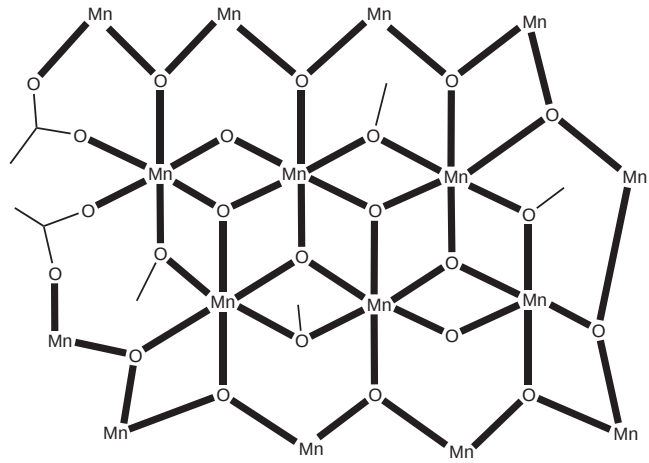


Figure 12 Core structure of $[Mn_{16}O_{16}(OMe)_6(OAc)_{16}(MeOH)_3(H_2O)_3]\cdot 6H_2O$ (**76**).

and 10 H_2O molecules. The complex is trapped valence, the Mn^{III} ions lying in the outer ring. The 21 Mn ions are not all in the same plane: the 9 Mn^{IV} ions and 2 Mn^{III} ions are coplanar, but the 2 Mn_5 crescents at top and bottom are slightly above and below this plane The structure can further be described as being composed of a $[Mn_{21}O_{24}(OMe)_8]$ core (Figure 13) as a CdI_2-like $[Mn_9{}^{IV}O_{20}]$ sheet held within a nonplanar $[Mn_{12}{}^{III}O_{12}]$ ring. There is thus a parallel between this cluster and the Mn_{12} complexes (see above). This complex is synthesized by the methanolysis of $[Mn_{12}O_{12}(O_2CCH_2Bu^t)_{16}(H_2O)_4]$ and has $S = 13/2$ and $D = -0.53\,cm^{-1}$, although no SMM behavior has been observed at $T > 1.8\,K$.

The largest Mn cluster known to date is $[Mn_{30}O_{24}(OH)_8(O_2CCH_2Bu^t)_{32}(H_2O)_2(CH_3NO_2)_4]$ (**78**) prepared by reacting $Mn(O_2CCH_3)_2\cdot 4H_2O$ and $KMnO_4$, followed by addition of *t*-butylacetic acid.[226] The complex is comprised of a $[Mn_{30}O_{24}(OH)_8]^{32+}$ core (Figure 14), with peripheral ligation provided by 32 *t*-butylacetate ligands, 4 nitromethane molecules, and 2 terminal H_2O molecules. The oxidation states of the manganese ions can best be described as trapped-valence $[Mn^{II}{}_3Mn^{III}{}_{26}Mn^{IV}]$. They have been assigned on the basis of relative Mn—O distances, bond valence sum calculations, and the presence of Jahn–Teller elongation axes on all 26 Mn^{III} centers. The metal ions are bridged by a combination of oxides and hydroxides. The coordination is terminated by *t*-butylacetate groups showing three types of binding mode: 24 are bridging 2 manganese ions in the familiar *syn,syn*-bridging mode, 6 are bridging 3 manganese ions in the *syn,syn,anti*-bridging mode, and 2 of them are monodentate to Mn^{II} ions. Magnetic studies indicate $S = 7$, $D = -0.79\,cm^{-1}$ and SMM behavior is seen at $T < 1.7\,K$. However, the theoretical model for the fitting assumes that the spin ground state is well isolated, which does not seem to be the case here, as commonly observed in high-nuclearity systems, especially those containing Mn^{II} for which exchange interactions are found to be weak.

5.1.5.4 Nitrogen, Oxygen, and Halide Ligands

A dinuclear bis-oxo-bridged Mn(III,IV) complex supported by two bpy ligands, $[Mn_2O_2(OAc)Cl_2(bpy)_2]$ (**79**), was synthesized where each Mn ion is bonded to a chloride ligand.[173] The chloride ions are *trans* to each other. The Mn···Mn separation is 2.67 Å and the Mn—O—Mn angle is about ~94.5°. The Mn—Cl bond distance is 2.3 Å on average. The manganese centers are antiferromagnetically coupled to give an $S = 1/2$ ground state similar to other bis-μ-oxo Mn(III,IV) complexes, and it has a multiline EPR signal in frozen solution below liquid N_2 temperature.

The complex $(H_2Im)_2[Mn_4O_3Cl_6(HIm)(O_2CMe)_3]\cdot 1.5MeCN$ (**80**) (H_2Im^+ = imidazolium cation) was the first reported in this series of distorted cubane complexes containing the $[Mn^{III}{}_3Mn^{IV}(\mu_3\text{-}O)_3X]^{6+}$ core by Christou and co-workers (X = Cl^- (**80**), Br^- (**81**)).[158,227,228] All of these complexes are prepared by the reaction of a μ_3-oxide $Mn_3{}^{III}$complex with Me_3SiC1, which leads to a disproportionation to give the $Mn^{IV}Mn_3{}^{III}$ complex and an Mn^{II} product. The reaction of $Mn(O_2CCH_3)_3\cdot 2H_2O$ with Me_3SiCl followed by addition of imidazole gives $(H_2Im)_2[Mn_4O_3Cl_6(HIm)(O_2CMe)_3]\cdot 1.5MeCN$ where H_2Im^+ is the imidazolium cation. Reaction of $[Mn_3O(O_2CR)_6(py)_3](ClO_4)$ (R = Me, Et) with Me_3SiCl leads to $[Mn_4O_3Cl_4(O_2CMe)_3(Im)_3]\cdot 3/2$

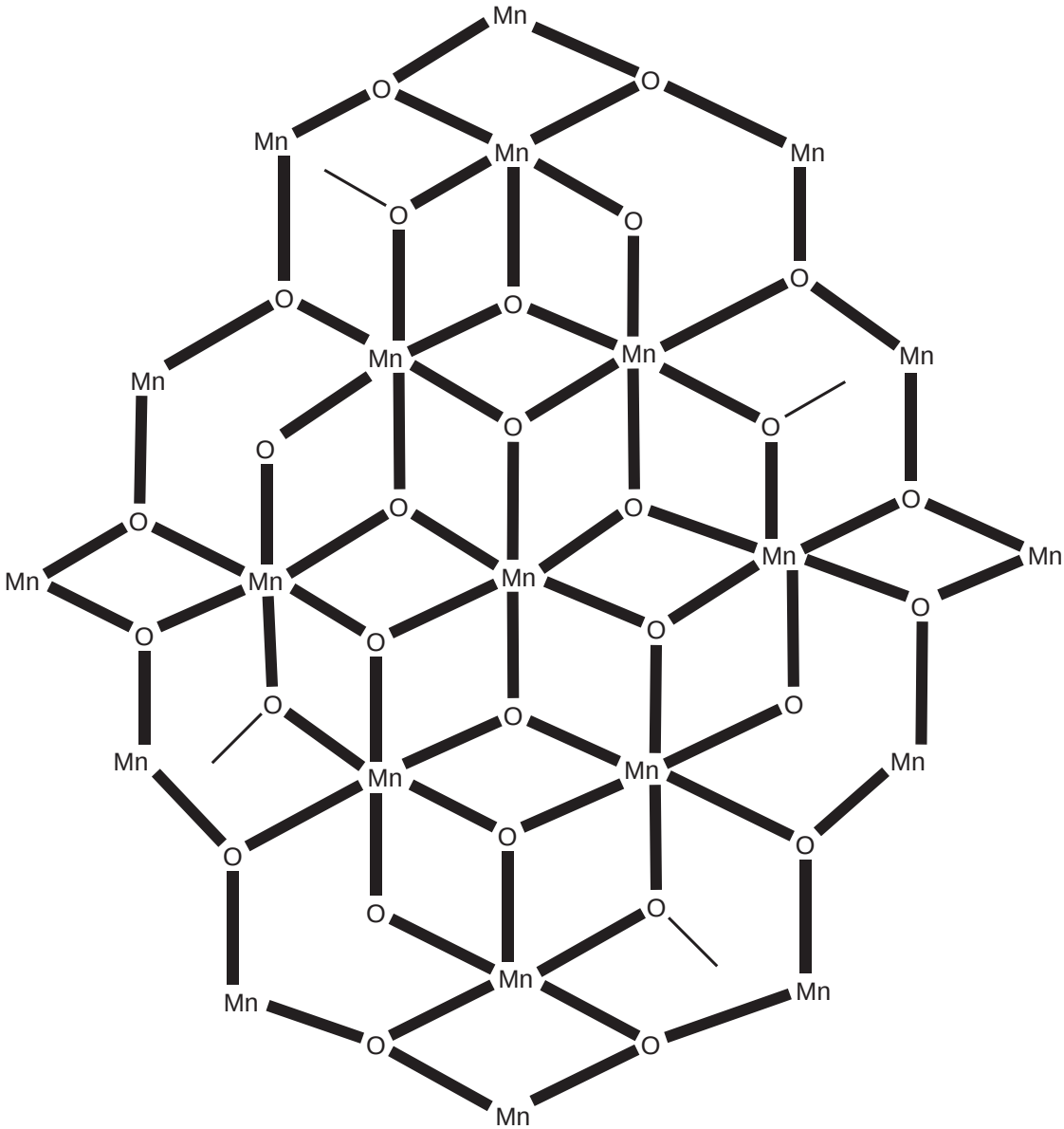


Figure 13 Core structure of $[Mn_{21}O_{24}(OMe)_8(O_2CCH_2{}^tBu)_{16}(H_2O)_{10}]$ (**77**) complex.

MeCN (**82**) and $[Mn_4O_3Cl_4(O_2CEt)_3(Im)_3]\cdot 5/2MeCN$ (**83**). A similar procedure but followed by addition of imidazole yields $[Mn_4O_3Cl_4(O_2CMe)_3(Im)_3]\cdot 5/2MeCN$. The central $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}C1)]^{6+}$ core of the anion in the complex consists of a Mn_4 pyramid with the Mn^{IV} ion at the apex, a μ_3-Cl^- ion bridging the basal plane, and a μ_3-O^{2-} ion bridging each of the remaining three faces. The Mn^{IV} ion has six oxygen atom ligands, three from the three μ_3-O^{2-} ions and three from the bridging acetates. Typical bond distances and structural information pertaining to these cubanes along with their biological relevance have been described in previous Section 5.1.5.3.2. The terminal imidazole ligand has also been replaced by pyridine in an isostructural complex, $[Mn_4O_3\text{-}Cl_4(O_2CMe)_3(py)_3]\cdot MeCN$ (**84a**).[158,229] The yield of the reaction can be improved if MeCOCl is used instead of Me_3SiCl. A family of complexes with arene-carboxylate ligation $[Mn_4O_3Cl_4(O_2CR)_3(py)_3]$ is also reported (R = 3,5-Cl_2-Ph, (**85**), Ph (**86**), 4-F-Ph (**87**), and 3,5-F_2-Ph (**88**)).[230] The presence of the aromatic rings in the ligand framework provides an additional handle for ^1H NMR interpretations. Studies conducted on these complexes show that the observed spectra can be interpreted using a spin delocalization mechanism. Contact shifts via π-delocalization as well as dipolar shifts are contributors to the chemical shifts. Treatment of $[Mn_3O(OAc)_6(py)_3](ClO_4)$ in MeCN with Me_3SiCl followed by addition of H_2O and acetic acid

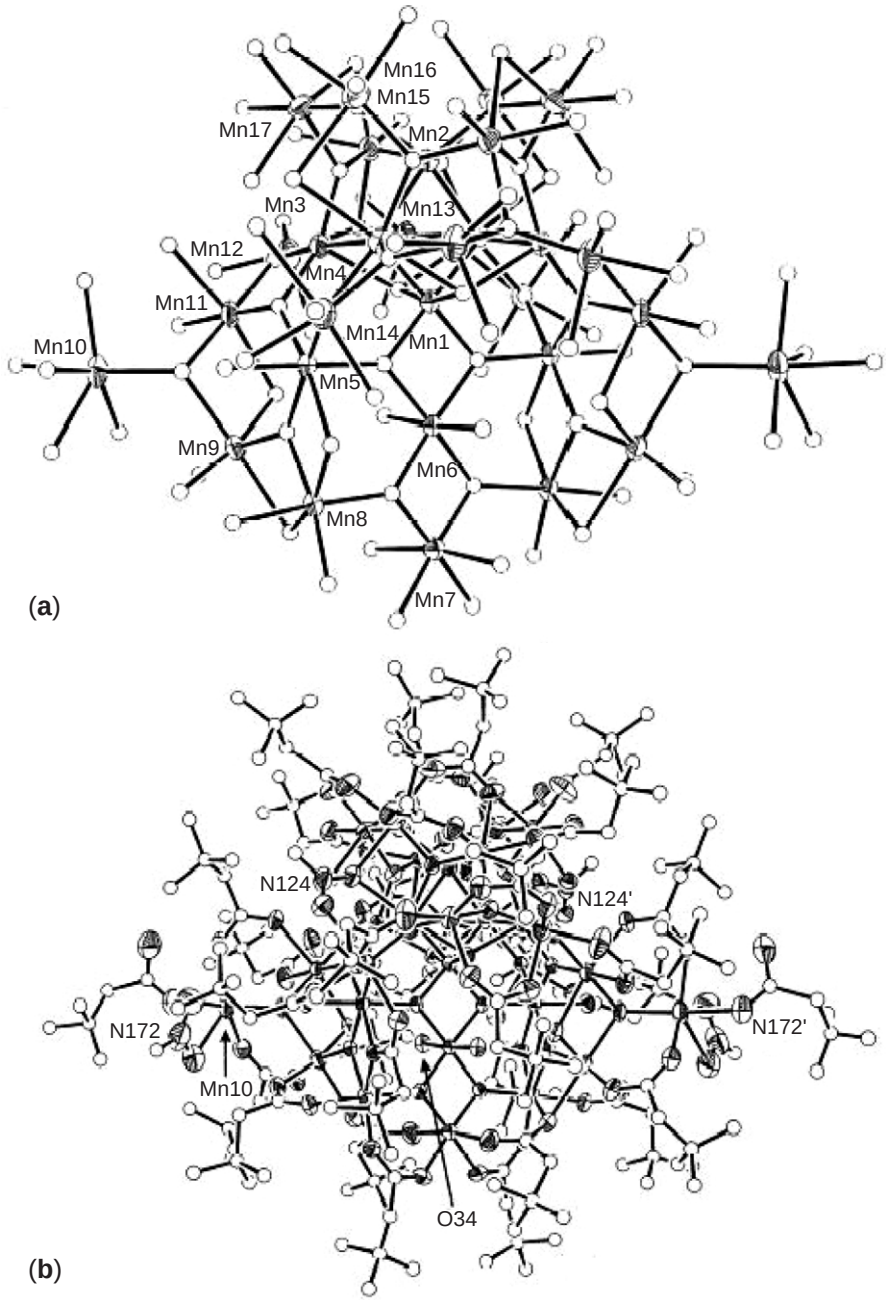


Figure 14 ORTEP representations: (a) the core and (b) complete complex $[Mn_{30}O_{24}(OH)_8(O_2CCH_2Bu^t)_{32}(H_2O)_2(CH_3NO_2)_4]$ (**78**) showing 50% probability ellipsoids.

results in crystallization of $(pyH)_3[Mn_4O_3Cl_7(OAc)_3]\cdot 2MeCN$ (**89**). As mentioned in the previous section, the distorted cubane class of complexes with an $S = 9/2$ ground state straddle the interface between classical and quantum mechanical behavior because they display quantum tunneling of magnetization and quantum phase interference. In this regard, QTM can be advantageous for some potential applications of SMMs, e.g., in providing the quantum superposition of states required for quantum computing. However, it is a disadvantage in other applications, such as information storage, where it would lead to information loss. Thus it is important to both understand and control the quantum properties of SMMs. In this respect, Wernsdorfer and co-workers have reported that $[Mn_4O_3Cl_4(O_2CEt)_3py_3]$ (**84b**)[158] behaves as a supramolecular SMM dimer in which antiferromagnetic coupling between the two components results in quantum behavior different from that of the individual SMMs. The experimental observations and further

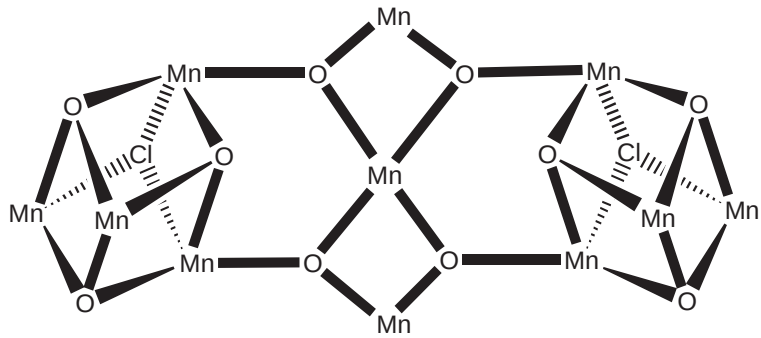


Figure 15 Core structure of $[Mn_{11}O_{10}Cl_2(OAc)_{11}(bpy)_2(MeCN)_2(H_2O)_2]^{2+}$ (**93**).

theoretical analysis suggest a means of tuning the QTM in SMMs. This system may also prove useful for studying quantum tunneling of relevance to mesoscopic antiferromagnets.[231]

The cubanes of the type $[Mn_4O_3X(O_2CR)_3(dbm)_3]$ ($X = F^-$ (**90**),[198] Cl^- (**91**), Br^- (**92**);[232] R = Me, Ph) containing both oxygen and halide atoms reported by Christou and co-workers have been prepared by a disproportionation reaction triggered by carboxylate abstraction from the $[Mn^{III}_4]$ butterfly clusters. They can also be prepared by ligand exchange reactions using Me_3SiX reagents from $[Mn_4O_3(O_2CR)_4(dbm)_3]$ complexes. Both of these reactions are initiated by treatment with Me_3SiX reagents that utilize the strength of Si—O bonds over Si—X ($X = Cl^-$, Br^-). Preparation of the F^- derivative requires a stronger fluoride donor, diethylammonium sulfur trifluoride (DAST). An analogous procedure involving addition of mineral acids (HX) on butterfly complexes and ligand exchange reaction on carboxylate-bridged distorted cubane clusters has also been reported.[201] The results have shown that the identity of the bridging ligand, X^-, has minimal influence on the resultant structures, magnetic properties, ^1H NMR and EPR spectral properties, or the redox behavior. All the complexes display a spin ground state of $S = 9/2$.

Treatment of $[Mn_4O_2(OAc)_7(bpy)_2](ClO_4)\cdot 3H_2O$ with Me_3SiCl in acetonitrile resulted in the high-valent $[Mn_{11}O_{10}Cl_2(OAc)_{11}(bpy)_2(MeCN)_2(H_2O)_2](ClO_4)_2$ (**93**) complex.[233] The crystal structure shows that two $[Mn_4O_3Cl]^{6+}$ cubane units are bridged by a nearly linear $[Mn_3O_4]^+$ unit to give the $[Mn^{III}_9Mn^{IV}_2]^{35+}$ core. The manganese centers in each cubane unit that are ligated to bpy ligand are in the +4 state. A schematic representation is shown in Figure 15.

5.1.6 OXIDATION STATE III

5.1.6.1 Introduction

The coordination chemistry of manganese(III) has been increasingly studied in an effort to simulate the biological systems that have been found to contain this oxidation state or go through this oxidation state in their catalytic cycles. However, the growth of manganese(III) chemistry has been slow due to the fact that manganese(III) is prone to disproportionation, particularly in aqueous solution, into manganese(IV) (as stable MnO_2) and manganese(II). Similarly, the synthesis of manganese(III) complexes from the oxidation of manganese(II) starting materials simply leads to the formation of insoluble and very stable MnO_2. While many of the manganese(III) complexes that have been discovered are polynuclear, mononuclear complexes of manganese(III) can be stabilized by Schiff base ligands, nitrogen-based ligands, and macrocyclic ligands. Di- and polynuclear complexes of manganese(III) require detailed investigation by spectroscopic and X-ray structural methods to confirm their structures. This is due to their propensities to be in mixed-valence states such as manganese(II,III) or manganese (III,IV) as well as the complex nature of the chemistry involved.

Manganese(III) has a d^4 electronic configuration and thus its octahedral complexes in the high-spin state, like those of copper(II), undergo a Jahn–Teller distortion. In fact, this distortion and the absence of an EPR signal in the regular X-band frequency often serve to identify manganese(III) centers in complexes with mixed valence states. There are a few examples of low-spin complexes of manganese(III) mostly with relatively high-field ligands, such as CN^-. High-spin manganese(III) complexes have spin-allowed *d–d* transitions and thus have some color compared their manganese(II)

analogues. The spin-only magnetic moment of the manganese(III) aqua ion is 4.9 μ_B and all high-spin complexes of manganese(III) have magnetic moments very close to this value. In general, manganese(III) complexes are good oxidizing agents and also act as strong Lewis acids. The labile nature of the manganese(III) center is indicated by the high water exchange rate constant, 100 times slower than manganese(II) center but 1,000 times faster than manganese(IV) center. The most commonly observed coordination numbers of manganese(III) are 5 or 6.

In this section, the treatment of complexes of different nuclearities is based on the ligand systems involved, but this is occasionally arbitrary as two different ligands may be present. The structures and abbreviations of ligands referred to in this section are shown in Figures 2 and 3 and 16–19.

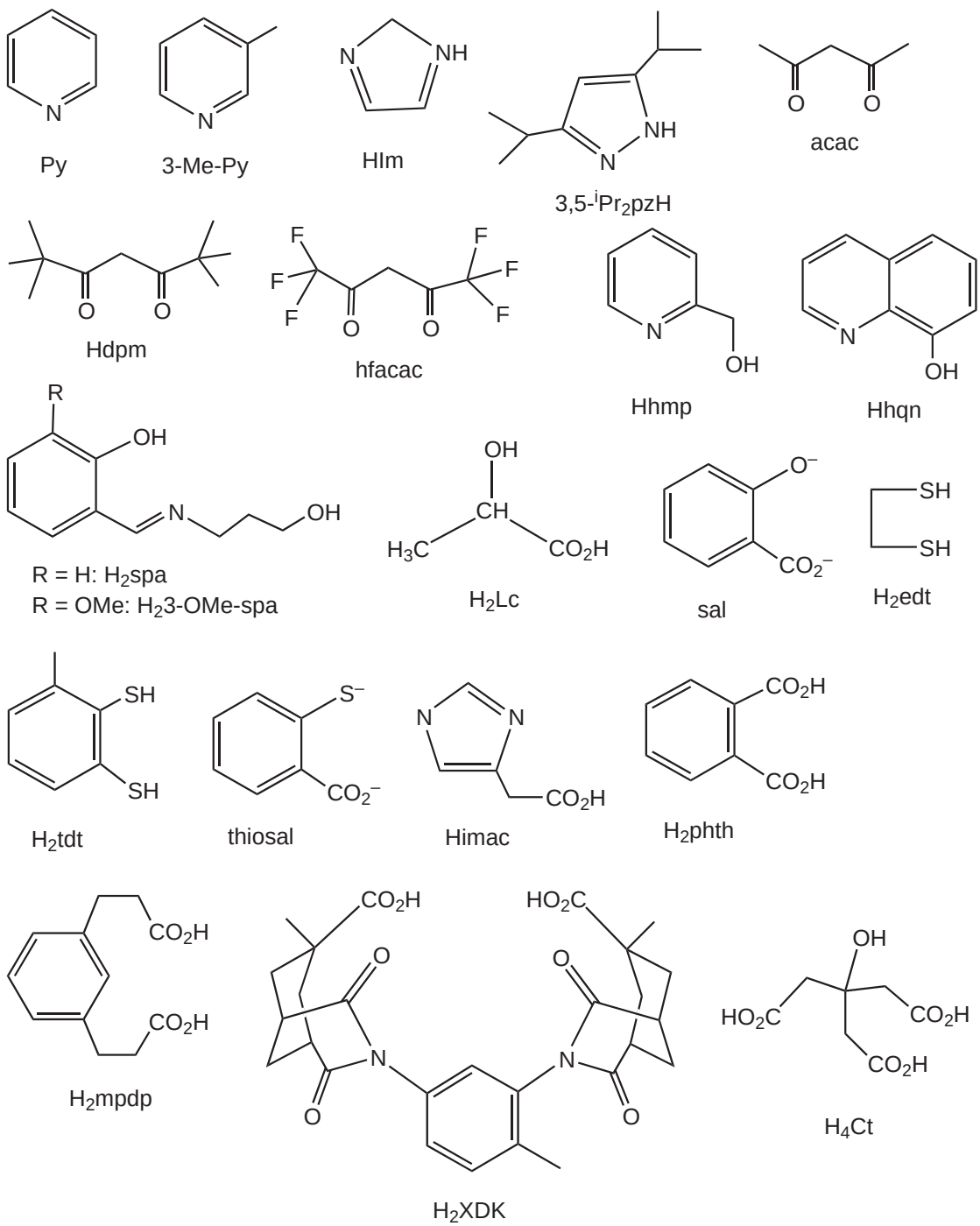


Figure 16

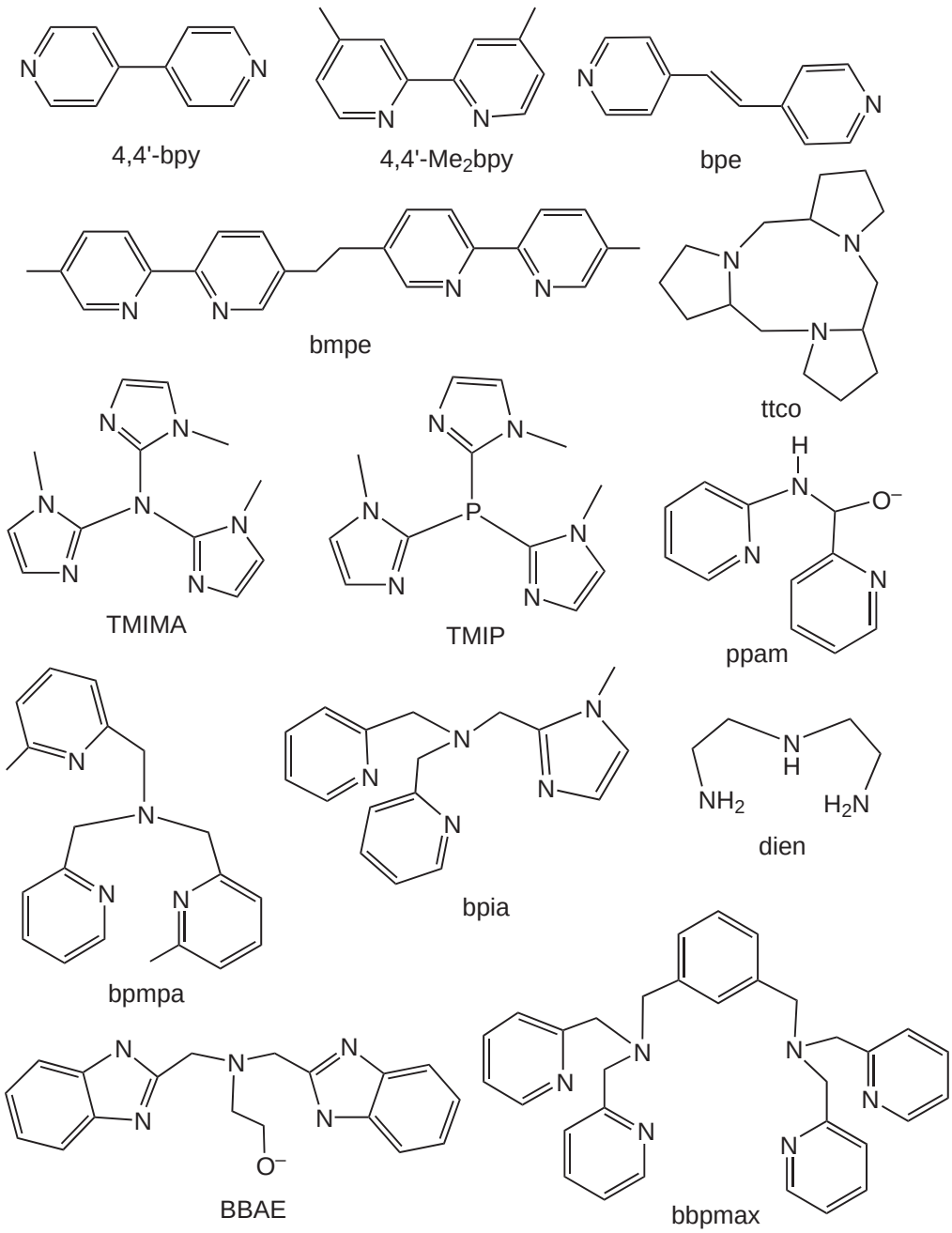


Figure 17

The chemistry of manganese(III) is dominated by dinuclear, trinuclear, and tetranuclear complexes and the core types observed are shown in Figures 20–22. Only a few complexes are reported with nuclearities >5 and there are as yet no known examples of pentanuclear manganese complexes. While there are three core types for dinuclear manganese(III) complexes with an (μ_2-O^{2-}) ion, no manganese(III) complexes with nuclearity >2 contain an (μ_2-O^{2-}) ion. There are no new manganese(III) complexes with carbon or tertiary phosphine ligands reported for the period of 1984 to the early 2000s.

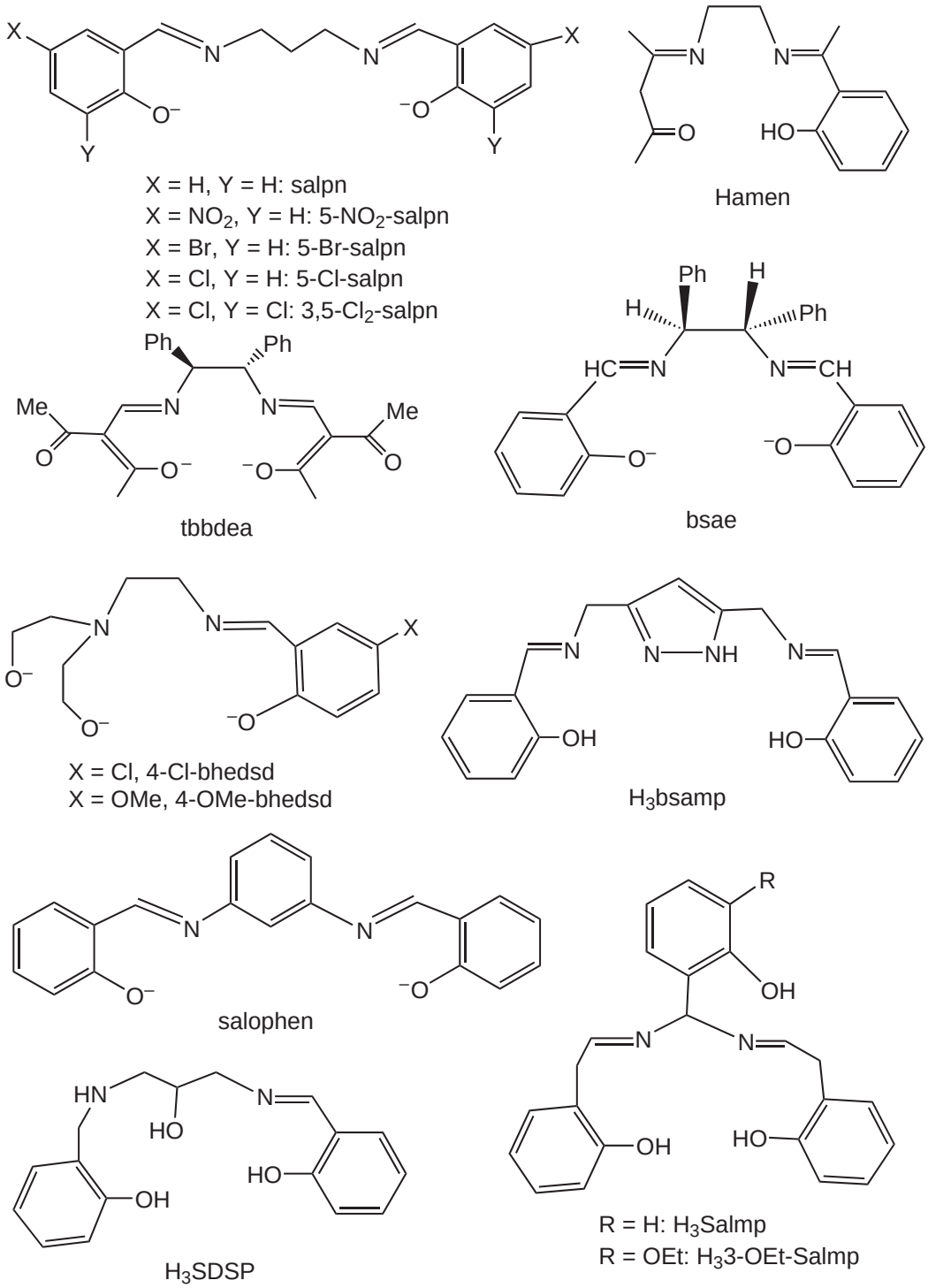
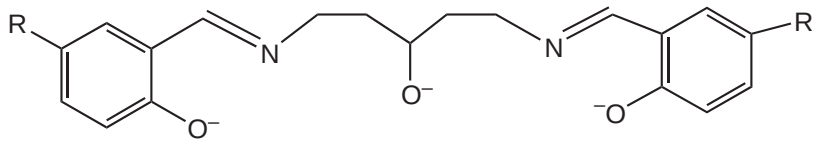


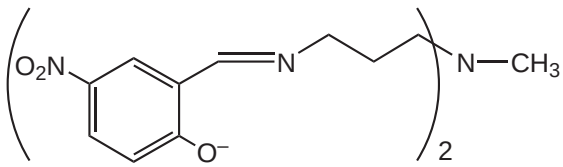
Figure 18

5.1.6.2 Oxygen Donor Ligands

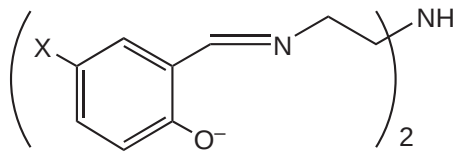
Manganese(III) complexes with a variety of oxygen ligands comprise the largest group next to those with mixed donor set polydentate ligands. The majority of these complexes are polynuclear.



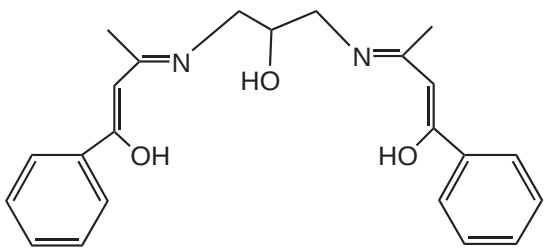
R = H: BSP; X = Cl: BCSP



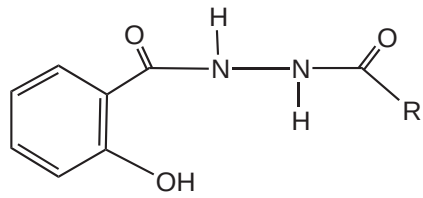
5-NO_2-sadpen



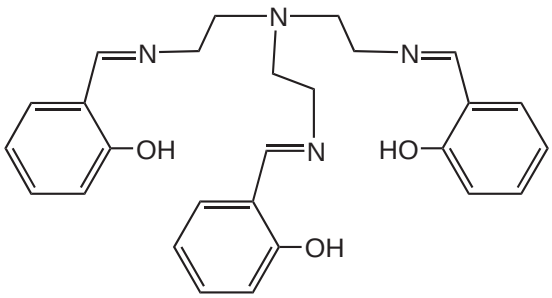
X = H, Saldien
X = NO_2, 5-NO_2-Saldien



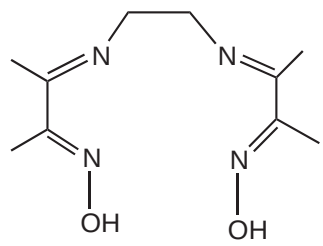
H_3bbdp



R = H, H_3fshz
R = CH_3, H_3ashz
R = C_2H_5, H_3pshz
R = C_6H_5, H_3bshz



H_3Saltren



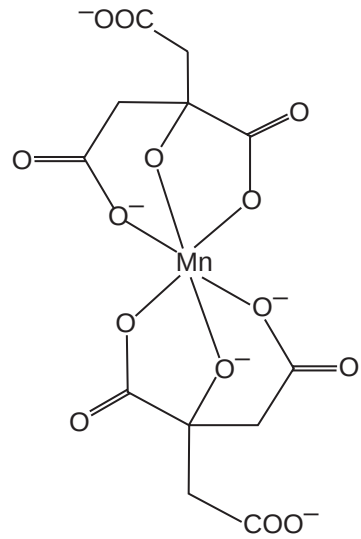
H_2bamen

Figure 19

5.1.6.2.1 Carboxylates

In order to isolate mononuclear complexes, the carboxylate has to be at least bidentate. However, there have been no new mononuclear manganese(III) complexes of simple carboxylates reported for the period 1984 to the early 2000s. The mononuclear complexes reported for this period are mostly with hydroxycarboxylate or β-diketone and related ligands. Examples of the former ligand type include $(NH_4)_5[Mn(Ct)_2]\cdot 2H_2O$ (**94**) (where H_4Ct = citric acid).[249] The structural data for this and other mononuclear Mn^{III} complexes are summarized in Table 3, and magnetic and spectroscopic data are displayed in Table 4. The manganese center in the anion of (**94**) is six coordinate and is bound by two fully deprotonated citrate ligands in a distorted octahedral fashion.

The chemistry of manganese(III) with monodentate carboxylates, such as acetate and benzoate or their derivatives, results in the formation of complexes with nuclearities of 2, 3, 4, 6, 7, 8, 9, 10, and 18. The chemistry of polynuclear carboxylate complexes is too extensive to detail here and coverage is confined to a brief discussion of the structural types involved.



(**94**)

(i) Dinuclear complexes

Dinuclear manganese(III) complexes with carboxylates fall into two categories: (i) those with one or two alkoxo bridge(s) and (ii) those with an (μ_2-O^{2-}) bridge. Structural, magnetic, and spectroscopic properties of some selected complexes are summarized in Tables 5 and 6. For both types, bridging carboxylates (one or two) are also present (see Figure 20). With the exception of the complex

Table 3 Structural information of selected mononuclear manganese(III) complexes.

Compound	*C.N. (geometry)*[a]	*Donor set*	*Mn–O* (Å)	*References*
$(NH_4)_5[Mn(Ct)_2]\cdot 2H_2O$	6 (octahedral)	O_6	1.885(1) 1.945(1) 2.224(1)	249
$(NEt_3H)_2[Mn(biphen)_2$ (biphenH)]	5 (trigonalbi pyramidal)	O_5	1.880(10)–1.984(9)	315
$[Mn(hfacac)_3]$	6 (octahedral)	O_6	1.9063(24)–2.1469(25)	317
$[Mn(Me_3tacn)(acac)$ $(H_2O)](ClO_4)_2$	6 (octahedral)	N_3O_3	2.005(4) 1.790(5) 2.067(5)	319
[Mn(5-NO_2-sadpen)(OH)]	6 (octahedral)	N_3O_3	1.827(3) 2.127(3) 1.920(3)	355
$[Mn(bsae)](PF_6)$	4 (square planar)	N_2O_2		370
$[Mn(salen)Cl]\cdot CH_3CN$	5 (square pyramidal)	N_2O_2Cl	1.878(2) 1.906(2)	340
[Mn(tbbdea)Cl]	5 (square pyramidal)	N_2O_2Cl		341
$(PPh_4)[Mn(thiosal)_2(HIm)]\cdot 2CH_2Cl_2$	5 (square pyramidal)	NO_2S_2	1.948(5) 1.932(5)	327
[Mn(salen)(S-p-NO_2-C_6H_4)]·CH_2Cl_2	5 (square pyramidal)	N_2O_2S	1.875(1) 1.883(1)	328
$(NEt_4)[Mn(edt)_2(HIm)]$	5 (square pyramidal)	NS_4		371
$[Mn(ppam)_2](ClO_4)$	6 (octahedral)	N_4O_2	1.856(3)	372
[Mn(3,5-iPr_2pzH) (HB(3,5-iPr_2pz)$_3$)(O_2)]	6 (octahedral)[b]	N_4O_2	1.851(5) 1.850(6)	332
cis-$[Mn(phen)_2Cl_2](NO_3)_2$ ·2.5CH_3CO_2H	6 (octahedral)	N_4Cl_2		373
$[Mn(terpy)(N_3)_3]$	6 (octahedral)	N_6	1.959(3)–2.258(2)	331

[a] C.N. = coordination number. [b] This is a six–coordinate structure with a side–on peroxo adduct.

Table 4 Selected physical properties of mononuclear manganese(III) complexes.

Compound	μ_{eff}, (μ_B)[a]	*UV–vis*[b] $\lambda(\varepsilon, M^{-1}cm^{-1})$, nm	*References*
$(NH_4)_5[Mn(Ct)_2]\cdot 2H_2O$		428(170), 520(59), 730(25)	249
$(NEt_3H)_2[Mn(biphen)_2(biphenH)]$	4.94	412(3370), 546(2080)	315
$(PPh_4)[Mn(thiosal)_2(HIm)]\cdot 2CH_2Cl_2$	5.11	415sh (2940), 450(2760), 500(2500)	327
$[Mn(salen)(S\text{-}p\text{-}C_6H_4NO_2)]\cdot CH_2Cl_2$	4.71[c]	550sh, 880	328
$[Mn(5\text{-}NO_2\text{-}sadpen)(OH)]$	5.07	363(23000)	355
$[Mn(Me_3tacn)(acac)(H_2O)](ClO_4)_2$	5.10	400sh (500), 530sh (300), 1050(273)	319
cis–$[Mn(phen)_2Cl_2](NO_3)_2\cdot 2.5CH_3CO_2H$	5.07	525(167)	373
$(NEt_4)[Mn(edt)_2(HIm)]$	4.97	290sh (4490), 355(13300), 390sh (6740), 610(545)	371
$[Mn(ppam)_2](ClO_4)$	4.95	460sh, 560(25), 800(14)	372
$[Mn(acac)_3]$	4.91	278(16491), 319(14490), 399(1941), 534(425)	374
$[Mn(pic)_3(H_2O)]$	4.90	260(17430), 428(380), 518(202)	374

[a] Spin only magnetic moment at around 298 K for the compound in the solid state. [b] In solution. [c] Measured in solution.

Table 5 Structural parameters for dinuclear manganese(III)–carboxylato complexes.

Compound	*Mn···Mn* (Å)	*Mn–O$_b$* (Å)	*Mn–O$_{carb}$* (Å)	*Mn–O$_b$–Mn* (deg.)	*References*
bis(μ-alkoxo)(μ-carboxylato)					
$(TMA)_3[Mn_2(Lc)_4(HLc)]\cdot H_2O$	3.094(4)	1.88(1) 2.080(9) 2.167(9) 1.81(1)	2.13(1) 2.05(1)	99.5(4) 101.6(3)	250
$[Mn_2(BCSP)(OCH_3)(OAc)(CH_3OH)(ClO_4)]$	2.921(2)	1.940(4) 1.905(5) 1.929(5) 1.925(5)	2.120(5) 2.123(6)	98.0(2) 99.4(2)	251
$[Mn_2(BSP)(OCH_3)(OAc)(CH_3OH)](ClO_4)$	2.931(2)	1.953(4) 1.920(5) 1.956(4) 1.935(5)	2.159(6) 2.172(6)	97.2(2) 99.0(2)	252
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)_2](Br)$	2.943(3)	1.953(7) 1.948(9) 1.958(7) 1.946(9)	2.140(10) 2.173(10)	101.6(2) 101.6(2)	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)_2](I)$	2.933(2)	1.928(7) 1.943(8) 1.962(8) 1.901(7)	2.179(9) 2.128(9)	97.8(3) 99.4(3)	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)(NCS)]$	2.940(3)	1.937(6) 1.934(6) 1.928(6) 1.969(7)	2.121(6) 2.209(6)	97.7(2) 99.0(3)	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)_2(N_3)]$	2.955(3)	1.952(8) 1.960(8) 1.957(8) 1.934(9)	2.149(10) 2.084(10)	97.9(3) 99.0(4)	253
$[Mn_2(5\text{-}Br\text{-}SALPN)(OCH_3)(OAc)(MeOH)_2](Br)$	2.932	1.934(4) 1.928(5) 1.935(4) 1.920(5)	2.146(5) 2.153(2)	98.3(2) 99.3(2)	254

Table 5 continued

Compound	*Mn···Mn* (Å)	*Mn–Ob* (Å)	*Mn–O_{carb}* (Å)	*Mn–O_b–Mn* (deg.)	*References*
Bis(μ-alkoxo)bis(μ-carboxylato)					
$[Mn_2(3\text{-OMe-spa})_2(OBz)_2]$	2.8720(15)	1.896(2) 1.939(2)	2.216(3) 2.262(3)		256
μ(oxo)(μ-carboxylato)					
$[Mn_2O(OAc)(TMIMA)_2](ClO_4)_2\cdot 2CH_3CN$	3.2503(8)	1.784(3) 1.789(3)	2.029(3) 2.042(4)	130.9(2)	257
$[Mn_2O(OAc)(bispicen)_2](ClO_4)_3$	3.276(3)	1.801(3)	2.031(5)	130.8(4)	258
$[Mn_2O(OAc)(bispicMe_2en)_2](ClO_4)_3$	3.29(1)	1.79(2)	1.90(3)	133(3)	258
$[Mn_2O(OAc)(bpia)_2](ClO_4)_3\cdot CH_3CN$	3.2544(8)	1.785(2)	2.028(2)	131.0(1)	259
(μ-oxo)bis(μ-carboxylato)					
$[Mn_2O(OAc)_2(bpy)_2(H_2O)(S_2O_8)]\cdot H_2O$	3.145(5)	1.735(10) 1.810(10)	1.949(12) 2.147(11) 1.933(11) 2.152(12)	125.1(6)	266
$[Mn_2O(OAc)_2(H_2O)_2(bpy)_2](PF_6)_2\cdot 1.75H_2O$	3.132(?)	1.781(5) 1.784(5)	2.142(6) 1.937(5) 1.939(5) 2.174(6)	122.9(?)	263
$[Mn_2O(OAc)_2(H_2O)_2(bpy)_2](ClO_4)_2$	3.152(2)	1.793(4) 1.800(4)	2.175(4) 1.946(4) 1.939(4) 2.164(4)	122.7(2)	267
$[Mn_2O(O_2CC_6H_5)_2(N_3)_2(bpy)_2]\cdot MeCN\cdot 4H_2O$	3.153(4)	1.802(4)	2.131(7) 2.043(7)	122.0(5)	267,268
$[Mn_2O(OAc)_2Cl_2(bpy)_2]\cdot CH_3COOH\cdot H_2O$	3.154(4)	1.788(11) 1.777(12)	2.214(12) 2.196(13) 1.955(13) 1.934(13)	124.3(7)	267
$[Mn_2O(OAc)_2(HB(pz)_3)_2]\cdot 4CH_3CN$	3.159(1)	1.773(2) 1.787(2)	2.044(2) 2.083(2) 2.085(3) 2.053(2)	125.1(1)	261
$[Mn_2O(OAc)_2(HB(pz)_3)_2]\cdot CH_3CN$	3.175(1)	1.790(3)	2.001(6) 2.133(6)	125.0(3)	261
$[Mn_2(\mu\text{-}O)(OAc)_2(tacn)_2](ClO_4)_2$	3.084(3)	1.80(1)	1.94(1) 2.05(1)	117.9(2)	260
$[Mn_2(\mu\text{-}O)(OAc)_2(Me_3tacn)_2](ClO_4)_2\cdot H_2O$	?	1.810(4)	2.047(4)	120.9(1)	260
$[Mn_2(\mu\text{-}O)(OAc)_2(Me_3tacn)_2](I_3)I\cdot H_2O$	3.096(2)	1.790(6) 1.787(6)	2.057(6) 2.059(6) 2.072(6) 2.063(6)	119.9(3)	262
$[Mn_2O(OAc)_2(bpea)_2](ClO_4)_2$	3.121(6) 3.106(6)	1.79(1) 1.75(2) 1.77(2) 1.78(2)	2.00(2)–2.09(2)	125.1(8) 122.1(8)	272
$[Mn_2O(OAc)_2(TMIP)_2](ClO_4)_2\cdot CH_3CN\cdot 0.5(CH_3)_2O$	3.164(5)	1.797(11) 1.781(11)	2.115(13) 2.155(13) 1.993(13) 1.965(13)	124.4(6)	270
$[(Mn_2O(OAc)_2)_2(bbpmax)_2](ClO_4)_4\cdot 3CH_3NO_2$	3.261(?)	1.834(5) 1.960(5)	2.124(5) 2.082(6) 1.984(6) 2.082(6)	118.5(3)	274
$[Mn_2O(XDK)(4,4'\text{–}Me_2bpy)_2(NO_3)_2]\cdot 2.5CH_3OH$	3.170(2)	1.781(7) 1.799(7)	1.968(8) 2.182(8) 2.185(8) 1.935(7)	124.6(4)	275

Table 6 Magnetic properties and related parameters for dinuclear manganese(III)–carboxylato complexes.

Compound	*μeff (BM)* [*Temp.* (K)]	*Temp. range* (K)	*J* (cm^{-1})[a]	*References*
$(TMA)_3[Mn_2(Lc)_4(HLc)]\cdot H_2O$	6.80[298]			250
$[Mn_2(BCSP)(OAc)_2](ClO_4)\cdot CH_3OH$	4.26[292]		−11.8	251
$[Mn_2(BSP)(OCH_3)(OAc)(CH_3OH](ClO_4)$	4.28[298.3] 3.08[81.5]	81.0–298.0	−10.6	252
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)_2](Br)$	4.21[295]	80.0–300.0	−13.2	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)_2](I)$	4.29[297]	80.0–300.0	−12.9	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)(NCS)]$	4.23[297]	80.0–300.0	−13.0	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)(N_3)]$	4.29[298]	80.0–300.0	−11.8	253
$[Mn_2O(OAc)(TMIMA)_2](ClO_4)_3\cdot 2CH_3CN$	4.99[288]		+1.33	257
$[Mn_2O(OAc)(bispicen)_2](ClO_4)_3$			+19.5	258
$[Mn_2O(OAc)_2(H_2O)_2(bpy)_2](PF_6)_2\cdot 1.75H_2O$		30.0–300.0	−3.4	263
$[Mn_2O(O_2CC_6H_5)_2(N_3)_2(bpy)_2]\cdot MeCN\cdot 4H_2O$	6.96[320] 8.12[30] 7.45[5.0]	5.0–330.0	+8.8	267
$[Mn_2O(OAc)_2Cl_2(bpy)_2]\cdot CH_3COOH\cdot H_2O$	6.33[327.7] 5.85[100] 2.09[5.0]	5.0–330.0	−5.1	267
$[Mn_2O(OAc)_2(HB(pz)_3)_2]\cdot CH_3CN$	4.96[300] 4.88[15.7] 4.61[5.4]	4.2–300.0	−0.2	261
$[Mn_2O(OAc)_2(HB(pz)_3)_2]\cdot 4CH_3CN$	4.89[278] 4.77[100] 4.43[20] 4.03[6.01]	4.2–300.0	−0.7	261
$[Mn_2O(OAc)_2(tacn)_2](ClO_4)_2$	6.16[26] 5.9[4.3]		+9.0	260
$[Mn_2O(OAc)_2(Me_3tacn)_2]\ (ClO_4)_2$			+9.0	260
$[Mn_2O(OAc)_2(tacn)(Me_3tacn)](ClO_4)_2$	7.16[293.5] 8.21[50.6]	4.2–298.0	+7.0	269
$[Mn_2O(OAc)_2(BBAE)_2](ClO_4)_2$	5.04[289.7] 5.16[81.4]	81.0–290.0	−1.72	264
$[Mn_2O(OAc)_2(mpepma)_2](PF_6)_2\cdot H_2O$	4.91[300] 5.17[52]	52.0–300.0	+1.0	375
$[Mn_2O(OAc)_2(TMIP)_2](ClO_4)_2$	5.01[298]	10.0–300.0	−0.2	270
$[Mn_2O(OAc)_2(tppn)](ClO_4)_2\cdot CH_3CN$	5.22[300] 6.05[30] 5.07[4.3]	4.3–300.0	+11	271

[a] Employing $H = -2JS_1\cdot S_2$ convention.

$(TMA)_3[Mn_2(Lc)_4(HLc)]\cdot H_2O$ (**95**) (where H_2Lc = lactic acid),[250] all complexes with a $[Mn_2(\mu\text{-alkoxo})_2(\mu\text{-carboxylato})]^{3+}$ core (type I) contain a Schiff base coligand.[251–254] Complex (**95**) can be prepared by the reaction of tetramethylammonium permanganate ($(TMA)MnO_4$), H_2Lc, and (TMA)OH in methanol. An excess of ligand allows for the reduction of the Mn^{VII} to Mn^{III}. The X-ray crystal structure of (**95**) provides the first example of an Mn^{III} dimer with axial compression.The Mn···Mn separation in (**95**) is 3.094 Å. The magnetic moment of (**95**) at room temperature is 6.80 μ_B.

Dinuclear complexes with Schiff base ligands, such as BSP, BCSP, and 5-Br-Salpn, have been synthesized from the reaction of $Mn(OAc)_3$ and the ligand in methanol. A representative structure is shown for the cation in $[Mn_2(BCSP)(OAc)_2](ClO_4)\cdot CH_3OH$ (**96**).

The Mn···Mn separations in these complexes lie in the range 2.931–2.955 Å and the magnetic moments at room temperature observed for these complexes vary in the range 4.21–4.29 μ_B with the exchange interaction (J) between the manganese centers in the range $-10.6\,cm^{-1}$ to $-13.2\,cm^{-1}$. Cyclic voltammetry studies in methanol show two quasireversible reduction waves at about −0.3 V and −0.7 V vs. SCE.

For the $[Mn_2(\mu\text{-alkoxo})_2(\mu\text{-carboxylato})_2]^{2+}$ core (type II), only the benzoate analogues, $[Mn_2(spa\ 3\text{-OMe-spa})_2(OBz)_2]$ (**97**) (where H_2spa = 3-salicylideneamino-1-propanol), of the acetate complex reported many years ago[255] has been synthesized and structurally characterized.[256] The Mn···Mn separation in (**97**) is 2.872 Å while the bridging Mn—O_{alkoxo} distances are 1.896 Å and 1.939 Å.

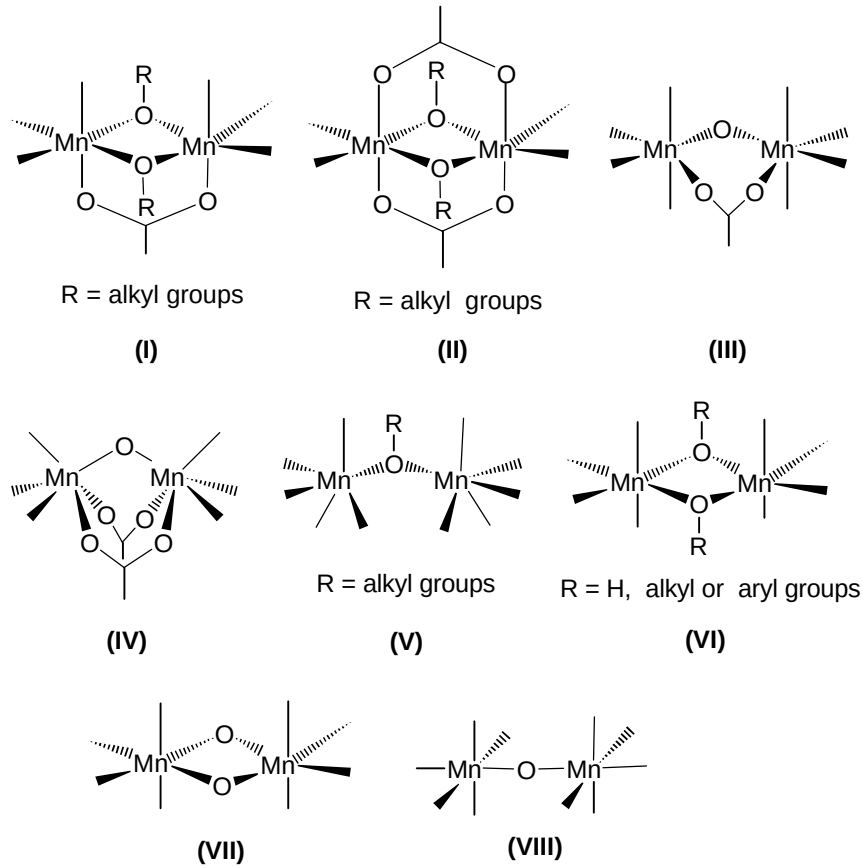
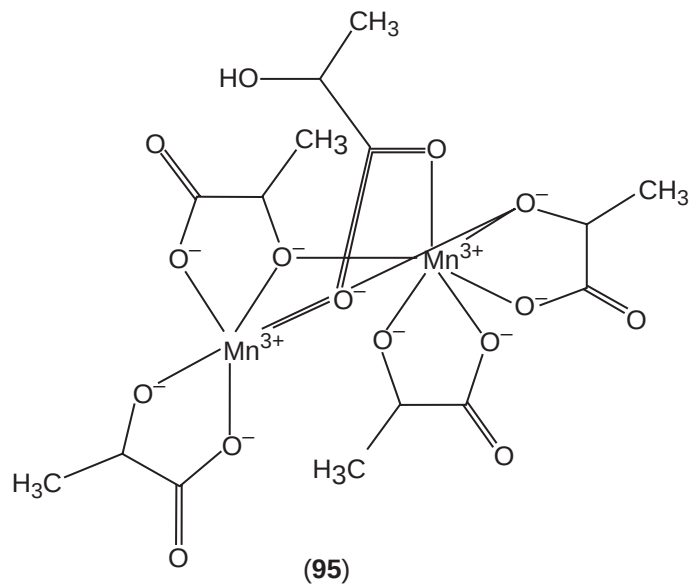


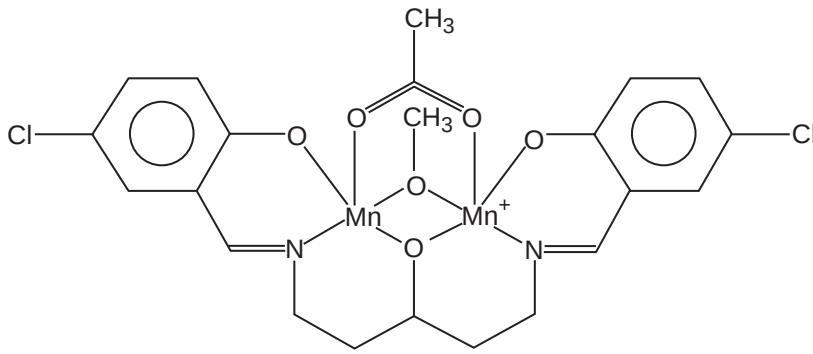
Figure 20 Core types observed for dinuclear manganese (II) complexes.

Much effort has been directed towards the chemistry of complexes with $[Mn_2(\mu\text{-O})(\mu\text{-OAc})]^{3+}$ (type III) and $[Mn_2(\mu\text{-O})(\mu\text{-OAc})_2]^{2+}$ (type IV) cores due to their relevance to biological systems (see Table 5). However, there are only four examples of complexes with type III core reported.[257–259] In order to obtain this type of complex, tetradentate ligands, such as TMIMA, bispicen, bispicMe_2en, and bpia (see Figures 3 and 17), are generally employed.

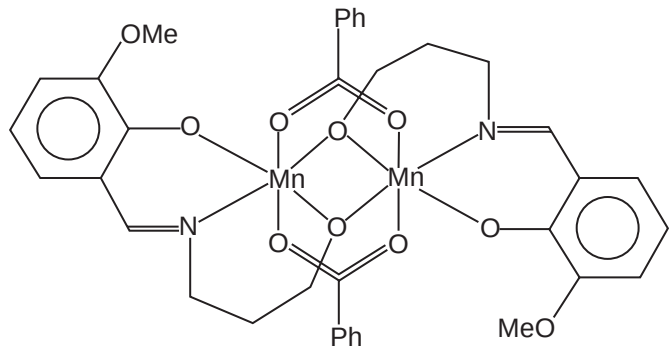
In these complexes, the manganese(III) centers are weakly ferromagnetically coupled with Mn···Mn separations and Mn—O—Mn angles of 3.25–3.29 Å and 130.8–131.0°, respectively.



(**95**)



(**96**)

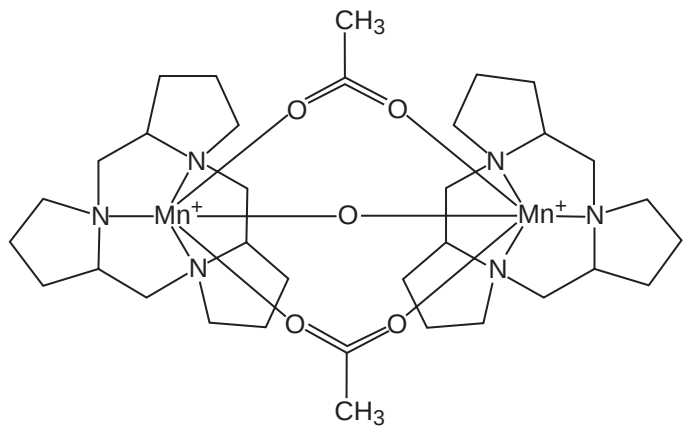


(**97**)

The solution electronic spectra of these complexes are typical of the $[Mn_2(\mu\text{-O})(\mu\text{-OAc})]^{3+}$ core and the observed bands are due to *d–d* transitions.

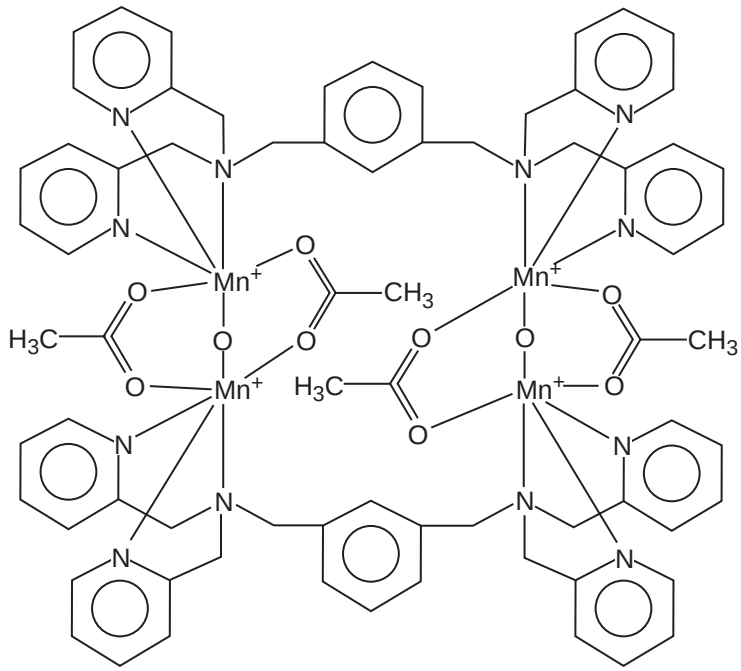
The first complexes with type IV core contained tridentate tacn, Me_3tacn, and $HB(pz)_3^-$ ligands (Figure 2).[260,261] Since the late 1980s a large number of complexes containing this core have been prepared with various bidentate, tridentate, and polydentate polypyridyl coligands (Figures 2, 3 and 17).[262–283,375] Tridentate or hexadentate ligands complete the coordination sites of each hexacoordinated manganese(III) center in these complexes. The use of bidentate ligands leaves one coordination site free on each manganese(III) center to be filled by easily exchangeable ligands, such as water, nitrate, chloride, hydroxide, or azide. While in most of these complexes monocarboxylates such as acetate, benzoate, etc., are used as bridging ligands, dicarboxylates such as mpdp or XDK (Figure 16) have also been employed.

The complex $[Mn_2O(OAc)_2(ttco)_2](PF_6)_2$ (**98**) reported by Bolm *et al.*[281] is an example with a capping tridentate ligand and has been found to be catalytically active in enantioselective epoxidations.



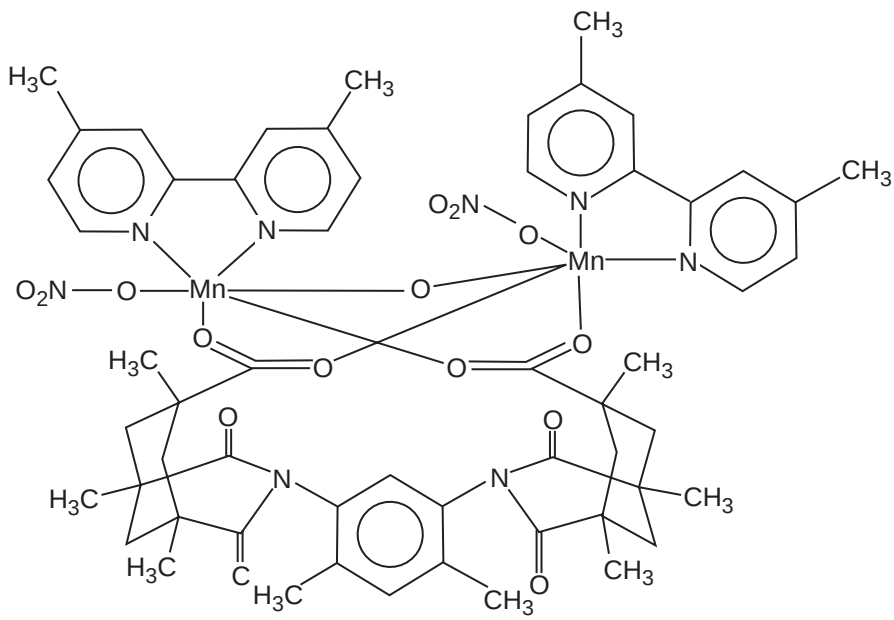
(**98**)

For the hexadentate ligands, such as tppn and bbpmax, tetranuclear complexes containing two $[Mn_2(\mu\text{-}O)(\mu\text{-}OAc)_2]^{2+}$ units are obtained. In the cation of the complex $[(Mn_2O(OAc)_2)_2(bbpmax)_2](ClO_4)_4$ (**99**) the two dinuclear units are related to each other by a mirror plane.



(**99**)

Using a sterically crowded dicarboxylate ligand XDK, Tanase and Lippard have reported a dinuclear complex $[Mn_2O(XDK)(4,4'\text{-}Me_2bpy)_2(NO_3)_2]$ (**100**).



(**100**)

The Mn···Mn separations in these complexes with type IV core range from 3.08 to 3.26 Å with tacn and bbpmax complexes lying at the extremes. The Mn—O—Mn angles vary between 117.9° and 125.1°. Based on the variable-temperature magnetic measurements for these complexes, both

weakly ferromagnetic and antiferromagnetic interactions between the manganese(III) centers are observed. Characteristic electronic absorption features observed for these complexes are now used as a tool to identify new complexes.

(ii) Trinuclear clusters

Trinuclear manganese(III) carboxylate complexes all have the same core structure as manganic acetate $[Mn(\mu_3\text{-}O)(\mu\text{-carboxlato})_6]^+$ (triangular b, Figure 21). The one-electron reduced species (II,III,III) were first reported in 1973 and structurally characterized in 1978[255] and many more such complexes have been made since. However, a limited number of complexes with a $[Mn(\mu_3\text{-}O)(\mu\text{-carboxlato})_6]^+$ core has been reported.[282,284–287] The first such complex, $[Mn_3O(O_2CCH_3)_6(py)_3](ClO_4)$ (**101**), was synthesized and spectroscopically characterized only in 1987[286] while the first crystallographically characterized complex, $[Mn_3O(O_2CC(CH_3)_3)_6(py)_3](ClO_4)\cdot CH_3CN$ (**102**), was reported in 1998.[287] To complete the sixth coordination site on each manganese center in these complexes, three neutral ligands, either py or 3-Me-py, have been used. Examples of complexes of this type together with selected structural parameters are summarized in Table 7. The typical Mn···Mn separation in these complexes is about 3.3 Å. While monocarboxylates are commonly used as bridging ligands, $[Mn_3O(mpdp)_3(py)_3](ClO_4)\cdot CH_3CN$ ((**103**)$\cdot CH_3CN$) is an example with a dicarboxylate, mpdp.

Weatherburn and co-workers[288] prepared the first and only trinuclear Mn_3^{III} complex, $[Mn_3O(OAc)_2(O_2)(dien)_3]I_3\cdot H_2O\cdot 0.33CH_3OH$ (**104**), which has a bridging peroxide group (triangular c, Figure 21). This complex was prepared from the reaction of either $Mn(OAc)_2$ or $Mn(OAc)_3$ with dien in methanol under reflux. The Mn···Mn separations in (**104**) are 3.32(3) Å and 3.14(4) Å.

(iii) Tetranuclear clusters

Tetranuclear manganese(III) carboxylate complexes have three different configurations for their metal centers: fused open cubane, planar, or butterfly (see Figure 22). There is only one example of the first type, namely $[Mn_4O_2(OAc)_2(BSP)_2]$ (**105**).[289] The Mn···Mn separations in (**105**) vary between 2.875(1) Å and 3.122(1) Å. Variable temperature magnetic measurements for (**105**) indicated weak antiferromagnetic interactions ($J = -10.0\,cm^{-1}$ and $J' = -3.7\,cm^{-1}$) between the manganese(III) centers. Cyclic voltammetry of (**105**) in methanol shows one quasireversible oxidation wave at 0.01 V and two quasireversible reduction waves at about −0.4 V and −0.7 V vs. SCE.

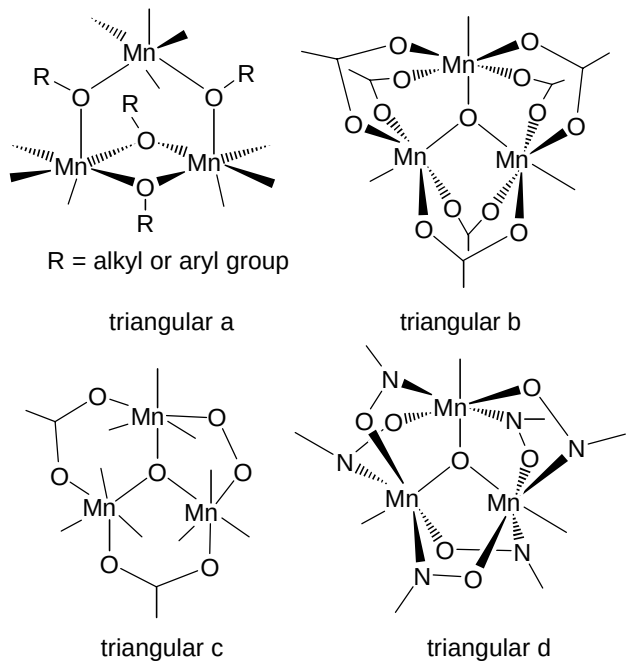


Figure 21 Core types observed for trinuclear manganese(III) complexes.

Table 7 Electronic spectral properties for dinuclear manganese(III)–carboxylato complexes.

Compound	*Solvent*	$\lambda(\varepsilon, M^{-1}cm^{-1})$, nm	*References*
$(TMA)_3[Mn_2(Lc)_4(HLc)]\cdot H_2O$	?	410(730)	250
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)_2]$ (Br)	MeOH	373(2,910), 427 sh(651), 610(137)	252
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)_2](I)$	MeOH	373(2,880), 420 sh(650), 610(135)	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)(NCS)]$	MeOH	373(2,950), 430 sh(616), 611(143)	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)(N_3)]$	MeOH	370(2,870), 430 sh(624), 612(136)	253
$[Mn_2(BSP)(OCH_3)(OAc)(MeOH)(ClO_4)]$	MeOH	373(3,070), 433 sh(600), 611(141)	253
$[Mn_2O(OAc)(TMIMA)_2](ClO_4)_3\cdot 2CH_3CN$	CH_3CN	496(405), 523(305), 733(308)	257
$[Mn_2O(OAc)(bispicen)_2](ClO_4)_3$	CH_3CN	260, 295, 380 sh, 490(225), 532(242)	258
$[Mn_2O(OAc)(bpia)_2](ClO_4)_3\cdot CH_3CN$	CH_3CN	495(524), 527(418), 711(176)	259
$[Mn_2O(OAc)_2(H_2O)_2(bpy)_2](PF_6)_2\cdot 1.75H_2O$	CH_3CN	240(5,800), 295(5,670), 385(300), 490(146), 640(108)	263
$[Mn_2O(O_2CPh)_2(N_3)_2(bpy)_2]$	DMF	280(17,000), 416 sh(492)	267
$[Mn_2O(OAc)_2Cl_2(bpy)_2]$	CH_2Cl_2	492(361), 556(246)	267
$[Mn_2O(O_2CEt)2Cl_2(bpy)_2]\cdot 3EtCO_2H\cdot H_2O$	DMF	283(7,000), 468 sh(275)	267
$[Mn_2O(O_2CPh)2Cl_2(bpy)_2]$	DMF	280(15,000), 340 sh(740), 502 sh(135)	267
$[Mn_2O(OAc)_2(HB(pz)_3)_2]$	CH_2Cl_2	283(6,000), 385 sh(405), 458 sh(165), 486(210), 503 sh (190), 524 sh(175), 540 sh(165), 582 sh(95), 760(58)	261
$[Mn_2O(OAc)_2(tacn)_2](ClO_4)_2$	CH_3CN	232(3,400), 280(3,800), 495(324), 520(250), 545 sh, 560 sh, 570 sh, 665(95), 910(40)	260
$[Mn_2O(OAc)_2(Me_3tacn)_2](ClO_4)_2\cdot H_2O$	CH_3CN	250 sh, 300(14,000), 486(667), 521(638), 720(104), 1,000(63)	260
$[Mn_2O(OAc)_2(tacn)(Me_3tacn)](ClO_4)_2$	CH_3CN	246(11,000), 304(12,000), 481(770), 521(740), 680 sh(200)	269
$[Mn_2O(OAc)_2(bpea)_2](ClO_4)_2\cdot 0.5H_2O$	CH_3CN	377 sh, 487(517), 521(372), 545 sh, 569 sh, 728(112)	272
$[Mn_2O(OAc)_2(TMIP)_2](ClO_4)_2$	CH_3CN	255(23,900), 376(844), 464(330), 484(405), 497(383), 521 sh(349), 568 sh(216), 736(106)	270
$[Mn_2O(OAc)_2(TMIP)_2](PF_6)_2$	CH_3CN	249(24,900), 372 sh(840), 464 sh(360), 485(460), 502(430), 521 sh(400), 568 sh(240), 757(130)	270

The difference between the planar tetranuclear complexes with a $[Mn_4O_2(OAc)_6]^{2+}$ core and the butterfly tetranuclear complexes with a $[Mn_4O_2(OAc)_7]^{+}$ core is due to the seventh bridging carboxylate in the latter. Interestingly, the butterfly type was discovered first. Examples of such complexes with various bidentate coligands, such as Hhmp, Hhqn, Himac, pic, Hdbm, Hdpm, and bpy (Figure 2 and 16), are summarized in Table 8.[290–301,376] Among all the planar tetranuclear manganese(III) carboxylate complexes, there are two with dbm or dpm ligands, $[Mn_4O_2(O_2\text{-}CEt)_6(dbm \text{ or } dpm)_2]$, that are different from the others in that these do not have two extra monodentate ligands. Thus, in these complexes two of the manganese centers are five coordinate (see the structure of $[Mn_4O_2(O_2\text{-}CEt)_6(dbm)_2]$ (**106**)). Interestingly, a complex with only one five-coordinated manganese center, $[Mn_4O_2(O_2CPh)_6(py)(dbm)_2]$ (**107**), has also been synthesized. Formation of these molecules with two monodentate ligands, one monodentate ligand, or no ligand is dependant on the starting materials used. All planar complexes with a monoanionic bidentate ligand are neutral.

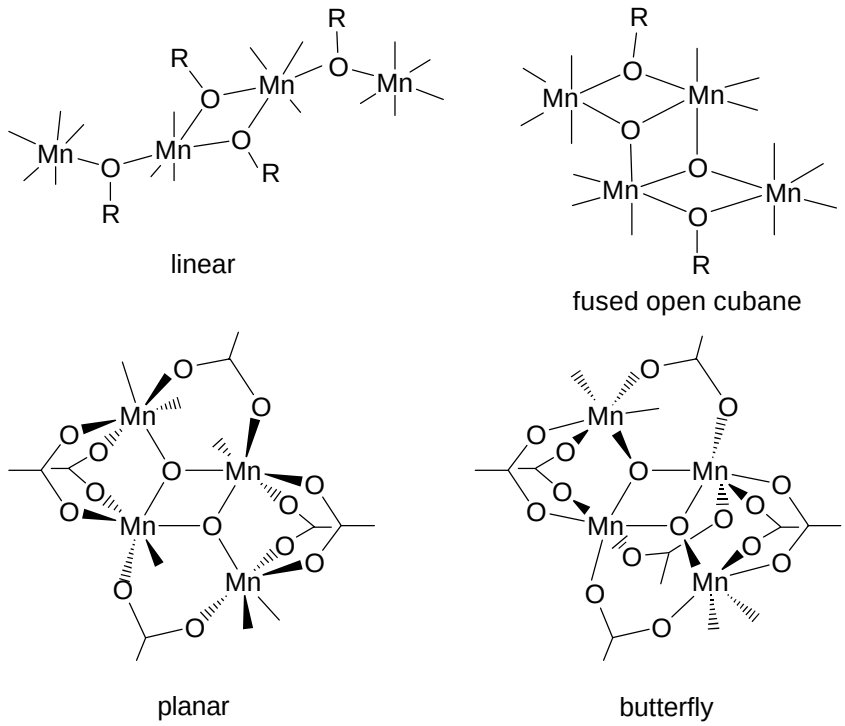
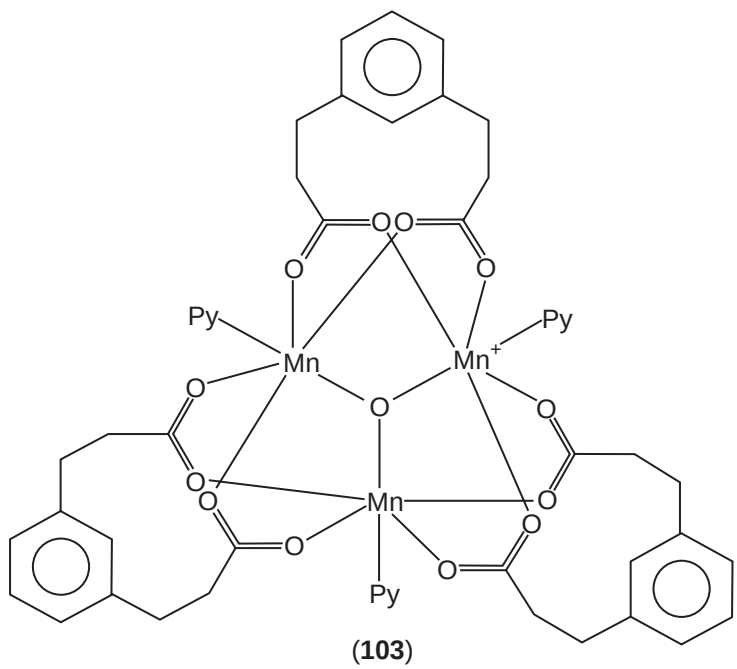


Figure 22 Core types observed for tetranuclear manganese(III) complexes.

Butterfly tetranuclear manganese(III) carboxylate complexes are monoanionic with the exception of the bpy complex. An example of a butterfly core complex is $(Bu^n_4N)[Mn_4O_2(O_2CPh)_7(imac)_2]\cdot 5CH_3CN$ (**108**).

The Mn···Mn separations in both planar and butterfly complexes are very similar and range between 2.80 Å and 3.45 Å. The magnetic properties of these complexes have been studied extensively, and showed antiferromagnetic interactions between the manganese(III) centers. Electrochemical behavior of the butterfly complexes is summarized in Table 9 and both oxidative and reductive processes are observed.[298,299,377]



(**103**)

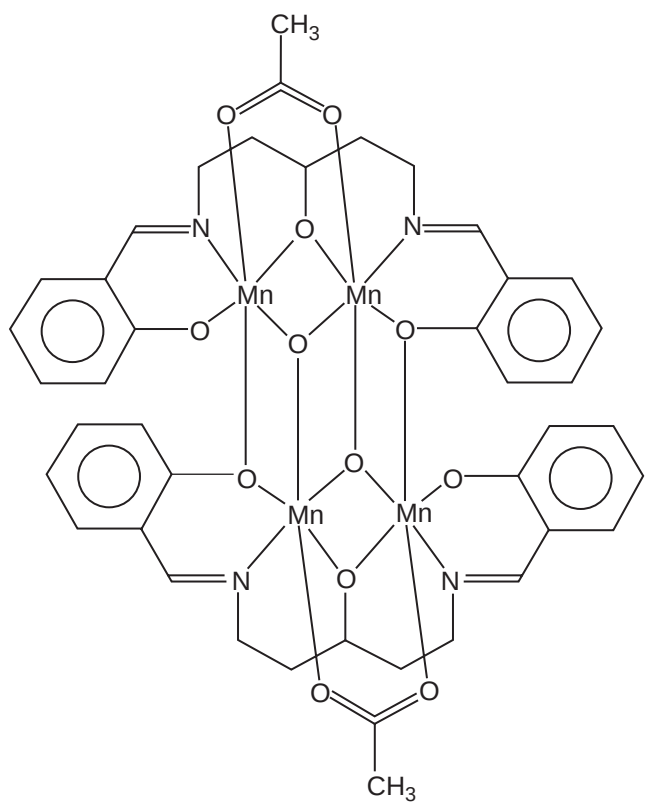
Table 8 Structural parameters for trinuclear manganese(III)–carboxylato complexes.

Compound	*Orientation of metals*	*Mn···Mn*(Å)	*MnO$_b$*(Å)	*References*
$[Mn_3O(OAc)_6(3\text{–}Me\text{–}Py)_3](ClO_4)$	triangular b	3.2754 3.3027 3.311	1.919(3) 1.881(1) 1.91(3)	285
$[Mn_3O(O_2CC_2H_5)_6(3\text{–}Me\text{–}Py)_3](ClO_4)$	triangular b	3.2662 3.2691 3.2800	1.883(4) 1.887(4) 1.897(4)	285
$[Mn_3O(O_2CC_3H_8)_6(Py)_3](ClO_4)$	triangular b	3.272 3.283 3.279	1.91(1) 1.84(1) 1.93(1)	284
$[Mn_3O(O_2CC(CH_3)_3)_6(Py)_3](ClO_4)\cdot CH_3CN$	triangular b		1.896(8) 1.867(8) 1.909(8)	287
$[Mn_3O(O_2)(OAc)_2(dien)_3]I_3\cdot H_2O\cdot 0.33CH_3OH$	triangular c	3.32(3) 3.14(4)	1.8(1) 1.9(1)	288

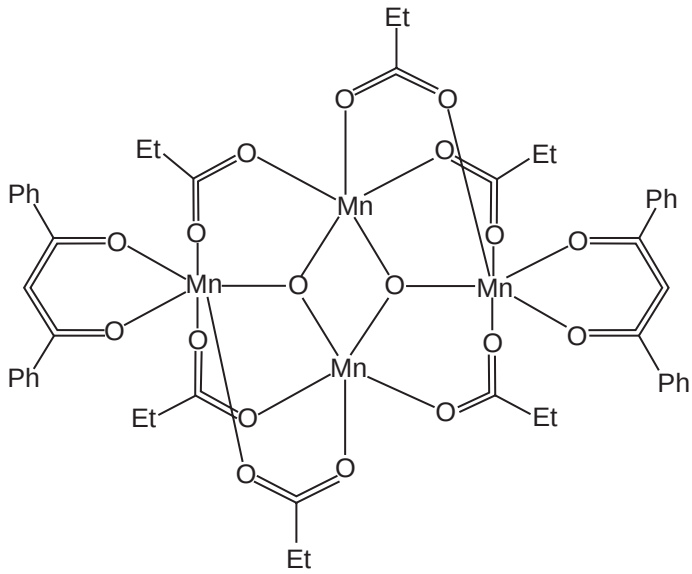
(iv) Higher nuclearity clusters

Manganese(III) carboxylate complexes of nuclearity >5 are limited and are summarized in Table 10. The first hexanuclear complex, $[Mn_6O_2(O_2CCMe_3)_{14}]$ (**109**), was prepared from $Mn(NO_3)_3$ and excess pivalic acid in dioxane.[302] This neutral complex has an $[Mn_6(\mu_4\text{-}O)_2(\mu_3\text{-}O_2CCMe_3)_4(\mu\text{-}O_2CCMe_3)_6]^{4+}$ core with both bridging and monodentate pivalates. All manganese centers have a distorted octahedral environment.

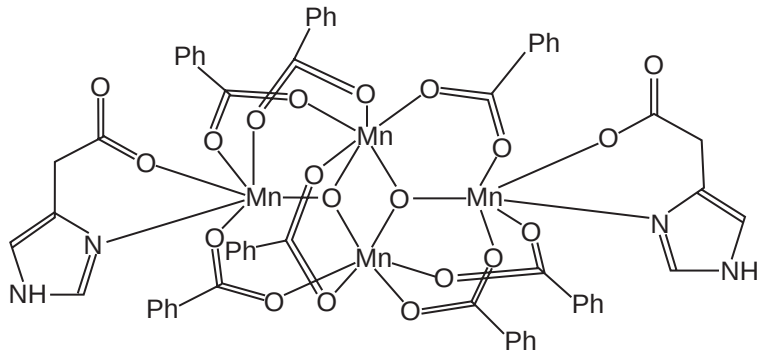
Employing asymmetric pentadentate ligands, such as H_3-4-X-bhedsd (H_3-4-X-bhedsd = *N*-(4-X-salicylidene)-*N*′,*N*′-bis(2-hydroxyethyl)ethylenediamine and X = Cl, Br, or OMe) (Figure 18), gave hexanuclear manganese(III) carboxylate complexes with an $[Mn_6(\mu_3\text{-}O)_2(\mu\text{-}OMe)_6]^{8+}$ core.



(**105**)



(**106**)



(**108**)

$[Mn_6O_2(OAc)_2(OMe)_6(4\text{-X-bhedsd})_2]\cdot 2H_2O$ (X = Cl (**110**) or OMe (**111**)) have been synthesized and structurally characterized.[303] These complexes have bridging oxo, alkoxo, and carboxylato groups.

A centrosymmetric complex, $[Mn_3O(O_2CPh)_4(PhPO_3)(PhPHO_2)(py)]_2\cdot 2.5CH_3CN$ (**112**), is a further type of hexanuclear complex that can be viewed as being a dimer of the triangular basic carboxylates described above (triangular b, Figure 21) linked by both phosphinate and phosphonate ligands.[304] It appears that the phosphonate ligands displace carboxylate ligands from one cluster and simultaneously act as a bridge to a second.

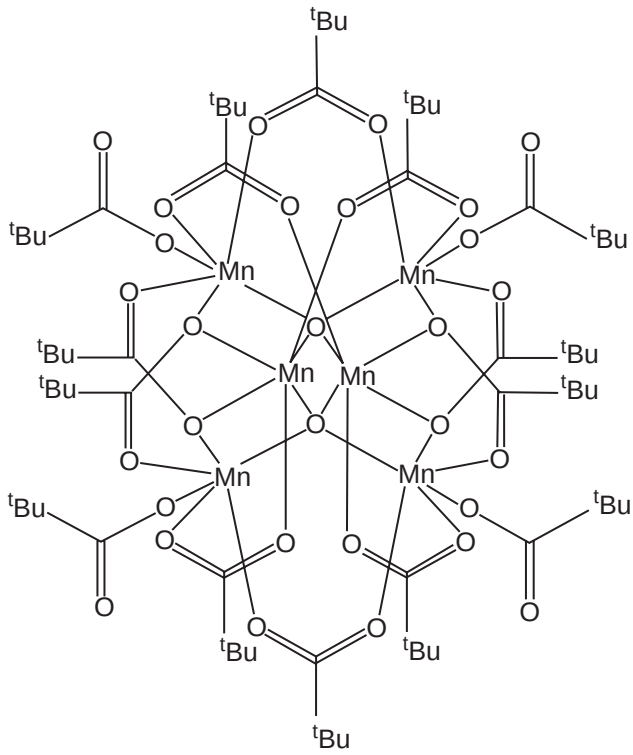
The only heptanuclear manganese(III) carboxylate complex, (NEt_4) $[Mn_7O_4(OAc)_{10}(dbm)_4]\cdot 3CH_2Cl_2\cdot 2C_6H_{14}$ (**113**),[305] has a ground spin state of 3 or 4 with a magnetic moment of 10.06 μ_B at 260 K. This complex was prepared from a dichloromethane solution of $[Mn_4O_2(O_2CPh)_6(py)_2(dbm)_2]$ and $Et_4N\cdot xH_2O$ by reaction at 0°C and layering with ether–hexane. The $[Mn_7(\mu_3\text{-}O)_4]^{13+}$ core in the anion of (**113**) consists of two $[Mn_4(\mu_3\text{-}O)_2]^{8+}$ butterfly units fused together by sharing of one wing-tip at each manganese center.

There are two types of octanuclear complexes: one with a core structure $[Mn_8(\mu_3\text{-}O)_4(\mu_4\text{-}O)_2(\mu_2\text{-}Cl)(\mu_4\text{-}Cl)(\mu\text{-}\eta^1,\eta^2\text{-carboxylato})_7]^-$[306,307] and others which are aggregates of the planar or butterfly tetranuclear complexes mentioned above connected by bidentate ligands, such as pic,[291,308] bpe,[292] and bmpe (Figures 2 and 17).[309]

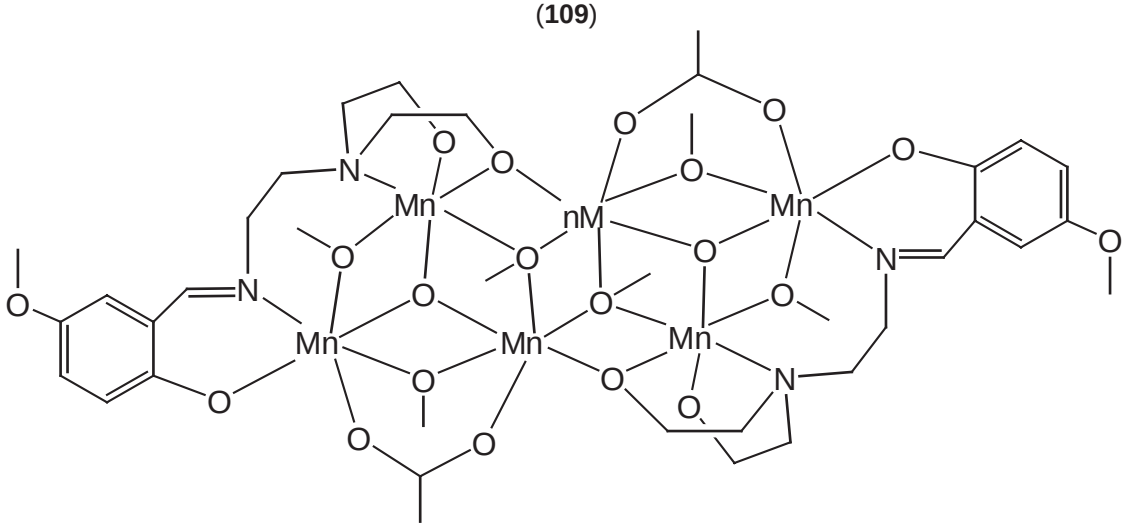
The octanuclear complex $(NBu^n_4)[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]\cdot 1.5CH_2Cl_2\cdot 2H_2O$ (**114**) was prepared from $(Bu^n_4N)[Mn_4O_2(O_2CPh)_9(H_2O)]$ and 4 equiv of Me_3SiCl in CH_2Cl_2 in 45–60% yield.

Table 9 Structural parameters for tetranuclear manganese(III)–carboxylato complexes.

Compound	*Orientation of metals*	*Mn···Mn*(Å)	*Mn–O$_b$*(Å)	*References*
$[Mn_4O_2(OAc)_2(BSP)_2]$	fused open cubane	2.933(1) 3.122(1) 2.875(1)	1.934(4) 1.889(5) 1.888(5) 1.941(4) 2.359(5) 2.142(4) 2.168(4) 1.892(4)	253,289
$[Mn_4O_2(OAc)_6(Py)_2(dbm)_2]$	planar	2.8749(11) 3.308(1) 3.398(1)	1.877(2) 1.885(2) 1.894(2)	294
$[Mn_4O_2(O_2CPh)_6(Py)(dbm)_2]$	planar	2.820(2)–3.425(2)	1.859(5)–1.892(5)	294
$[Mn_4O_2(O_2CEt)_6(dbm)_2]\cdot$hexane	planar			295
$[Mn_4O_2(O_2CEt)_6(NO_3)(bpy)_2](ClO_4)\cdot 1.5CH_2Cl_2$	planar	2.854(3)	1.858(8)–1.900(8)	295
$[Mn_4O_2(O_2CCF_3)_8(bpy)_2]\cdot CF_3CO_2H$	planar			301
$[Mn_4O_2(3,5-F_2\text{-}C_6H_3CO_2)_6(py)_4Cl_2]\cdot 2Et_2O$	planar	2.875(2)–3.418(2)	1.864(5)–1.922(5)	293
$[Mn_4O_2(O_2CPh)_6(EtOAc)_2(dbm)_2]$	planar			292
$[Mn_4O_2(O_2CPh)_6(dpm)_2]$	planar	2.841(1)–3.362(1)	1.865(3)–1.922(3)	296
$[Mn_4O_2(O_2CPh)_6(Pic)_2(MeCN)_2]$	planar	3.282(1) 2.892(2) 3.390(1)	1.859(5) 1.887(5) 1.905(6)	291
$[Mn_4O_2(OAc)_7(bpy)_2](ClO_4)\cdot 3H_2O$	butterfly	2.848(5) 3.312(5) 3.385(5) 3.371(5) 3.299(5)	1.918(12) 1.911(15) 1.844(13) 1.889(13) 1.930(13) 1.804(16)	297,376
$(Bu^n_4N)[Mn_4O_2(OAc)_7(hqn)_2]\cdot 2CH_2Cl_2$	butterfly	3.349(4) 2.818(4) 3.414(4) 3.399(4) 3.319(4)	1.907(6) 1.875(7) 1.882(6) 1.894(7) 1.879(6) 1.861(6)	298
$(Me_4N)[Mn_4O_2(O_2CPh)_7(hmp)_2]$	butterfly	3.325(7) 2.829(7) 3.404(7) 3.386(7) 3.301(7)	1.892(12) 1.889(12) 1.857(12) 1.891(12) 1.907(11) 1.874(13)	298
$(Bu^n_4N)[Mn_4O_2(OAc)_7(Pic)_2]\cdot CH_3CN$	butterfly	3.308(2) 2.842(2) 3.386(2) 3.406(2) 3.313(2)	1.890(5) 1.910(5) 1.908(4) 1.888(5) 1.847(5) 1.840(5)	299
$(Bu^n_4N)[Mn_4O_2(O_2CPh)_7(imac)_2]\cdot 5CH_3CN$	butterfly	2.816(1)–3.446(1)	1.848(3)–1.915(3)	300
$(Bu^n_4N)[Mn_4O_2(O_2CPh)_9(H_2O)]$	butterfly	2.816(4) 3.367(4) 3.296(4) 3.302(4) 3.365(4)	1.900(11) 1.913(10) 1.823(11) 1.909(10) 1.905(11) 1.825(10)	306



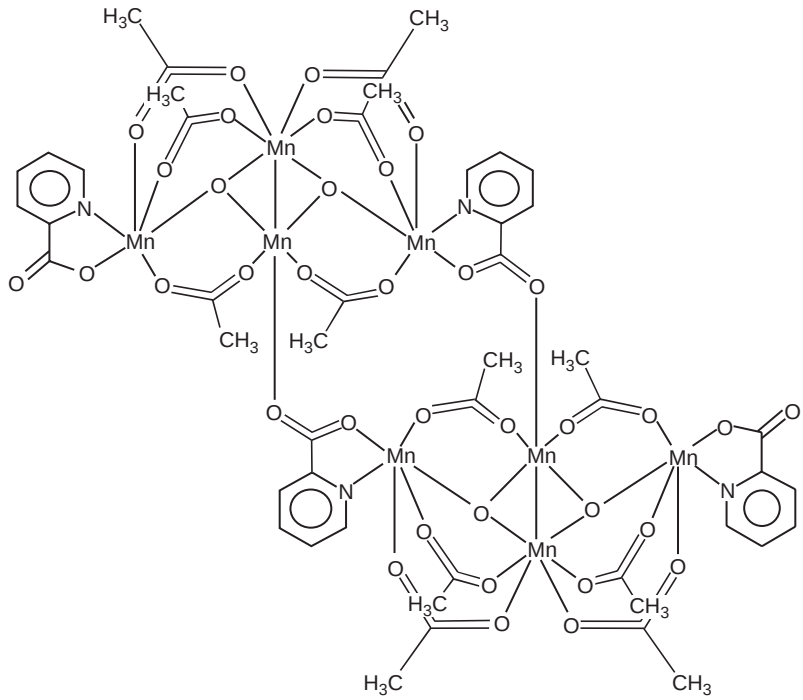
(**109**)



(**111**)

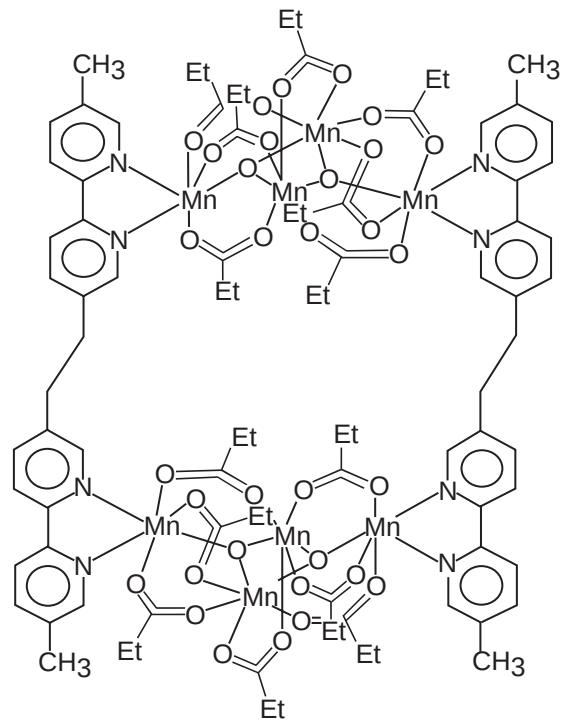
Table 10 Electrochemical properties for tetranuclear manganese(III)–carboxylato butterfly complexes.

Compound	*Solvent*	$E_{1/2}^{ox}$ (ΔE_p)	$E_{1/2}^{red}$ (ΔE_p)	*References*
$(Bu^n{}_4N)[Mn_4O_2(OAc)_7(hqn)_2]\cdot 2CH_2Cl_2$	CH_2Cl_2	+0.35 +0.81	−1.6	298
$(Me_4N)[Mn_4O_2(O_2CPh)_7(hmp)_2]$	CH_2Cl_2	+0.25 +0.95	−1.5	298
$(NBu^n{}_4)[Mn_4O_2(OAc)_7(Pic)_2]\cdot CH_3CN$	CH_2Cl_2	+0.52(180)	−0.86	299
$(NBu^n{}_4)[Mn_4O_2(O_2CPh)_7(dbm)_2]$	CH_3CN	+1.17 +0.48	−0.66	377



(**115**)

It has a ground spin state of 11 with a magnetic moment of 13.8 μ_B at 300 K. The core structure in the anion of (**114**) can be considered as arising from the addition of an eighth Mn^{III} ion connected to the $[Mn_7(\mu_3\text{-}O)_4]^{13+}$ unit in (**113**) by two additional bridging O^{2-} ions. The structures of the complexes of pic and bmpe ligands, $[\{Mn_4O_2(OAc)_6(pic)_2\}_2]$ (**115**) and $[Mn_4O_2(O_2\text{-}CEt)_7(bmpe)]_2(ClO_4)_2$ (**116**) are shown.



(**116**)

The nonanuclear complex $[Mn_9O_7(O_2CPh)_{13}(py)_2]$ (**117**) was prepared from the reaction of $[Mn_3O(O_2CPh)_6(py)_2(H_2O)]$ with PhIO in acetonitrile.[310] The room temperature magnetic moment of this compound is 13.2 μ_B. The other nonanuclear manganese complexes $[M_2Mn_9O_7(O_2CR)_{15}(L)_2]$ ((**118**): M = Na, R = Ph and L = CH_3CN;[306,307] (**119**): M = K, R = $C(CH_3)_3$) and L = $(CH_3)_3CCO_2$)[311] can be considered as mixed-metal clusters. The sodium salt was synthesized from the reaction of $(NBu^n_4)[Mn_4O_2(O_2CPh)_9(H_2O)]$ with $(PhCO)_2O_2$ in the presence of $NaClO_4$. Based on the variable temperature magnetic measurement, the compound was found to have a ground spin state of 4. All nonanuclear complexes contain two types of bridging acetates: μ^2-η^1-acetato and μ-η^1,η^2-acetato but in different ratios. Reactions of $[Mn_4O_2(O_2CPh)_6(pic)_2(H_2O)_2]$ with Hpic or Hdbm result in the decanuclear complexes $[Mn_{10}O_8(O_2CPh)_6(pic)_8]$ (**120**) and $[Mn_{10}O_8(O_2CPh)_6(pic)_6(dbm)_2]$ (**121**), respectively.[312] Both have the same $[Mn_{10}(\mu_3\text{-}O)_6(\mu_4\text{-}O)_2]^{14+}$ core, but differ in the nature of the chelated ligands at two positions. The simulation of the magnetic data at 320–2 K for (**121**) indicates a ground spin state of 0; however, a ground spin state of 1 or 2 with very low lying excited state cannot be ruled out without data measured below 2 K. Interestingly, reactions of the corresponding butterfly tetramer, such as $(NBu^n_4)[Mn_4O_2(O_2CPh)_9(H_2O)]$, with potassium hydrogen phthalate or 4,4′-bpy result in the octadecanuclear complexes $[K_4Mn_{18}O_{16}(O_2CPh)_6(phth)_2(H_2O)_4]$ (**122**)[313] and $[(Mn_9O_7(O_2CC_6H_4(OMe))_{13}(4,4'\text{-bpy}))_2]$ (**123**)[314], respectively. While the former is a mixed-metal cluster, the latter is a dimer of the derivative of the nonanuclear complex reported by Low *et al.*[310] The mixed-metal cluster has 18 Mn^{III} ions held together by 16 μ_3-O^{2-} ions to give an $[Mn_{18}O_{16}]^{22+}$ core. The two phthalate groups each bridge a total of four Mn atoms with each of their oxygen atoms terminally ligated. The $[Mn_{18}O_{16}]^{22+}$core can be described as arising from the fusion of five $[Mn_4(\mu_3\text{-}O)_2)]^{8+}$ units. The central $[Mn_{10}O_6]^{18+}$ unit, which results from the body-to-body fusion of three such units, connects after two $[Mn_4O_2]^{8+}$ units at the six "wing-tip" positions. It has an $S = 0$ ground state based on the magnetic measurements for the temperature range 320–2 K. This is unusual for polynuclear Mn^{III} complexes, and may be explained in terms of the spin frustration that is likely to be present in the $[Mn_4O_2]^{8+}$ butterfly building blocks.

5.1.6.2.2 Alkoxide and aryloxide ligands

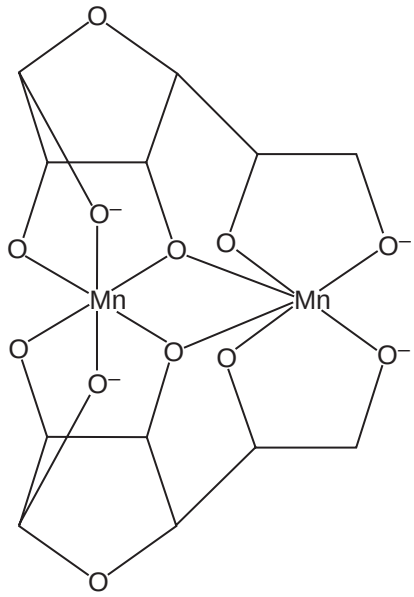
If 2,2′-biphenol ($biphenH_2$) is deprotonated (using NEt_3 base) prior to reacting with trinuclear basic carboxylates in acetonitrile, it forms a mononuclear manganese(III) complex $(NEt_3H)_2[Mn(biphen)_2(biphenH)]$ (**124**).[315] An X-ray structure determination indicated a trigonal bipyramidal geometry around the metal center. This is a rare example of five-coordinate manganese(III) surrounded by five oxygen atoms. It has a magnetic moment of 4.94 μ_B and shows two absorptions in the electronic spectroscopy at 412 nm and 546 nm (see Tables 3 and 4 for details).

The dinuclear complex $Ba_2[Mn_2(\beta\text{-D-Man}f)_2]\cdot 13H_2O$ ((**125**)·$13H_2O$) (where Man*f* = mannofuranose) is an example of a homoleptic coordination compound of mannofuranose pentaanions with manganese(III).[316] The Mn···Mn separation and the average Mn—O—Mn angle in the anion of (**125**) are 3.323(3) Å and 103.4°, respectively. In (**125**) the high-spin manganese(III) centers are weakly antiferromagnetically coupled ($J = -3\,cm^{-1}$).

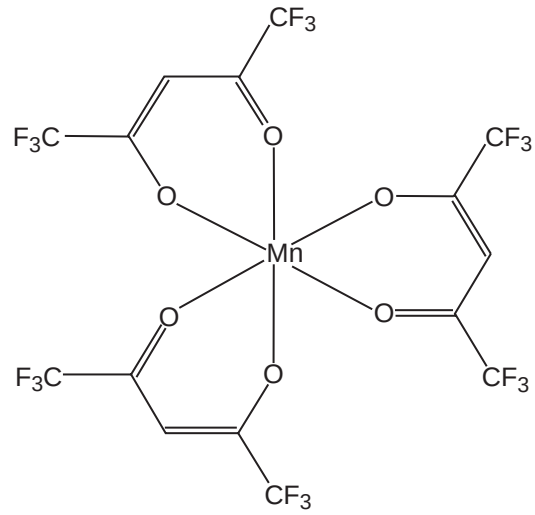
5.1.6.2.3 Diketones and related ligands

A number of mononuclear manganese(III) complexes of diketones (mostly acac or its derivatives) have been reported (see Tables 3 and 4).[317–320,372,374] However, most of the products resulted from attempts to prepare complexes with higher nuclearity, and $[Mn(acac)_3]$ (**126**) and $[Mn(acac)_2(H_2O)_2](ClO_4)$ (**127**) are the most studied complexes in this category. For the $[Mn(Me_3tacn)(acac)(H_2O)](ClO_4)$ complex (**128**) the Mn—OH_2 distance (1.790(5) Å) is shorter than those for the acac ligand (2.005(4) Å and 2.067(5) Å). All these complexes show magnetic behavior typical of manganese(III) ions. The hfacac analogue, $Mn(hfacac)_3$ (**129**), where hfacac = hexafluoroacetylacetone, has been reported.[317] The Mn—O distances in (**129**) vary between 1.91 Å and 2.15 Å.

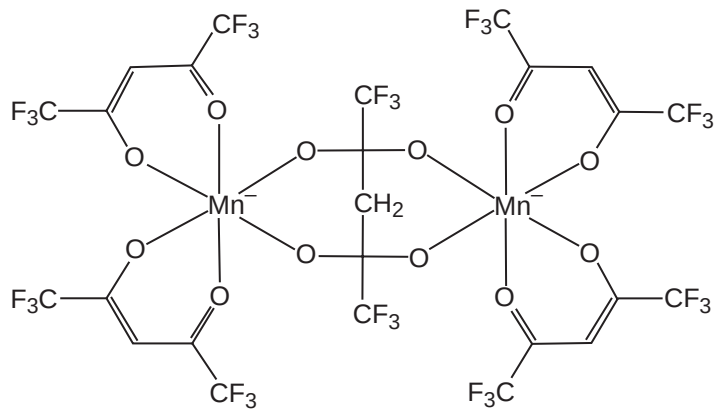
The chemistry of the doubly hydrated form of hexafluoroacetylacetone, 1,1,1,5,5,5-hexafluoropentane-2,2,4,4-tetraolato (hfpt), is worth mentioning. A dinuclear manganese(III) complex $(pyH)_2[Mn_2(hfpt)(hfacac)_4]$ (**130**) was formed from a mixture of $[Mn_3O(OAc)_6(py)_3](ClO_4)$,



(**125**)



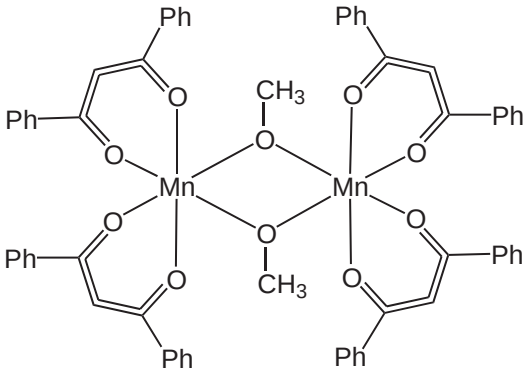
(**129**)



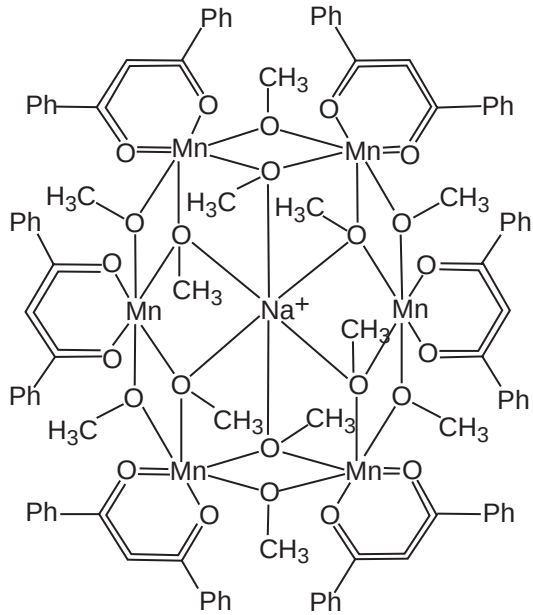
(**130**)

hfacacH, $hfptH_4$, and pyridine (py) in a 1:6:1.5:9 ratio in CH_2Cl_2 in a 58% yield.[317] Two $Mn(hfacac)_2$ units in the anion of (**130**) are bridged by the $hfpt^{4-}$ group; acting as a bidentate chelate ligand. A variable-temperature magnetic study over the range 5–320 K shows weak ferromagnetic interaction between the Mn^{III} centers for a fitting of the data with $J = +0.21\,cm^{-1}$, $D = 0.9\,cm^{-1}$, $g = 1.99$. Vacuum thermolysis of this molecule at 111–150°C yields $(pyH)[Mn(hfacac)_3]$ and lesser amounts of *cis*-$[Mn(py)_2(hfac)_2]$, $[Mn(hfac)_3]$, the tetraol, and manganese oxides. The initiation of the thermolysis is by proton transfer from pyH^+ to the tetraolate oxygen to which it is hydrogen bonded, causing cleavage of the carbon–oxygen bonds.

A simple example of a bis(μ-alkoxo) manganese(III) complex with diketones as coligands is $[Mn_2(OCH_3)_2(dbm)_4]$ (**131**).[321] It is obtained by controlled oxidation and aggregation from slow diffusion of methanol vapor into a chloroform solution of the brown solid isolated from the reaction between $MnCl_2$, NaOMe, and Hdbm (in a 1:1:4 ratio) in dry methanol. The two manganese(III) centers (the Mn···Mn distance is 3.1037(6) Å) are related by an inversion center and symmetrically bridged by two methoxide ions. Variable-temperature magnetic measurement and its analysis for (**131**) provide a realistic set of parameters for tetragonally elongated manganese(III) complexes with $D = -2.5(4)\,cm^{-1}$, $J = 0.28(4)\,cm^{-1}$, and $g = 1.983(2)$.



(131)



(132)

A hexanuclear manganese(III)-alkoxo complex with the same ligand set as (**131**), $[NaMn_6(OMe)_{12}(dbm)_6](BPh_4)\cdot 2CHCl_3$ (**132**), was made in a similar manner to (**131**) except that the brown solid was recrystallized from a solution of chloroform/methanol mixture in the presence of $NaBPh_4$.[322] The $[Mn_6(OMe)_{12}]$ ring in (**132**) displays a 12-metallacrown-6 structure and acts as a host for the sodium ion, which has a trigonally distorted octahedral environment. With an average Mn···Mn separation of 3.21(2) Å in (**132**), the observed geometry of the managanese ions and the UV–visible spectra in the solid state are both typical of Jahn–Teller-distorted high-spin manganese(III). Detailed magnetic studies for (**132**) indicate that it has ground spin state of 12.

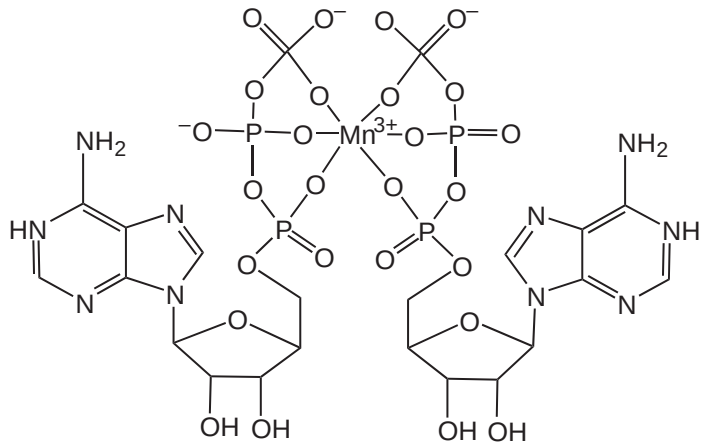
Christou, Hendrickson and co-workers have synthesized and structurally characterized the non-alkoxo hexanuclear manganese(III) clusters $[Mn_6O_4X_4(Me_2dbm)_6]$ ((**133**): X = Cl; (**134**): X = Br), with ground spin states of 12.[378] These clusters were synthesized by slow evaporation of MeCN/CH_2Cl_2 solutions of the corresponding mononuclear complexes $[MnX(Me_2dbm)_2]$ (X = Cl or Br), presumably via their hydrolysis. The structure of (**133**) consists of a core comprising a Mn_6^{III} octahedron whose four nonadjacent faces are bridged by μ_3-O^{2-} ions and the other four faces bridged by μ_3-Cl^- ions. Chelating Me_2dbm groups complete the octahedral geometry around each metal center. The Mn···Mn separations in (**133**) are 3.204(9) Å and 4.531(3) Å. Compound (**134**) is isostructural with (**133**), except that the chlorides are replaced by bromides.

5.1.6.2.4 Other oxygen ligands

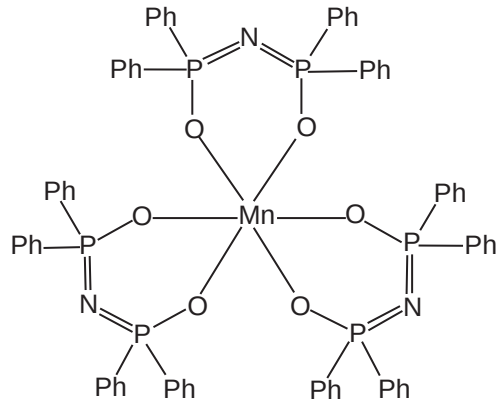
Two mononuclear complexes with phosphate ligands have been reported: $[Mn(H_2O)_6]$-$[Mn(ATP)_2]\cdot 10H_2O\cdot 2DPA$ (**135**)[323] where ATP = adenasine-5′-triphosphate and DPA = 2,2′-dipyridylanine and $[Mn(Ph_2P(O)NP(O)Ph_2)_3]\cdot CH_2Cl_2$ (**136**).[324]

5.1.6.3 Sulfur Donor Ligands

Manganese(III) complexes with sulfur ligands are very rare. This is due to the fact that manganese(III) ions tend to oxidize sulfur ligands with the formation of manganese(II) complexes. Nevertheless Henkel *et al.*[325] have prepared the complex $(Ph_4P)_2$ $[Mn(tdt)_2][Mn(tdt)_2(MeOH)]$ (**137**) from the reaction of $MnCl_2\cdot 4H_2O$ with Na_2tdt (where tdt = toluene-3,4-dithiolate) in the presence of oxygen and $[Ph_4P]Br$. Complex (**137**) has two mononuclear manganese(III) anions, one with tetrahedral geometry and the other with trigonal bipyramidal geometry. The



(**135**)



(**136**)

one-electron oxidized species of the anion, $[Mn(tdt)_2]$, is square planar. A mononuclear complex of 1,2-dithioethane (edt), $(NEt_4)[Mn(edt)_2(HIm)]$ (**138**), was isolated from the air oxidation of a mixture of manganese(II) salt, edt^{2-}, and HIm.[326,371] It has a square pyramidal geometry with S_4N donor set. The anion of (**138**) contains high-spin manganese(III) and exhibits interanion antiferromagnetic exchange interactions ($J = -0.15\,cm^{-1}$, $g = 1.91$) propagated by interanion NH···S hydrogen bonds. Attempts to mimic the active site of manganese(III) acid phosphatase have resulted in two mononuclear manganese(III) complexes containing sulfur ligands. Both complexes, $(PPh_4)[Mn(thiosal)_2(HIm)]\cdot 2CH_2Cl_2$ (**139**)[327] and $[Mn(salen)(S\text{-}p\text{-}C_6H_4NO_2)]\cdot CH_2Cl_2$ (**140**)[328], are square pyramidal with NO_2S_2 and N_2O_2S donor sets, respectively. The magnetic moment of the former complex measured in solution (5.11 μ_B at 298 K) and that of the latter measured on a solid sample (4.71μ_B at 281 K) are close to the expected values for manganese(III) complexes.

5.1.6.4 Nitrogen Donor Ligands

The chemistry of manganese(III) with nitrogen ligands other than macrocycles (see Section 5.1.7) or mixed N,O donors is still quite limited (see (Figures 3 and 17) for ligands described below). The synthesis and characterization of $[Mn\{N(SiMe_3)_2\}_3]$ (**141**) provides the first well-characterized example of a three-coordinate Mn compound.[329] It was prepared by treatment of $[Mn\{N(SiMe_3)_2\}_2]$ with one equivalent of $BrN(SiMe_3)_2$. The violet compound was characterized by X-ray diffraction, UV–visible and ^{1}H NMR spectroscopy, and magnetic studies. It has a trigonal planar MnN_3 framework with an Mn—N distance of 1.890(3) Å. The corresponding manganese(II) complex is dinuclear. Most other complexes have been generated either from

the reaction of manganese(III) halides or pseudohalides with mono-, bi-, or tridentate ligands or the reaction between oxo-bridged dinuclear complexes and NaN_3 (see Table 3). Octahedral mononuclear complexes, $[Mn(tacn)(N_3)_3]$ (**142**)[330] and $[Mn(terpy)(N_3)_3]$ (**143**),[331] result from the latter reaction and show a strong tetragonal elongation as a result of the Jahn–Teller distortion expected for a high-spin manganese(III) complex.

The first mononuclear manganese(III) peroxo species without a porphyrin ligand, $[Mn(3,5\text{-}Pr^i{}_2pzH)(HB(3,5\text{-}Pr^i{}_2pz)_3)(O_2)]$ (**144**),[332] was prepared from the reaction of $[\{Mn^{II}(HB(3,5\text{-}Pr^i{}_2pz)_3)\}_2](OH)_2$ with excess of H_2O_2 (10–20 equivalents) in the presence of $3,5\text{-}Pr^i{}_2pzH$ (2 equivalents) at room temperature. It is a six-coordinate complex with a "side-on" peroxo group.

The only μ-oxo-bridged dinuclear manganese(III) complex with a non-Schiff base ligand, $[Mn_2O(bpia)_2Cl_2](ClO_4)_3\cdot 2CH_3CN$ (**145**),[259] was reported by Pecoraro and co-workers (see Section 5.1.6.5.3 for other such complexes with a Schiff base ligand). It was prepared by reacting a DMF solution of $[Mn_2O(OAc)_2(bpia)_2Cl_2](ClO_4)_3$ with a 0.12 M solution of HCl in acetonitrile. The bridging oxygen atom lies on a crystallographic inversion center generating a linear Mn—O—Mn unit, with Mn···Mn and Mn—O distances of 3.5326(9) Å and 1.7663(5) Å, respectively. The cyclic voltammogram of (**145**) exhibits two quasireversible oxidation waves ($E_{1/2}$ values of 1.09 V and 1.54 V vs. SCE) and one quasireversible reduction wave ($E_{1/2}$ value of 0.63 V vs. SCE).

Compared to numerous bis(μ-oxo) dimanganese(III,IV) complexes, there are only a few examples of the corresponding dimanganese(III,III) species. N-donor ligands, such as the tetradentate polypyridyl ligands bpen, bpmpa, bped, and $bispicMe_2en$, as well as a hindered tris(pyrazolyl)borate ligand stabilize the manganese(III) oxidation state (see Table 11).[333–336]

In these complexes, the manganese(III) centers are strongly antiferromagnetically coupled with Mn···Mn separations and Mn—O—Mn angles in the ranges 2.674–2.699 Å and 92.1–97.0°, respectively. All complexes with tetradentate ligands have octahedral geometry around the manganese centers. However, steric crowding of the tridentate ligands resulted in five-coordinate manganese. The solution electronic spectra of these complexes are typical of the $[Mn_2(\mu\text{-}O)_2]^{2+}$ core.

5.1.6.5 Mixed Donor Polydentate Ligands

Most of the polydentate ligands that stabilize manganese(III) are Schiff bases. In this section, complexes containing various polydentate ligands are summarized (see (Figures 3, 18 and 19) for

Table 11 Magnetic and structural parameters for higher nuclearity (>Mn_5) manganese(III)–carboxylato complexes.

Compound	*Ground spin state (S)*	μ_{eff} (μ_B) [temp., K]	*Mn···Mn*(Å)	*References*
$(NEt_4)[Mn_7O_4(OAc)_{10}(dbm)_4]\cdot 3CH_2Cl_2\cdot 2C_6H_{14}$	3 or 4	10.06[260]	2.849(4)– 3.380(3)	305
$(NBu^n{}_4)[Mn_8O_6Cl_6(O_2CPh)_7(H_2O)_2]\cdot 1.5CH_2Cl_2\cdot 2H_2O$	11	13.8[300] 20.60[15] 17.7[5]	2.791(3)–3.625(2)	306,307
$[Mn_4O_2(OAc)_6(Pic)_2]_2$		2.876(7)–3.450(7)		291,308
$[Mn_4O_2(O_2CPh)_6(dbm)_2(bpe)]_2$				292
$[Mn_4O_2(O_2CEt)_7(bmpe)]_2(ClO_4)_2\cdot 4CH_2Cl_2$				309
$[Mn_9O_7(O_2CPh)_{13}(Py)_2]$		13.2[298]	2.869(6)–5.533(6)	310
$[Na_2Mn_9O_7(O_2CPh)_{15}(MeCN)_2]\cdot 3MeCN$	4	12.23[320] 6.94[5]	2.871(3)–3.393(3)	306,307
$[K_2Mn_9O_7(O_2CCMe_3)_{15}(HO_2CCMe_3)_2]$	2		3.26–3.36	311
$[Mn_{10}O_8(O_2CPh)_6(pic)_8]\cdot 6CH_2Cl_2$	0	14.28[320] 4.94[2]	2.956(3)–3.645(3)	312
$[Mn_{10}O_8(O_2CPh)_6(pic)_6(dbm)_2]\cdot 3CH_2Cl_2$			2.992(2)–3.668(2)	312
$[K_4Mn_{18}O_{16}(O_2CPh)_{22}(phth)_2(H_2O)_4]\cdot MeCN$	0	15.1[320] 1.73[2]	2.740(2)–3.478(2)	313
$[Mn_9O_7(O_2CC_6H_4(p\text{–}OMe))_{13}(4,4'\text{–}bpy)]_2$	2	11.68[300]	2.880 2.872	314

Table 12 Structural parameters for dinuclear noncarboxylato–manganese(III) complexes.

Compound	*Mn···Mn*(Å)	*Mn–O$_b$*(Å)	*Mn–O$_b$–Mn*(deg.)	*References*
(μ–alkoxo)				
[Mn_2(2–OH–5–Cl–SALPN))$_2$ (MeOH)]·MeOH	3.808(1)	2.317(4) 1.900(4)	128.9(2)	359
[Mn_2(2–OH–SALPN)$_2$(THF)]	3.756(2)	2.353(3) 1.883(3)	128.9(2)	360
bis(μ–alkoxo)				
[Mn(spa)Cl(CH_3OH)]$_2$	3.011(1)	1.926(3) 1.955(4)	101.8(1)	338
[Mn_2(SDSP)$_2$]·2CH_3CN	3.243(2)	1.939(6) 2.265(7)	100.7(3)	362
[Mn_2(3,5–Cl_2(SALPN))$_2$(OCH_3)$_2$]	3.192(3)	1.899(5) 2.209(5) 2.220(5) 1.910(5)	101.1(3) 101.4(2)	350
[Mn_2(BSP)(OCH_3)Cl_2(MeOH)$_2$]	3.006(2)	1.937(5) 1.944(5) 1.942(5) 1.938(5)	101.6(2) 101.6(2)	253
[Mn_2(BSP)(OCH_3)(NCO)$_2$(H_2O)$_2$]	2.980(3)	1.962(9) 1.935(9) 1.942(10) 1.926(9)	99.5(5) 101.0(5)	253
[Mn_2(OCH_3)$_2$(dbm)$_4$]	3.1037(6)	1.874(1) 2.136(1)		321
[Mn_2(OCH_3)$_2$(Sal)$_2$(CH_3OH)$_4$]	3.00	1.917(3)	102.5(1)	337
Ba_2[Mn_2(β–D–ManfH$_{-5}$)$_2$]·13H_2O	3.323(3)	1.970(8) 2.189(9) 2.055(7) 2.244(9)	103.9(4) 103.0(4)	316
bis(μ–phenoxo)				
[Mn(EtOH)$_4$][Mn_2(Sal)$_4$(Py)$_2$]	3.247(1)	1.911(3) 2.320(3)	99.78(13)	339
[Mn_2(amen)$_2$(H_2O)$_2$](ClO_4)$_2$	3.318(1)	1.912(3) 2.305(2)	?	352
[Mn_2(Salmp)$_2$]·2CH_3CN	3.111(1)	2.239(3) 1.900(3)	97.1(1)	363
[Mn_2(salen)$_2$(H_2O)$_2$](ClO_4)$_2$·H_2O	3.361(2)	2.490(3) 1.891(3)		351
(μ–oxo)				
[Mn_2O(5–NO_2-Saldien)$_2$]	3.490(2)	1.757(4) 1.751(4)	168.4(2)	357
[Mn_2O(bpmsed)$_2$](ClO_4)$_2$	3.516(2)	1.758(2)	180	358
[Mn_2O(bpia)2Cl_2](ClO_4)$_3$·2CH_3CN	3.5326(9)	1.7663(5)	180	259
bis(μ–oxo)				
[Mn_2O_2(BPEN)$_2$](ClO_4)$_2$·H_2O	2.676(3)	1.814(8) 1.853(9) 1.830(9) 1.863(8)	94.5(4) 92.1(4)	333,334
[Mn_2O_2(BPMPA)$_2$](NO3)$_2$·6H_2O	2.674(4)	1.818(9) 1.841(6)	93.9(3)	334
[Mn_2O_2(BPED)$_2$](ClO_4)$_2$·7H_2O	2.686(1)	1.855(4) 1.851(4) 1.839(4) 1.824(4)	93.3(2) 93.9(2)	334
[Mn_2O_2(HB(3,5–iPr_2pz)$_3$)$_2$]	2.696(2)	1.806(5) 1.813(6) 1.808(6) 1.787(6)	96.5(3) 97.0(3)	335
[Mn_2O_2(bispicMe$_2$en)$_2$](ClO_4)$_2$·5H_2O	2.699(2)	1.846(4) 1.851(4)	93.8(2)	336

Table 13 Magnetic properties and related parameters for dinuclear non–carboxylato–manganese(III) complexes.

Compound	μ_{eff} (μ_B) [*temp.* (K)]	*Temp. range* (K)	J (cm^{-1})	*References*
$[Mn_2(2–OH–SALPN)_2\ (MeOH)]\cdot MeOH$	4.85[298]		−3.55	359
$[Mn_2(SDSP)_2]\cdot 2CH_3CN$	5.08[280] 5.56[81]	80.0–300.0	+4.5	362
$[Mn_2(BSP)(OCH_3)Cl_2(MeOH)_2]$	5.16[292]	80.0–300.0	−15.6	253
$[Mn_2(BSP)(OCH_3)(NCO)_2(H_2O)_2]$	4.08[202]	80.0–300.0	−16.5	253
$[Mn(EtOH)_4][Mn_2(Sal)_4(Py)_2]$	3.14[298]			339
$[Mn_2(amen)_2(H_2O)_2](ClO_4)_2$	4.84[298] 1.70[4.4]	4.2–300	−1.68	352
$[Mn_2(salmp)_2]\cdot 2DMF$		2.0–300.0	−13	363
$[Mn_2(salen)_2(H_2O)_2](ClO_4)_2\cdot H_2O$	5.0[298]	77.0–292.0		351
$[Mn_2O(5–NO_2\text{-}Saldien)_2]$	1.44[280]	6.0–280.0	−120.0	357
$[Mn_2O_2(BPEN)_2](ClO_4)_2\cdot H_2O$	3.05[298] 1.17[30]	4.0–296.0	−86.4	333,334
$[Mn_2O_2(bispicMe_2en)_2](ClO_4)_2\cdot 6.5H_2O$	2.72[298] 0.36[30]	4.0–296.0	−100.5	356

[a] Employing $H = -2JS_1\cdot S_2$ convention.

Table 14 Electronic spectral properties of dinuclear non–carboxylato–manganese(III) complexes.

Compound	*Solvent*	$\lambda(\varepsilon, M^{-1}cm^{-1})$, nm	*References*
$[Mn_2(BSP)(OCH_3)Cl_2(MeOH)_2]$	MeOH	374(2860), 430 sh(775), 627(145)	253
$[Mn_2(BSP)(OCH_3)(NCO)_2(H_2O)_2]$	MeOH	377(2910), 433 sh(765), 610(160)	253
$[Mn(EtOH)_4][Mn_2(Sal)_4(Py)_2]$	DMSO	282(16,500), 323(8400), 424(336), 460 sh (274), 522(215)	339
	DMF	282(16,500), 323(8400), 460(271), 534(235)	
$[Mn_2(3–OtE–Salmp)_2]$	DMF	332(16200)	363
$[Mn_2(Salmp)_2]\cdot 2DMF$	DMF	332 sh(20200), 480 sh(4080)	363
$[Mn_2O_2(BPEN)_2](ClO_4)_2\cdot H_2O$	?	461(141), 545	333,334
$[Mn_2O_2(BPMPA)_2](NO_3)_2\cdot 6H_2O$		443(361), 575(249)	333,334
$[Mn_2O_2(HB(3,5-iPr_2pz)_3)_2]$	C_7H_8	468(315)	335
$[Mn_2O_2(bispicMe_2en)_2](ClO_4)_2\cdot 6.5H_2O$	H_2O	308 sh(503), 475(294), 492(323), 575 sh(145), 760(113)	336

structures of ligands). Complexes with carboxylates are not included here, as these have been already covered in Section 5.1.6.1. Structural data and some physical properties of such complexes are listed in Tables 11–17.

5.1.6.5.1 Bidentate and tridentate

Dinuclear Mn^{III} complexes with alkoxide or aryloxide ligands are detailed in Table 11. Examples of bis(μ-alkoxo) complexes with bidentate or tridentate ligands are $[Mn_2(OCH_3)_2(Sal)_2(CH_3OH)_4]$ (**146**) (where H_2Sal = salicylic acid)[337] and $[Mn(spa)Cl(CH_3OH)]_2$ (**147**).[338] The Mn···Mn separations in (**146**) and (**147**) are very similar (about 3.00 Å). Magnetic susceptibility data for (**146**) have been measured in the temperature range 80–300 K and indicated that an antiferromagnetic spin-exchange interaction operates between the manganese(III) centers ($J = -10.33\,cm^{-1}$). In the absence of any methoxide ligand, a bis(μ-phenoxo) complex, $[Mn(EtOH)_4][Mn_2(Sal)_4(py)_2]$

Table 15 Structural parameters of selected trinuclear manganese(III)–Schiff base complexes.

Compound	*Orientation of metals*	*Mn···Mn*(Å)	*Mn–O$_b$*(Å)	*References*
$[Mn_3(BBDP)_2(OCH_3)_2(CH_3OH)(EtOH)](ClO_4)\cdot CH_3OH$	Triangular a	3.141(3) 3.686(3) 3.686(3)	2.195(10) 2.205(10) 1.894(9) 1.891(9) 1.981(9) 1.940(9) 2.066(8) 2.144(10)	364
$[Mn_3O(bamen)_3](ClO_4)\cdot 2H_2O$	Triangular d	3.2999(6) 3.2952(6) 3.3026(6)	1.908(2) 1.909(2) 1.898(2)	368

Table 16 Structural parameters of selected tetranuclear manganese(III)–Schiff base complexes.

Compound	*Orientation of metals*	*Mn···Mn*(Å)	*Mn–O$_b$*(Å)	*References*
(μ_3–alkoxo)				
$[Mn_4(bsamp)_2(OCH_3)_4(CH_3OH)](ClO_4)_2\cdot 4CH_3OH$	Linear	3.485(3) 3.127(2)	1.885(2) 2.169(2) 1.876(5) 2.177(5)	353
(μ_3–oxo)				
$[Mn_4O_2(Saltren)_2][MnCl_4]\cdot 2CH_3CN$	Fused open cubane	2.992(2) 2.898(2) 3.035(2)	1.900(4) 1.944(4) 1.920(3) 2.093(4) 1.893(4) 2.273(3) 2.304(3)	369
(μ_4–oxo)				
$[Mn_4(O)(Salen)_4(Na(diglyme))_2]$	Oxo–centered tetrahedral	?	2.073(6) 2.059(6)	354

Table 17 Magnetic and structural parameters of selected higher nuclearity (>Mn_4) noncarboxylato–manganese(III) complexes.

Compound	*Ground spin state (S)*	$\mu_{eff}(\mu_B)$ [*temp.*, K]	*Mn···Mn*(Å)	*References*
$[Mn_6O_4Cl_4(Me_2dbm)_6]$	12	16.01[320] 13.69[2]	3.204(9) 4.531(3)	378
$[Mn_6O_4Br_4(Me_2dbm)_6]$	12		3.212(11) 4.541(4)	378
$[NaMn_6(OMe)_{12}(dbm)_6](BPh_4)\cdot 2CHCl_3$	12		3.2258(10) 3.20119(11) 3.1972(10)	322 366

(**148**),[339] is formed. The Mn···Mn separation in (**148**) (3.25 Å) is longer than that observed for (**146**) and (**147**). At 298 K the value of the effective magnetic moment for (**148**) is 3.14 μ_B.

5.1.6.5.2 Tetradentate

The most common tetradentate Schiff base ligands used are Salen (where H_2Salen = *N*,*N*′-ethylene-bis(salicylideneamine) and its derivatives (see (Figures 3, 18 and 19) for structures).

Square planar and square pyramidal mononuclear manganese(III) complexes with tetradentate ligands have been investigated extensively in the context of the enantioselective epoxidation of unfunctionalized olefins. In particular, tetracoordinate manganese(III) complexes with various tetradentate ligands of the general formula LMn, where L = a tetradentate dianionic ligand, such as base (see Figure 18), or pentacoordinate manganese(III) complexes with various tetradentate ligands of the general formula LMnX, where L = tetradentate dianionic ligand, such as tbbdea (see Figure 18), and X = halide, have been studied in depth.[340–346,370] This topic is covered in more detail in Volume 9 of this work.

[Mn_2(3,5-Cl_2(SALPN))$_2$(OCH_3)$_2$] (**149**) is the first bis(μ-alkoxo) dinuclear Mn(III) complex having John–Teller distortions along two of the Mn–OMe bonds. It contains a pseudo C_2 axis with a highly distorted [Mn_2(μ-OCH_3)$_2$] core. The Mn···Mn separation in **149** is 3.19 Å.[350]

[Mn_2(salen)$_2$(H_2O)$_2$](ClO_4)$_2$·H_2O ((**150**)·H_2O)[351] and [Mn_2(amen)$_2$(H_2O)$_2$](ClO_4)$_2$ (**151**)[352] are examples of bis(μ-phenoxo) complexes. The Mn···Mn separations in (**150**) is 3.361(2) Å and 3.318(1) Å, respectively. Variable-temperature magnetic measurements for (**151**) at 4.4–298 K indicate weak antiferromagnetic coupling between the metal centers ($J = -1.68\ cm^{-1}$).

Tetranuclear complexes [Mn_4(bsamp)$_2$(OCH_3)$_4$(CH_3OH)](ClO_4)$_2$·4CH_3OH ((**152**)·4CH_3OH)[353] and [Mn_4(O)(salen)$_4$(Na(diglyme))$_2$] (**153**)[354] have been synthesized. Complex (**152**) is an example of linear tetranuclear manganese(III) complex while (**153**) is an oxo-centered tetrahedral complex with no bridging ligands between the manganese centers.

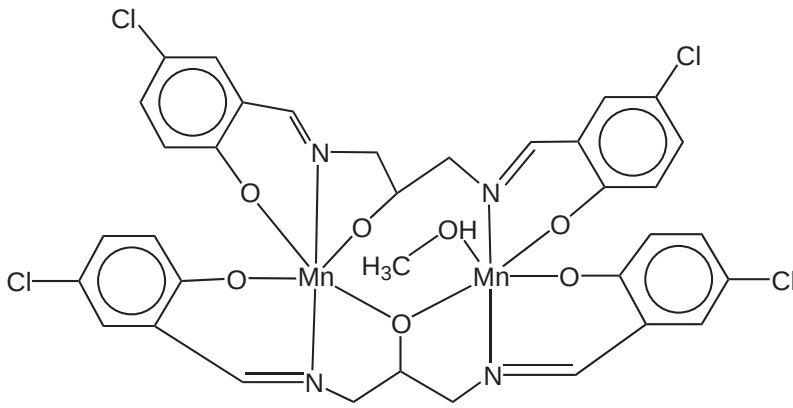
5.1.6.5.3 Pentadentate

A remarkably stable mononuclear manganese(III) hydroxide, [Mn(5-NO_2-sadpen)(OH)] (**154**), is the only example with this class of ligand (see Figures 18 and 19 for structures) reported to date.[355] It should be noted that the porphyrin ligands do not stabilize a mononuclear species and form hydroxo-bridged dimers.[356] Two μ-oxo dinuclear manganese(III,III) complexes have been reported with pentadentate Schiff base ligands [Mn_2O(5-NO_2Saldien)$_2$] (**155**) and [Mn_2O(bpmsed)$_2$](ClO_4)$_2$ (**156**).[357,358] Complex (**155**) reported by Armstrong and co-workers shows very strong antiferromagnetic interaction between the metal centers ($J = -120.0\ cm^{-1}$) that are separated by 3.490(2) Å with an Mn—O—Mn angle of 168.4(2)°. In contrast, the Mn···Mn separation and the Mn—O—Mn angle in (**156**) are 3.516(2) Å and 180°, respectively. Due to the linearity of the Mn—O—Mn vector, the antiferromagnetic interaction between the manganese centers in (**158**) is $-108\ cm^{-1}$.

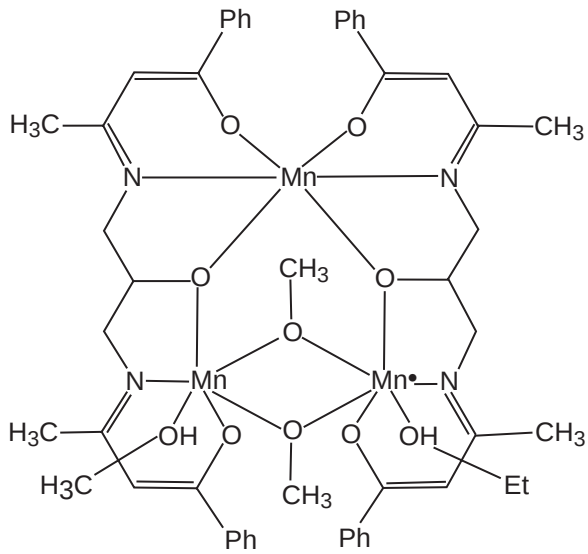
Three μ-alkoxo dinuclear complexes with pentadentate ligands have been reported: [Mn_2-(2-OH-5-Cl-SALPN)$_2$(MeOH)]·MeOH ((**157**)·MeOH),[359] [Mn_2(2-OH-SALPN)$_2$(THF)] (**158**),[360] and [Mn_2(2-OH-SALPN)$_2$(H_2O)]·3MeOH (**159**).[361] It is unexpected that the two metal centers in this complex are not equivalent. The Mn···Mn separation in (**159**) is the longest yet reported for a monoalkoxy-bridged species.

Several bis(μ-alkoxo) complexes have been reported for various pentadentate ligands. Some examples are [Mn_2(2-OH-3-NO_2-SALPN)$_2$]·2DMF (**160**·DMF),[347] [Mn_2(2-OH-5NO_2-SALPN)$_2$)](**161**),[348,349], [Mn_2(SDSP)$_2$]·2CH_3CN (**162**),[362] [Mn_2(BSP)(OCH_3)Cl_2(MeOH)$_2$] (**163**),[253] and [Mn_2(BSP)(OCH_3)(NCO)$_2$(H_2O)$_2$] (**164**).[253] An example of a bis(μ-phenoxo) complex with a pentadenate ligand is [Mn_2(Salmp)$_2$]·2CH_3CN ((**165**)·2CH_3CN).[363]

Employing the pentadentate ligand H_3bbdp, a trinuclear complex with a triangular core (see Figure 21), [Mn_3(bbdp)$_2$(OCH_3)$_2$(CH_3OH)(EtOH)](ClO_4)·CH_3OH (**166**) was prepared from $Mn(OAc)_2$·4H_2O in a mixture of MeOH/EtOH in the presence of triethylamine.[364] The manganese centers at the base of the isosceles triangle are bridged by two methoxide ions resulting much shorter Mn···Mn distance (3.141(3) Å) compared to the other two Mn···Mn separations (3.686(3) Å). At 298 K, the value of effective magnetic moment of (**166**) was 7.31 μ_B. Analysis of variable temperature magnetic susceptibility measurements for (**166**) indicated antiferromagnetic interactions between the metal centers.



(**163**)



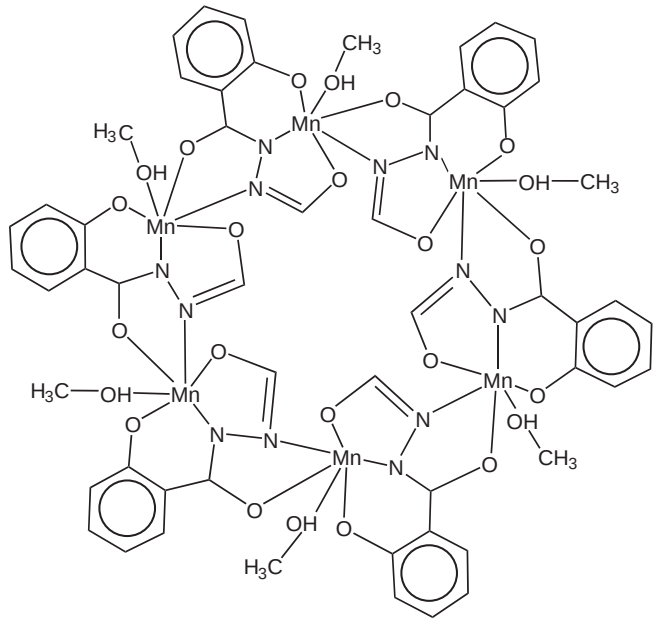
(**166**)

The nuclearity of the manganese(III) metallamacrocycles with the unsymmetrical ligands shown in (Figure 19) depends on the R group. For H_3fshz, H_3ashz, and H_3pshz ligands, hexanuclear complexes $[Mn_6(Rshz)_6(solvent)_6]\cdot 4solvent$ ((**167**): R = H, solvent = MeOH; (**168**): R = CH_3, solvent = DMF; (**169**): R = C_2H_5, solvent = DMF) were formed.[365,366] The H_3bshz ligand generated a decanuclear complex $[Mn_{10}(bshz)_{10}(MeOH)_{10}]$ (**170**).[367] Due to the meridional coordination of the ligands to the metal center, the ligands are not only bridging the ring metal ions using a hydrazide N—N group but also enforcing a propeller-like configuration. The sixth coordination site on each manganese center contains a solvent molecule. All complexes are neutral. Structures of complexes (**167**) and (**169**) are shown.

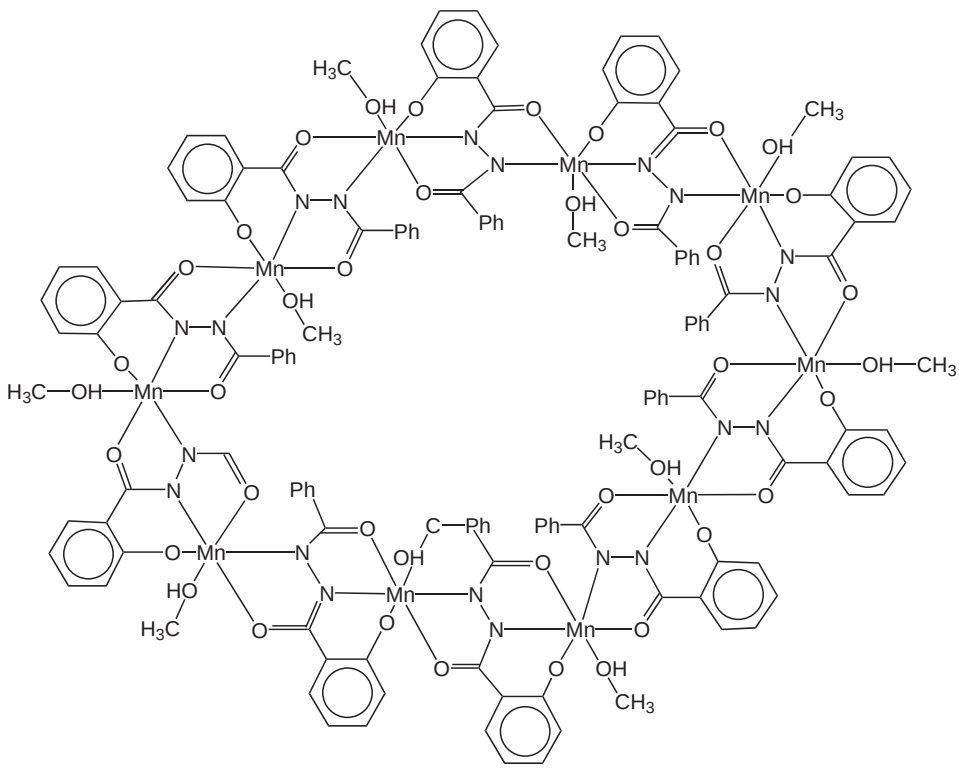
5.1.6.5.4 Hexadentate

There are only trinuclear and tetranuclear manganese(III) complexes reported with hexadentate Schiff base ligands. Two such hexadentate ligands, bamen and Saltren (Figure 19), form unique core structures.

The trinuclear complex $[Mn_3O(bamen)_3](ClO_4)\cdot 2H_2O$ (**171**), where H_2bamen = 1,2-bis(biacetylmonoximeimino)ethane, is of great interest, as it is a triangular d-type Figure 21 molecule without any bridging carboxylates.[368] It was prepared from the reaction of $Mn(ClO_4)_2\cdot 6H_2O$ with

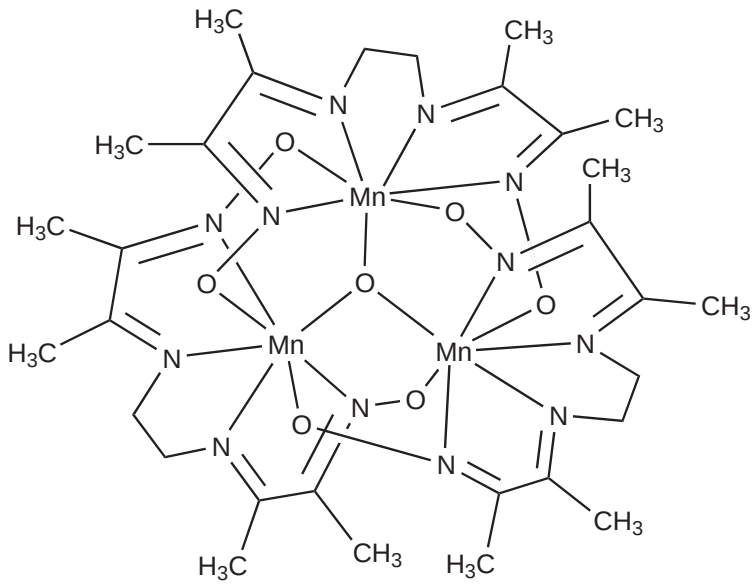


(**167**)



(**170**)

H_2bamen in methanol in the presence of triethylamine. The structure of (**171**) consists of a symmetric planar $\{Mn^{III}{}_3(\mu\text{-O})\}$ unit, where each hexadentate N_4O_2 donor ligand binds all three manganese centers. The N_4O_3 coordination sphere around each manganese center is very close to pentagonal bipyramidal. The average Mn···Mn separation in (**171**) is 3.30 Å. Cyclic voltammetry of (**171**) in MeCN shows three oxidation responses at $E_{1/2} = 0.87$ V, 1.45 V, and 1.98 V vs. Fc^+/Fc. The first two responses are very close to reversible processes and the last one is



(**171**)

irreversible. Analysis of variable-temperature magnetic susceptibility measurements for (**171**) indicates ferromagnetic interactions between the metal centers ($J = 22.3\,cm^{-1}$, $g = 2.06$).

Use of the tripodal ligand Saltren creates a tetranuclear complex $[Mn_4O_2(Saltren)_2][MnCl_4]\cdot 2CH_3CN$ (**172**)[369] having a fused open cubane structure without a carboxylate group. At 300 K the value of the effective magnetic moment for (**172**) is 5.1 μ_B, which decreases to 2.0 μ_B at 4.2 K. The redox properties of (**172**) in propylene carbonate have been studied by cyclic voltammetry. Two oxidation responses are observed at $E_{1/2} = -0.32$ V and 0.43 V vs. SCE.

5.1.7 COMPLEXES WITH MACROCYLIC LIGANDS

5.1.7.1 Oxidation States IV, V, and VI

5.1.7.1.1 Nitrogen donor macrocycles

Manganese is used by nature to catalyze a number of important biological reactions that include the dismutation of superoxide radicals, the decomposition of hydrogen peroxide, and the oxidation of water to dioxygen. The dinuclear manganese centers that occur in *Lactobacillus plantaraum* catalase[379] and *Thermus thermophilus catalase*[380,381] have attracted considerable attention and many model compounds have now been synthesized that attempt to mimic aspects of these biological systems.[382] The catalases have at least four accessible oxidation states ($Mn^{II}Mn^{II}$, $Mn^{II}Mn^{III}$, $Mn^{III}Mn^{III}$, and $Mn^{III}Mn^{IV}$); it is believed that the $Mn^{II}Mn^{II}/Mn^{II}Mn^{III}$ redox couple is effective in catalyzing the disproportionation of water.[383]

The tetranuclear manganese(IV) complex $[Mn_4O_6(1,4,7\text{-triazacyclononane})_4](ClO_4)_4\cdot 2H_2O$ in which the macrocycles are present as capping ligands, has been characterized by X-ray diffraction.[384] Each manganese ion is in a distorted octahedral environment comprised of three facially coordinated amine nitrogen atoms and three oxygen atoms with the $[Mn_4O_6]^{4+}$ core corresponding to an adamantane skeleton.

Individual ligands from a series of eight N-substituted 1,4,7-triazacyclononanes (L) incorporating combinations of H, Me, Et, or Pr substituents on the nitrogens have been employed to prepare both dinuclear Mn^{III} $[Mn_2(\mu\text{-}O)(\mu\text{-}CH_3COO)_2L_2]X_2$ ($X = ClO_4$ or PF_6) complexes and Mn^{IV} complexes of type $[Mn_2(\mu\text{-}O)_3L_2]^{2+}$ (the latter starting from L, a Mn^{II} salt and a counterion and subsequently treated with alkaline hydrogen peroxide).[385] The crystal structure of $[Mn^{IV}{}_2(\mu\text{-}O)_3L_2][PF_6]_2\cdot 0.5KPF_6$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) was determined. The

($Mn^{IV}{}_2\mu$-O)$_3$ core is near identical to that of the known tri-Et analogue. The Mn—Mn distance is exceptionally short at 2.295 Å and the value for the Mn—O—Mn bond angle of 77.9° is also low.

The ability of particular triazacyclononane derivatives to stabilize manganese in its higher oxidation states has resulted in the use of such complexes as oxidation catalysts.[382] One reaction of this type is the epoxidation of alkenes or alkynes, for which hydrogen peroxide is employed as the terminal oxidant. The use of such complexes to overcome the problems of hydrogen peroxide disproportionation has enabled the development of efficient epoxidation protocols. In one such study the catalytic activity of a higher-valent manganese complex of chiral 2,6-dimethyl-1,4,7-trimethyl-1,4,7-triazacyclononane, generated *in situ* from manganese(II), for the hydrogen peroxide (enantioselective) epoxidation of styrene was successfully demonstrated.[386] Other 2,6-substituted derivatives of the parent trimethylated parent ring were also shown to be effective ligands for similar asymmetric epoxidation reactions.[386] In a related study, the epoxidation of a considerable number of olefins with hydrogen peroxide using tris-N-substituted (methyl, 2-hydroxybutyl, or carboxymethyl) 1,4,7-triazacyclononane manganese species has been performed.[387]

The synthesis, structure, and characterization of the mixed-valence $Mn^{III}Mn^{IV}$complex [MnO(cyclam)]$_2$(ClO$_4$)$_3$·2H$_2$O (where cyclam = 1,4,8,11-tetraazacyclotetradecane) has been reported.[388] The X-ray structure of the cation (as its triflate salt) shows that the Mn_2O_2 core remains relatively unchanged in this complex from other related (μ-oxo) complexes prepared previously from different organic ligands.[388] A number of nitridomanganese(V) and (VI) complexes incorporating aza macrocyclic ligands have been generated. Photolysis of *trans*-[Mn^{III}(cyclam)(N$_3$)$_2$](ClO$_4$) in methanol at −35 °C with light at ~350 nm produced blue [{*trans*-[Mn^{V}(cyclam)(N)]}^{2}-(μ-N$_3$)](ClO$_4$)$_3$·3H$_2$O and dinitrogen.[389] Several six-coordinate complexes of type *trans*-[Mn^{V}(cyclam)(N)Y]$^{n+}$ (Y = Cl, n = 1; Y = MeCN, n = 2; Y = ClO_4^-, n = 1; Y = $CF_3CO_2^-$, n = 1) were also prepared. Each contains the nitridomanganese(V) (M≡N) unit and displays a temperature-independant paramagnetism corresponding to the presence of a low-spin d^2 configuration. *Cis*-[Mn^{V}(cyclam)(N)(CN)](ClO$_4$) was also isolated in this study from a solution of [{*trans*-[Mn^{V}(cyclam)(N)]}$_2$(μ-N$_3$)](ClO$_4$)$_3$·3H$_2$O in methanol after the addition of sodium cyanide. *Trans*-[Mn^{V}(cyclam) (N)(MeCN)]$^{2+}$ was demonstrated to undergo an electrochemically reversible one-electron oxidation to give a stable nitridomanganese(VI) species (d^1 configuration) which was characterized by UV–visible and EPR spectroscopy. In this study photolysis of [Mn^{III}(1,4,7-trimethyl-1,4,7-triazacyclononane)(N$_3$)$_3$] in acetonitrile at 20 °C with light at 253.7 nm was also investigated and shown to lead to photoreduction to afford colorless crystals of [{Mn^{II}(1,4,7-trimethyl-1,4,7-triazacyclononane)(N$_3$)}$_2$(μ-N$_3$)$_2$];[389] in contrast, photolysis with 350 nm light at −35 °C yielded the blue photooxidation product [Mn^{V}(1,4,7-trimethyl-1,4,7-triazacyclononane)-(N)(N$_3$)$_2$].

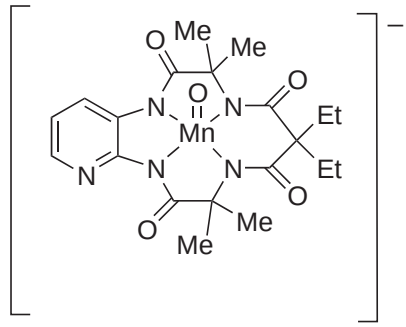
Photolysis of the monoazido species [$Mn^{III}L^1$(acac)L]BPh$_4$ (where L is 1,4,7-triazacyclononane, L^1 is its N-methylated derivative, and acac is pentane-2,4-dionate) in the solid state has been demonstrated to yield the six-coordinate nitrido species [Mn^{V}L(N)(acac)]BPh$_4$.[390]

An anilino radical complex of manganese(IV) has been prepared for comparison with its phenoxyl analogue.[391] The pendant arm aniline ligand 1,4,7-tris(2-amino-3,5-di-*t*-butylbenzyl)-1,4,7-triazacyclononane (L) yields the anilido complex [Mn^{IV}L]X (X = ClO$_4$ or BPh$_4$). The cyclic voltammogram of this species displays three ligand-centered one-electron-transfer oxidation waves corresponding to complexes incorporating one-, two-, and three-coordinated anilino radicals, respectively. These anilino radical species were characterized by UV–visible, EPR, and resonance Raman spectroscopy.

Manganese-oxo species of both salen[392,393] and porphyrin ligands[394] have been implicated as reaction intermediates in O-transfer processes. Groves *et al.* have demonstrated the formation of both Mn^{IV} and Mn^{V} oxo-porphyrins.[394,395] Following earlier studies in which synthetic ligand species gave rise to stable Mn^{V} oxo complexes[396–399] but did not yield useful O-atom transport agents,[396,398] the related tetraamide macrocyclic anionic complex (**173**) incorporating Mn^{V} was demonstrated to be activated towards O-atom transfer by the addition of secondary ions.[400] The effect of different activating ions on the reactivity was initially studied for the conversion of Ph$_3$P to Ph$_3$PO but then extended to a number of other reaction types. Overall, the system provides a mild, selective and stable catalyst for undertaking such O-atom transfers.

5.1.7.1.2 Mixed donor macrocycles

Under mildly basic conditions the manganese(II) species [MnLH$_3$][MnCl$_4$] [where LH$_3$ = *N*,*N*′*N*″-tris[(2S)-2-hydroxypropyl]-1,4,7-triazacyclononane (LH$_3$)] partially deprotonates and on aerial



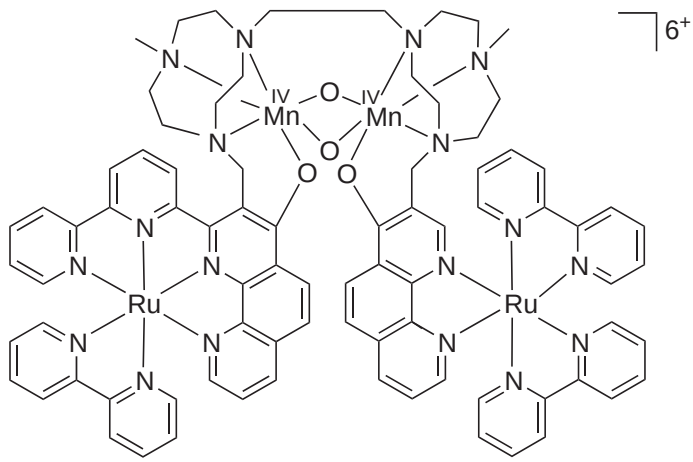
(**173**)

oxidation yields the mixed-valence dimer $[Mn^{II}LH_3L\ Mn^{IV}](PF_6)_3$ in which the manganese(II) and manganese(IV) sites show different coordination geometries, with the manganese(II) environment being trigonal prismatic and that of manganese(IV) pseudooctahedral.[401] Weighardt *et al.* suggested that the reason a manganese(II)/manganese(IV) complex is formed rather than a manganese(III) species arises because of the exacting stereochemical requirements of this ligand type. Manganese(III) would be expected to be Jahn–Teller distorted but it appears that this ligand will not favor the adoption of such a tetragonal distortion; this appears to be the driving force behind the stabilization of the relatively less-common manganese(IV) oxidation state in this case. Under the influence of a strong base, further oxidation of the above mixed-valence species occurs to yield a new manganese(IV) species which was assumed to be of type $[MnL]^+$.

As a consequence of the presence of bulky Pr^i groups (and in contrast to the methyl substituted ligand species), the more sterically hindering ligand, *N*,*N*′*N*″-tris[(2R)-2-hydroxy-3-methylbutyl]-1,4,7-triazacyclononane has been postulated to be unable to form a mixed-valence dinuclear species.[402] Rather, the corresponding monomeric complex of type $[Mn^{IV}L]PF_6$ was obtained and characterized by X-ray diffraction.

It is noted that a similar manganese(IV) complex cation, $[MnL]^+$, where LH_3 is *N*,*N*′,*N*″-tris(2-hydroxyethyl)-1,4,7-triazacyclononane, may be produced directly as its perchlorate salt on oxidation of a solution of manganese perchlorate and ligand with hydrogen peroxide or by oxidation using a solution of "manganese(II) acetate" and ligand in air. This product was shown by X-ray diffraction to have a pseudooctahedral geometry.[401]

There has been considerable interest in the potential of polynuclear manganese complexes to oxidize water to molecular oxygen catalytically and in doing so to thus act as models for photosystem II. Thus, with an aim of providing models for the photoactive components along the electron-transfer pathway of photosystem II, heterooligonuclear complexes incorporating one, two, or three manganese ions, oxidizable (radical forming) phenolates, and tris(2,2′-bipyridyl)-ruthenium(II)-derived units (as photosensitizers) have been prepared[403] and an example is the bridged 1,4,7-triazacyclononane derivative (**174**). The tris(dipyridyl)ruthenium(II) units were



(**174**)

employed because of their ability to induce light energy driven charge separation and thus act as mimics for the P680 reaction center in photosystem II. In general, the manganese ions in these complexes exist in the II, III, or IV oxidation states and readily undergo metal-centered reversible one-electron transfer steps.

In photosystem II an intermediate tyrosyl radical is formed which then repetitively oxidizes an adjacent manganese cluster leading to a four-electron oxidation of two water molecules to dioxygen. In broad detail, the model compounds[403] described above were demonstrated to undergo similar reactions on photochemical excitation of the respective ruthenium centers.

Linear homo- and heterotrinuclear complexes incorporating manganese(III/IV) with tris-(dimethylglyoximato)metalate(II) tetraanions (dimethylglyoximato = dmg) as bridging ligands have been prepared.[404] Two series of complexes, $Mn^{III}M^{II}Mn^{III}$ and $Mn^{IV}M^{II}Mn^{IV}$, where M^{II} (metalate) may be Mn^{II}, Ni^{II}, Cu^{II}, or Zn^{II} in individual complexes. 1,4,7-Trimethyl-1,4,7-triaza-cyclononane (L) acts as a capping ligand for the terminal Mn^{III} or Mn^{IV} ions. The X-ray structures of $[LMn^{III}\{(\mu\text{-dmg})_3Mn^{II}\}Mn^{III}L](ClO_4)_2$ and $[LMn^{III}\{(\mu\text{-dmg})_3Cu^{II}\}Mn^{III}L](ClO_4)_2$ have been determined. All these trinuclear complexes are quasi-isostructural, with the terminal manganese ions showing distorted N_3O_3 octahedral geometries, and the divalent metal ions M^{II} being six-coordinate (with $M^{II}N_6$ coordination spheres).

5.1.7.2 Oxidation State III

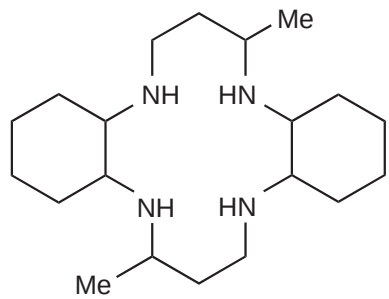
5.1.7.2.1 Nitrogen donor macrocycles

A number of studies of the interaction of the nine-membered, N_3-donor ring 1,4,7-triazacyclono-nane and its N-substituted derivatives manganese(III) have appeared.

Paramagnetic, dinuclear manganese(III) complexes incorporating the capping ligands 1,4,7-triazacyclononane (L) and 1,4,7-trimethyl-1,4,7-triazacyclononane (L′) have been investigated using ^{1}H NMR spectroscopy.[405] It was demonstrated that this technique can be employed to follow a slow interconversion starting from symmetric $[Mn^{III}{}_2(\mu\text{-O})(\mu\text{-}CH_3OO)_2L_2]^{2+}$ and $[Mn^{III}{}_2(\mu\text{-O})\ (\mu\text{-}CH_3OO)_2L'_2]^{2+}$ to asymmetric $[LMn^{III}(\mu\text{-O})(\mu\text{-}CH_3OO)_2Mn^{III}L']^{2+}$. The X-ray structure of the latter complex has been determined: each manganese(III) ion has facial octahedral coordination involving an O_3N_3 donor set, with the Mn···Mn distance being 3.121(3)Å. The latter is a typical separation for complexes of this type.[406]

Cohydrolysis of $MnLCl_3$ (L = 1,4,7-triazacyclononane) and $RuL'Cl_3{\cdot}H_2O$ (L′ = 1,4,7-trimethyl-1,4,7-triazacyclononane) in equimolar amounts in methanol containing an excess of sodium acetate gives rise to the asymmetric heterodinuclear species $[L'Ru(\mu\text{-O})(\mu\text{-}CH_3COO)_2MnL]PF_6$ on addition of sodium hexafluorophosphate. A model to interpret the strong spin-exchange coupling in this complex was presented.[407]

Pseudooctahedral complexes of the N_4 donor cyclam of type $[Mn(cyclam)X_2]Y$, where X and Y are a range of monovalent anions, have been reported.[408] The efficacy of a complex of this type (with X = Y = Cl) as an oxidation catalyst has been probed. In another study both manganese(II) and manganese(III) complexes of the tetraaza macrocycle (**175**) have been characterized and were shown to be of types $[MnLCl_2]{\cdot}0.5HCl$ and $[MnL(N_3)_2]N_3$. The *trans*-octahedral structures of both species have been confirmed by X-ray diffraction studies.

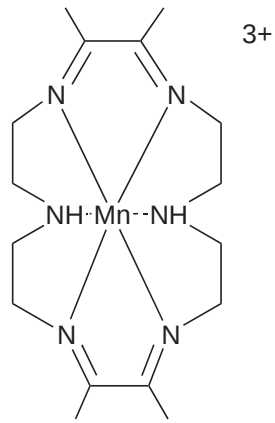


(**175**)

The characterization, redox properties, and pulse radiolysis study of manganese(III) complexes of type $[MnLCl_2]^+$ (where L = cyclam, *meso*-, and *rac*-5,7,7,12,14,14-hexamethylcyclam (tet a and tet b, respectively)) have been reported.[409] An X-ray crystal structure of the *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane complex shows that the coordination geometry of the "tet a" complex is close to octahedral with the macrocycle coordinated equatorially and the chlorides occupying *trans* axial sites.

The effect of solvent on the charge-transfer bands of thiocyanato-tetraazamacrocycle manganese(III) complexes has been investigated and shown to be influenced by the donor and acceptor (H bonding) properties of the respective solvents.[410]

The synthesis of the manganese(III) complex of the hexaaza macrocyclic ligand (**176**), derived from 2,3-butanedione and diethylenetriamine, and its use as a catalyst for the epoxidation of olefins using iodosylbenzene as oxidant has been reported.[411]



(**176**)

Mixed-metal complexes of tri- and tetraaza macrocycles incorporating manganese(III) and a second metal ion have been synthesized.[412,413] For example, the synthesis, ESR spectrum, and magnetic properties of the heterobinuclear complex $[LFe^{III}(\mu\text{-}O)(\mu\text{-}CH_3COO)_2Mn^{III}L]^{2+}$, formed by hydrolysis of a 1:1 mixture of $FeLCl_3$ and $MnLCl_3$ (where L = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane) in aqueous sodium acetate solution, have been reported.[412] The dinuclear complex displays strong intramolecular antiferromagnetic exchange coupling reflecting the presence of a doublet ground state.

Reaction of cyclam with $Mn(ClO_4)_2$ coupled with air oxidation results in formation of the formally Mn^{III} Mn^{IV} species $[Mn(cyclam)(\mu\text{-}O)]_2(ClO_4)_3$.[414] In this complex, the manganese ions are in fact crystallographically equivalent with each adopting a close to octahedral coordination geometry.

5.1.7.2.2 Mixed donor macrocycles

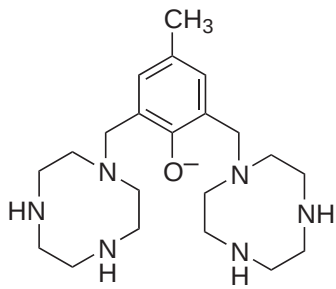
The 1:1 complex of the tris-*N*-propionate derivative of 1,4,7-triazacyclononane has been synthesized and X-ray diffraction has confirmed that all ligand donors are bound to the manganese(III) ion; surprisingly there was no evidence for a Jahn–Teller distortion of the type expected for a high-spin d^4 system of this type.[415]

Manganese(III) complexes of a number of phenolate pendant arm macrocycles related to the above have also been reported. Thus, both 1,4,7-tris(2-hydroxybenzyl)-1,4,7-triazacyclononane and 1,4,7-tris(3-*t*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane, on tris-deprotonation, afford monomeric pseudooctahedral complexes with this ion.[416]

The potentially tetradentate macrocycles 1,4-dimethyl-7-(3-*t*-butyl-5-methoxy-2-hydroxybenzyl)-1,4,7-triazacyclononane (L) and 1,4-diisopropyl-7-(3,5-di-*t*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane (L′), on loss of a proton, yield very stable octahedral complexes of type $[Mn^{III}L(Ph_2acac)]ClO_4$ and $[Mn^{III}L'(Bu_2acac)]ClO_4$ when prepared in the presence of the bidentate coligands 1,3-diphenyl-1,3-propanedionate (Ph_2acac) or 1,3-dimethyl-1,3-propanedionate (Bu_2acac), respectively. In this study, the corresponding neutral manganese(II) complex $[Mn^{II}L'(Bu_2acac)]$, was also isolated.[417]

A sodium ion template reaction employing sodium 2,6-diformyl-4-chlorophenolate and *N*,*N*-bis(2-aminoethyl)-*N*-hydroxyethylamine followed by an *in situ* transmetalation using $Mn(ClO_4)_2$ yields a mononuclear manganese(III) complex of a 21-membered asymmetric [2 + 2] Schiff base macrocycle.[418] In this species a hydroxyethyl group of the amine was eliminated such that ring contraction of one "cavity" of the macrocycle occurred with the formation of an imidazolidine ring. X-ray diffraction indicates that the manganese(III) ion in the resulting complex has a distorted octahedral coordination geometry.

The binuclear complex $[Mn_2L(\mu\text{-}CH_3OO)]^{2+}$ (where L = (**177**)) has been shown to be a "valence trapped" Mn^{II}/Mn^{III} species using a combination of ESR, electrochemistry, magnetic susceptibility measurements, and X-ray diffraction.[419,420] Each manganese ion adopts a distorted octahedral coordination geometry involving three nitrogens of one N_3-cyclononane fragment, an oxygen from a bridging phenoxy ion, and two oxygens from each of two bridging acetate ligands. The above mixed-valent species undergoes one-electron oxidation as well as one-electron reduction to form Mn^{III}/Mn^{III} and Mn^{II}/Mn^{II} species, respectively.



(**177**)

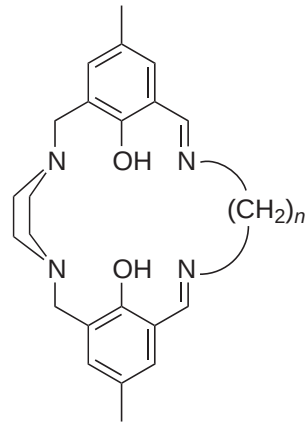
Other mixed-valence Mn^{II}/Mn^{III} species involving macrocyclic complexes have been reported.[421–424]

The complexes $[Mn_2LCl_2Br]\cdot H_2O$, $[Mn_2LBr_3]\cdot 0.5CH_2Cl_2$, and Mn_2LCl_2 have been reported, where LH_2 is the macrocyclic ligand formed by the [2 + 2] Schiff base condensation product of 1,3-diaminopropane and 2,6-diformyl-4-*t*-butylphenol.[425,426] The X-ray structure of the latter complex shows the bound macrocycle to be essentially planar; however, each manganese(II) ion is displaced 0.69 Å on either side of the ligand plane towards a bound chloro ligand such that the geometry of each metal center is distorted square pyramidal. The Mn···Mn distance is 3.168 Å. The structure of $[Mn_2LCl_2Br]\cdot H_2O$ has also been determined and confirms that this complex is "valence trapped" with the manganese(III) ion showing an average Mn—O length of 1.936 Å while the manganese(II) ion exhibits Mn—O lengths of 2.129 Å and 2.386 Å. The former ion has two chloro ions in axial positions and lies 0.15 Å out of the donor atom plane; the manganese(II) ion is displaced 1.25 Å from the donor plane (but to its opposite side) towards a coordinated bromo ligand; it also interacts with one of the chloro ions coordinated to the manganese(III) center. The cyclic voltammograms of the species $[Mn_2LX_2]$ (X = Cl or Br) in CH_3CN/CH_2I_2 each show two one-electron oxidation waves at ca. +0.6 V and ca. +1.2 V vs. NHE. The variable-temperature magnetic susceptibilities yield magnetic exchange parameters of $+0.24\,cm^{-1}$, $-2\,cm^{-1}$, and $-1\,cm^{-1}$ for complexes $[Mn_2LCl_2]$, $[Mn_2LCl_2Br]\cdot H_2O$, and $[Mn_2LBr_3]\cdot 0.5CH_2Cl_2$, respectively. Similar ESR data are found for I and II. At 7.5 K a glass of II gives an X-band spectrum with a broad $g = 2$ signal and apparent fine structure signals at $g = 29.0$, 7.4, 5.4, and 5.1. It was noted that relatively weak antiferromagnetic interactions are seen for such binuclear $Mn^{II}Mn^{III}$ complexes, which contrasts with the strong antiferromagnetic interactions that are generally observed for binuclear $Mn^{III}Mn^{IV}$ complexes.

Crystals of $[Mn_2(H_2L)(\mu\text{-}CH_3COO)(\mu\text{-}OH)(MeOH)_2][ClO_4]_2\cdot 2MeOH$ were obtained from condensation of 2,6-diformyl-4-methylphenol and 2,6-bis(aminomethyl)-4-methylphenol in the presence of Mn^{2+} and dioxygen.[427] The manganese(III) centers show identical distorted octahedral environments. The magnetic moment per manganese is 4.61 μ_B at room temperature and falls to 1.8 μ_B at 10 K, in accordance with the presence of weak antiferromagnetic coupling.

The synthesis as well as spectral and electrochemical properties of a series of unsymmetrical bis(phenoxo)-bridged macrocyclic binuclear manganese(III) complexes based on (**178**), incorporating dissimilar coordination sites, have been reported.[428] The bis(phenoxo)-bridged complexes yielded two reduction waves in the region 0.00 V to −1.60 V assigned to the process $Mn_2^{III} \rightarrow Mn^{II}Mn^{III} \rightarrow Mn_2^{II}$]. In the positive region (0.00 V to +1.00 V), two oxidation couples were

present corresponding to $Mn_2^{III} \rightarrow Mn^{III}Mn^{IV} \rightarrow Mn_2^{IV}$]. Small variations in the electronic and structural coordination environment of each manganese ion were demonstrated to be reflected in corresponding changes in the redox potentials of the individual complexes.



(**178**)

5.1.7.3 Oxidation State II

5.1.7.3.1 Nitrogen donor macrocycles

Since the early 1980s there has been a large number of studies involving coordination of manganese(II) to a wide variety of synthetic macrocyclic ligand types. In particular, nitrogen donor macrocycles have collectively formed the major ligand category employed for these studies.

As for the higher oxidation states of manganese, a significant number of investigations involving pendant arm, polyaza macrocycles have been carried out.

A number of reports of the interaction of the nine-membered, N_3 donor ring 1,4,7-triazacyclononane and its derivatives with manganese(II) have appeared. For example, hydrolysis of a solution containing equimolar amounts of the mononuclear complexes $L'RuCl_3.H_2O$ and $LMnCl_3$ (where L = 1,4,7-triazacyclononane and L′ = 1,4,7-trimethyl-1,4,7-triazacyclononane) in methanol with an excess of sodium acetate yields the asymmetric, heteronuclear species $[L'Ru(\mu\text{-}O)(\mu\text{-}CH_3COO)_2MnL)]^{2+}$ as its dihexafluorophosphate salt on addition of sodium hexafluorophosphate.[407] This complex has an $S = 3/2$ electronic ground state and the X-ray structure shows it to contain a (μ-oxo)bis(μ-CH_3COO)Ru core, with the ruthenium ion capped by the tridentate macrocycle L′ and the manganese ion capped by L. Assignment of the metal oxidation states in this complex is not trivial but on the basis of the results of physical measurements, the complex was formulated as a $[Ru^{III}OMn^{III}]^{2+}$ species. The product exhibits strong spin exchange coupling and also undergoes reversible one-electron electrochemical oxidation. Chemical oxidation employing $Na_2S_2O_8$ in aqueous solution yields $[L'Ru(\mu\text{-}O)\text{-}(\mu\text{-}CH_3COO)_2MnL)]^{3+}$.

A manganese(II) complex of the bis-pendant-arm ligand 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane (L) of type $[MnLCl]ClO_4$ has been demonstrated by X-ray diffraction to adopt a coordination geometry in the solid state that lies between octahedral and trigonal prismatic.[429] An electrochemical investigation indicated that this complex undergoes a one-electron oxidation from manganese(II) to manganese(III) followed by a further oxidation step to manganese(IV) at a significantly more positive potential. A related dinuclear complex, $[Mn_2L'Cl_2](CLO_4)_2 \cdot 2DMF$, in which L′ is the dinucleating ligand formed by the attachment of 2-pyridylmethyl arms to each of the four secondary amines in a species of type ethylene-*N*,*N*′-linked bis(1,4,7-triazacyclononane) (L′), has also been reported. A number of analogues of this latter (dimeric) complex, incorporating various other bridging linkages, also have been synthesized. Electrochemical measurements indicate that as the metal–metal separation increases, electrostatic repulsions are reduced and oxidation of the respective complexes occurs at lower potentials.

Tris-N-functionalization of 1,4,7-triazacyclononane has yielded a variety of sexadentate ligands, which form stable complexes with manganese(II). For example, the 1,4,7-tris(2-pyridylmethyl) derivative gives a complex of type $[MnL](ClO_4)_2$ in which the manganese ion has a

distorted prismatic, N_6 environment. The cyclic voltammogram of this species in acetonitrile shows a quasireversible, one-electron Mn^{II}/Mn^{III} couple.[430] A related complex of type $[MnLCl]^+$, where L = 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane, has also been characterized.[431] The corresponding species $[MnL(H_2O)]^{2+}$ exhibits a reversible Mn^{III}–Mn^{II} couple, which is less positive than that for the 1:1 complex of 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane, indicating greater stabilization of the Mn^{III} state in the case of the former system.

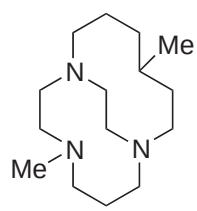
A study of manganese(II) complexation by the linked 1,4,7-triazacyclononane moiety, 1,2-bis (1,4,7-triaza-1-cyclononyl)ethane (L), in which two potentially tridentate N_3 units are joined by an ethane bridge linked to a nitrogen of each ring, has been reported.[432] Reaction of $MnCl_2{\cdot}4H_2O$ with this species (in a 2:1 ratio) gives colorless $[Cl_2Mn(L)MnCl_2]{\cdot}0.5H_2O$. Addition of sodium hexafluorophosphate to an aqueous solution of this complex yielded the monomeric species $[MnL](PF_6)_2$ which may be oxidized in alkaline solution with oxygen, yielding the tetrameric manganese(IV) complex $[Mn_4(L)_2(\mu\text{-}O)_6]^{4+}$. In each of these complexes the respective N_3 units are postulated to occupy three facial coordination sites about each metal center—a mode of coordination well documented to occur for the parent single ring, 1,4,7-triazacyclononane.[433]

A series of structural, spectroscopic, and electrochemical studies were reported for mono- and dinuclear manganese(II) complexes of type $[MnLCl]^+$ (where L = 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane)) and $[Mn_2L'Cl_2]^{2+}$ (where L′ represents a series of bis(pentadentate) ligands derived from bis(1,4,7-triazacyclononane) macrocycles linked by ethylene, propylene, butylene, *m*-xylylene, and 2-hydroxypropylene bridges joining an amine on each 1,4,7-triazacyclononane fragment, with 2-pyridylmethyl arms attached to the two remaining secondary ring nitrogens of each ring).[434] X-ray structures of the above complexes show the geometry of each manganese center to be intermediate between octahedral and trigonal prismatic and, for the dinuclear complexes, there is a systematic increase in the M···M distance as the length of the alkyl chain is increased.

Electrochemical, ESR, and H_2O_2 reactivity studies have been reported for the above mononuclear and binuclear complexes. Cyclic and square-wave voltammetric studies show that a one-electron oxidation (from Mn^{II} to Mn^{III}) occurs for the mononuclear complex, followed by a further oxidation to Mn^{IV} at a significantly more positive potential. The binuclear manganese(II) complexes are each oxidized to the manganese(III) species in two unresolved one-electron steps and then to manganese(IV) species. In an extension of these studies, reaction of hydrogen peroxide with the dinuclear complex incorporating an ethylene bridge yielded an oxo-bridged $Mn^{III}Mn^{IV}$ intermediate with a characteristic 16-line ESR signal.

The use of the *N*,*N*,*N*″,*N*‴-tetramethylcyclam derivative, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc), leads to formation of the five-coordinate manganese(II) derivative $[Mn(tmc)Cl]BPh_4{\cdot}CH_3CN$ in which the macrocycle is coordinated in an equatorial fashion with the chloro ligand occupying an axial site.[435] The divalent oxidation state of the manganese was confirmed by a variable-temperature magnetic susceptibility study ($S = 5/2$). The cyclic voltammogram of this complex showed two reversible waves that were interpreted in terms of the presence of a chemical equilibrium between isomeric species.

The binding for the cross-bridged macrocycle (**179**) to act as a proton sponge and hence inhibit metal ion binding was overcome by the use of vigorously dried acetonitrile.[436] Thus reaction of $[Mn(pyridine)_2Cl_2]$ with (**179**) in an inert atmosphere in this solvent yielded $[MnLCl_2]$ (L = (**179**)) whose distorted octahedral structure, incorporating the macrocycle in a folded configuration, was confirmed by an X-ray diffraction study. Magnetic susceptibility data for this complex indicated its d^5 high-spin nature.



(**179**)

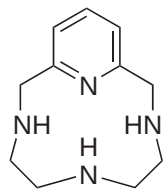
The redox behavior of [MnLY], where L is the dianionic form of dibenzotetramethyltetraaza[14]annulene and Y is tetrahydrofuran or nothing, has been investigated.[437] A two-electron oxidation and one- and two-electron reductions have been determined for this complex. The

former behavior yielded a variety of functionalized species of type $[Mn^{III}LX]$ (X = Cl, I or NCS) as well as cationic species that included one of type $[MnLY_2]^+$ (Y = tetrahydrofuran).

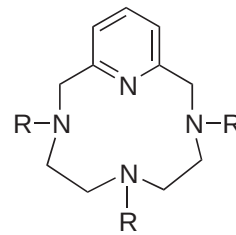
High-spin, five-coordinate complexes are known of type $[MnLX]PF_6$ (X = F, Cl, Br, or I and L = 2,9-dimethyl-3,10-diphenyl-1,4,8,11-tetraazacyclotetra-1,3,8,10-tetraene). Electrochemical investigation of these complexes revealed that they are surprisingly resistant to oxidation in dimethylsulfoxide.[438]

Other aza-donor macrocyclic ligand complexes of manganese(II) have been synthesized using metal template procedures.[439–442]

Stability constants represent primary data when considering a ligand type for use in a medical application. Stability constant determinations have been undertaken for the N_4 donor macrocyclic ligand derivatives (**180**) and (**181**) with a range of divalent first-row transition and post-transition metal ions (including Mn^{2+}).[443,444] In all cases the "natural" (Irving–Williams) stability order was observed to obtain for the 1:1 (M:L) complexes.



(**180**)



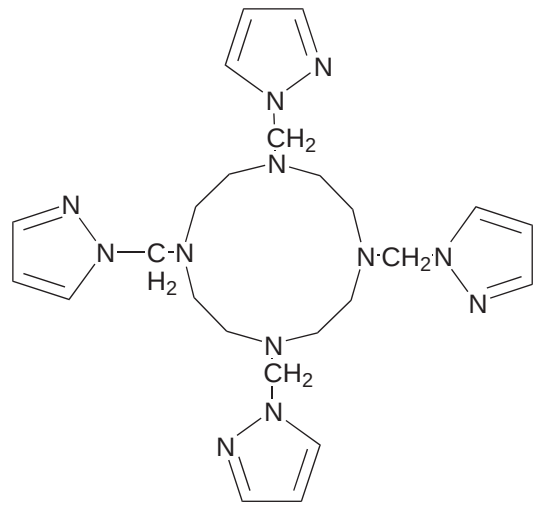
R' = Me, R = H
R' = R = H
R' = R = CH_2COOH
R' = H, R = CH_2COOH

(**181**)

There have been a number of other reports of the use of largely unsaturated, N_4 donor macrocycles to generate 1:1 manganese(II) complexes.[445–451] The majority of these have been assigned octahedral geometries in which two monodentate ligands occupy the remaining positions in the coordination sphere.

Two manganese(II) complexes have been reported of type $[MnL](ClO_4)_2$ that incorporate the 12-membered N_4 donor "cyclen" macrocycle functionalized with four and three pyridyl donor pendants, respectively (namely 1,4,7,10-tetrakis(2-pyridylmethyl)-1,4,7,10-tetraazacyclododecane and 1-methyl-4,7,10-tris(2-pyridylmethyl)-1,4,7,10-traazacyclododecane). In the first of these the manganese ion is eight-coordinate with all donor nitrogens of the ligand bound to the central ion to yield a distorted square prism coordination geometry. The metal ion in the second complex is seven-coordinate with a distorted monocapped octahedral geometry with again all of the nitrogen donors of the ligand bound to the manganese ion.[452]

The potentially octadentate, pendant arm ligand 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane (L; (**182**)) gives $[MnL][PF6]_2 \cdot Me_2CO$ with manganese(II).[453] The crystal structure of this complex shows that the central metal is coordinated by eight nitrogens of L.



(**182**)

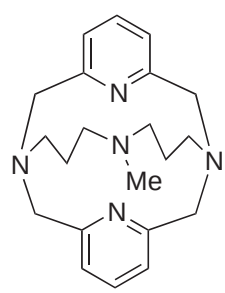
Within the overall context that manganese(II) species are potential NMR contrast agents, structure–function relationships underlying the observed ^{1}H NMR relaxation enhancement for the protons of coordinated water have been investigated for a series of manganese(II) complexes of pentaaza macrocyclic ligands with 15- to 18-membered rings showing various degrees of unsaturation.[454] The ligands range from a fully saturated, 15-membered pentaazacrown through to Schiff base derivatives formed between 2,6-diacetylpyridine and triethylenetetramine or its longer-chain analogues.

Manganese(II) complexes of a number of other polyaza macrocyclic ligands have also been investigated as solvent proton relaxation reagents.[455–457] For example, over 20 such complexes of 1,4,7,10,13-pentaazacyclopentadecane have been investigated to examine the effects of substituents on the nuclear magnetic relaxation of water protons.[457] Enhanced relaxation rates were observed for those complexes incorporating hydrogen bonding substituents, such as hydroxyalkyl or aminoalkyl groups, on the carbon backbone of the macrocycle.

In a major series of papers, Riley *et al.*[458–466] have demonstrated that the manganese(II) complexes of particular polyaza macrocycles, such as 1,4,7,10,13-pentaazacyclopentadecane, act as highly active and stable mimics of superoxide dismutase. This research group has developed a wide-ranging program to design, synthesize, and test complexes of this type in chosen disease models (both *in vitro* and *in vivo*) as potential pharmaceutical agents. The superoxide dismutase-like activity of other manganese(II) complexes of a aza macrocycles has been reported.[467,468]

Manganese(II) complexes of pentaaza macrocyclic ligand types have been reported, with these typically being assigned six-coordination[469] or seven-coordination[470] geometries. These include the six-coordinate complex, $[MnLCl][BF_4]\cdot 4H_2O$ (where L is a 1,10-phenanthroline-containing, unsaturated system incorporating peripheral hydroxyethyl tails),[471] and a complex of the flexible aliphatic macrocycle, 1,4,7,10,13-pentaazacyclopentadecane, for which the complex cation also is of similar stoichiometry to the above. This latter species has been demonstrated to promote ^{1}H NMR relaxation enhancement of coordinated water molecules. For this system it was concluded that water is rapidly exchanged in the coordination sphere of the manganese ion.[472]

The X-ray structure of $[MnLCl](PF_6)$, incorporating the topologically constrained high-spin ($\mu = 5.96\ \mu_B$) pentadentate ligand (**183**), shows that the manganese ion adopts a pseudooctahedral coordination geometry in which five donors of the organic ligand and a chloride ion occupy the coordination sphere.[469] In part, the ligand is "preorganized" for metal coordination and the above manganese complex is remarkably kinetically stable in 0.1 M HNO_3—the visible spectrum of the solution being unchanged after more than two weeks. The complex exhibits weak ferromagnetism; it reacts with *t*-butyl hydroperoxide and hydrogen peroxide to yield the *t*-butyl peroxyl and hydroperoxyl radicals, as shown by ESR spectroscopy.

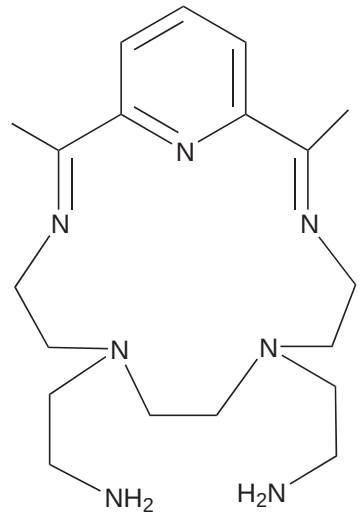


(**183**)

Other studies involving ligands of the above general type describe a seven-coordinate manganese(II) species[473] of the macrocycle formed *in situ* from reaction of 1,10-phenanthroline-2,9-dicarboxaldehyde dihydrazone with 2,6-bis(bromomethyl)pyridine. The magnetostructural behavior of a second seven-coordinate (distorted pentagonal bipyramidal) species of the 15-membered Schiff base macrocycle derivative obtained from diacetylpyridine and triethylenetetramine has also been reported.[474]. With respect to this latter ligand type, it is noted that complexes (including manganese complexes) of Schiff base macrocycles derived from heterocyclic dicarbonyls were reviewed by Fenton in 1986.[475]

The complex $[MnL](PF_6)_2$, where L is the pendant arm ligand (**184**), also based on a N_5 diimine macrocycle, was obtained directly by a template procedure.[476]. The coordination geometry is pentagonal bipyramidal with the pendant amino groups occupying the axial sites. The aqueous ^{1}H NMR relaxation rate enhancement in the presence of this complex is small in comparison to

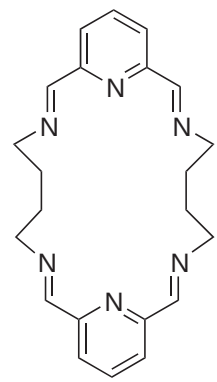
those obtained for other complexes (see above)—indicative of relaxation via an outer-sphere mechanism only.



(**184**)

A number of pendant arm ligand derivatives based on hexamine macrocyclic backbones have been reported.[477] One such species was formed by the [2 + 2] Schiff base condensation between 3,3-iminobis(propylamine) and diformyl-*p*-cresol followed by sodium borohydride reduction of the four imine functions so generated. Potentiometric studies indicate that a range of both mononuclear and dinuclear species are formed in solution with manganese(II) incorporating various both protonated and nonprotonated forms of the ligand.

The observation of a strong infrared absorption at below 2,000 cm^{-1} for the dinuclear complex of (**185**) incorporating manganese thiocyanate was taken as indicating that rare (single atom) N-bound NCS bridges occur in this manganese(II) species.[478,479]

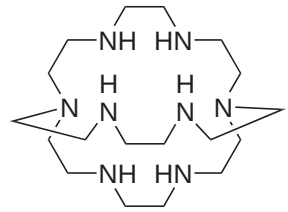


(**185**)

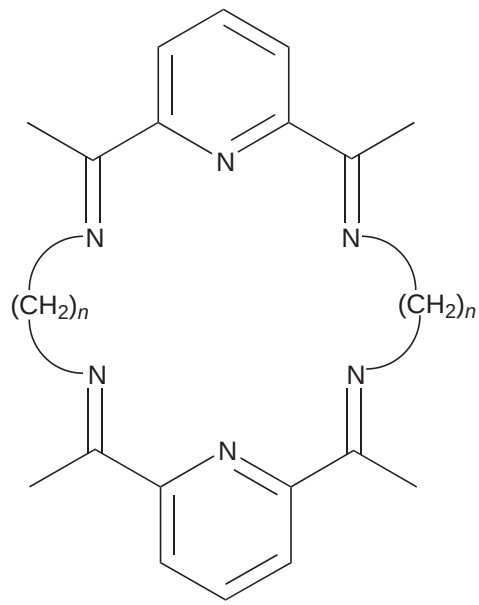
Stability constants for the manganese(II) complexes of two polyaza cycloalkanes incorporating six and eight secondary nitrogens atoms have been reported for aqueous media at 25 °C along with the corresponding enthalpy changes determined using a microcalorimetric technique. The log *K* values for the 1:1 complexes of the above ligands are 10.50 and 6.27, respectively, indicating a substantial stability loss for the larger ring complex.[480]

Transition metal ion cryptates of the tris(2-aminoethyl)amine-capped cryptand (**186**) showed enhanced stability of the +2 oxidation state compared with a related tighter-capped cage ligand.[481] An X-ray structure determination of the former showed that the cationic manganese(II) cryptate adopts a pseudooctahedral geometry with the capping nitrogens remaining unprotonated (while cryptates of smaller, more highly Lewis acidic cages, are obtained in a protonated form). The manganese(II) ion was found to be symmetrically placed within a slightly elliptical cryptand structure, which is present in an overall *lel* conformation.

A heterobinuclear complex of type $PbMnL(NCS)_4]$ containing the 24-membered macrocycle (**187**) ($n = 5$) has been synthesized. The X-ray structure shows a Pb—Mn separation of 4.857 Å, with the metals bridged by two —NCS— groups.[482]



(**186**)



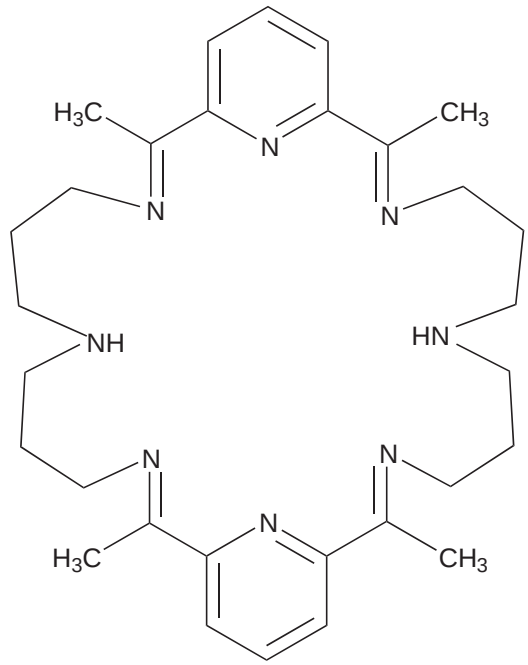
(**187**)

The Schiff base complex $[SrL](BPh_4)_2$ (L = (**188**)) was obtained by an *in situ* metal template procedure.[483] This species undergoes a transmetallation reaction in dry ethanol to yield $[Mn_2NCS_4]$ (L = (**188**)). No evidence for a magnetic exchange interaction was observed in this case.

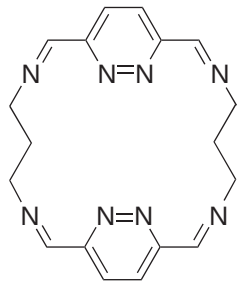
Ring opening of the cryptand derived from condensation of the branched tetraamine "tren" with 2,6-diacetylpyridine (in a 2:3 molar ratio) in the presence of manganese(II) acetate, $NaBF_4$,[484] and NEt_3 yielded the dinuclear complex $Mn_2L(CH_3COO)](BF4)_3$ (where L = XH5) which was proposed as a structural model for active sites in natural systems. The Mn—Mn separation is 4.82 Å compared with that of 4.9 Å found in the D-xylose isomerase from *Streptomyces rubiginosus*.

Reaction of lead(II) (as a template), 3,6-diformylpyridazine, and 1,3-diaminopropane in 1:1:1 and 2:2:1 ratios yielded the corresponding lead(II) complexes of (**189a**) and (**189b**), respectively.[485] Transmetallation of either of these products by reaction with manganese(II) perchlorate in the presence of excess sodium thiocyanate gave $[Mn_2L(NCS)_4]$ (where L = (**189a**)). The X-ray structure of this product confirmed that it contained the corresponding [2 + 2] Schiff base condensation product. The two manganese ions are non-equivalent, with one having a six-coordinate and the other a seven-coodinate geometry. An unusual single nitrogen bridge involving the nitrogen of one thiocyanate group occurs between the manganese ions.

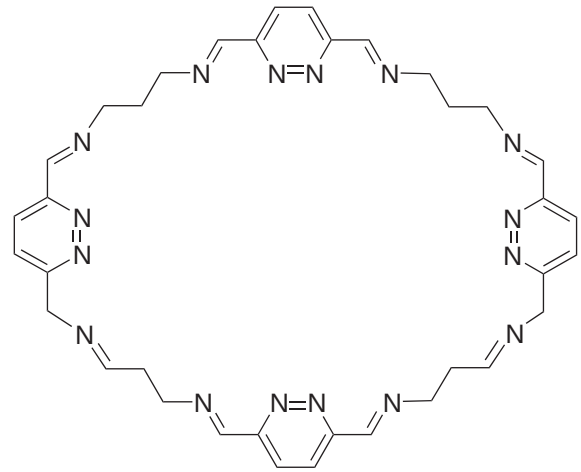
Polyaza macrocycle derivatives have been employed in a number of analytical applications.[486,487] For example, polymer-immobilized cyclam has been employed for the preconcentration of manganese in seawater prior to analysis.[487]



(**188**)



(**189a**)



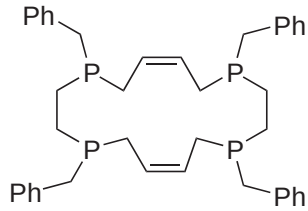
(**189b**)

5.1.7.3.2 Phosphorus donor macrocycles

Macrocyclic complexes of type [$MnLX_2$] (where L = (**190**) and X = Cl, Br, I, and NCS) have been synthesized.[488] These complexes appeared exceptionally stable relative to other manganese(II) phosphine complexes. They can be manipulated in air for minutes without decomposition, a finding that was ascribed to the steric protection afforded by this macrocyclic ligand species.

5.1.7.3.3 Oxygen donor macrocycles

Mass spectrometry studies have demonstrated the formation of a number of 1:1 crown polyether complexes of manganese(II) as cationic species in the gas phase.[489,490]



(**190**)

A number of solvent extraction experiments have demonstrated that individual crown ethers in combination with a lipophilic sulfonic acid (such as didodecylnaphthalene sulfonic acid) are efficient, synergistic phase transfer agents for manganese(II) from aqueous solution into an organic phase.[491,492] The X-ray structure of the manganese di-*t*-butylnaphthalenesulfonate with cyclohexano-15-crown-5 ether as its toluene solvate has been reported.[493]

5.1.7.3.4 Sulfur donor macrocycles

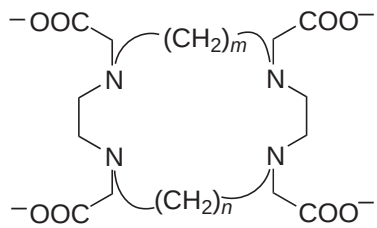
An electrospray mass spectrometric study of the interaction of manganese(II) salts with the tetrathia analogue of cyclam showed the utility of this technique for detecting complex formation for both manganese and a series of other metal cations.[488]

5.1.7.3.5 Mixed donor macrocycles

Manganese(II) has been commonly employed as a templating metal ion for the synthesis of a wide range of other mixed donor (oxygen/nitrogen) Schiff base macrocycles (and/or their imine-reduced derivatives).[494–510]

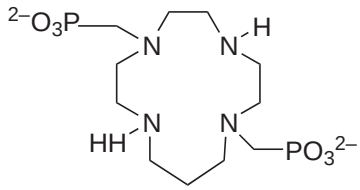
Log *K* values (25 °C; $I = 0.1$) for the manganese(II) complexes of the, 12- to 14-membered tetraaza rings of type (**191**) incorporating N-pendant, tetracaboxymethyl groups have been reported as 20.20, 16.74, and 11.27, respectively, for formation of the fully deprotonated ligand species of type $[MnL]^{2-}$; values for the 2:1 $[Mn_2L]$ as well as for protonated-ligand complex species were also determined.[511] The corresponding stabilities of the 1,7-diacetic acid and 1,4-diacetic acid derivatives of the 12-membered 1,4,7,10-tetraazacyclododecane ring are 11.29 and 11.07, respectively.[512]

Potentiometric titrations of the 1,7-disubstituted derivatives of the 12-membered ring 1,4,7,10-tetraazacyclododecane incorporating bis(methanephosphoric acid) or bis(methanephosphoric acid monoethylester) pendant arm substituents (**192a**) and (**192b**) with base in the presence of manganese(II) confirm the 1:1 stoichiometries of the corresponding complexes in aqueous solution. The former ligand also demonstrated an ability to yield species of type $MnHL^{+}$ and MnH_2L^{2+} (where H_2L is the neutral ligand).[513]

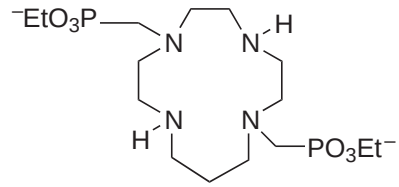


(**191**)

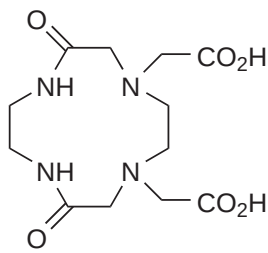
Formation constants for the manganese(II) complexes of the 12- and 13-membered, N_4 macrocyclic systems incorporating two carboxymethyl arms (**193a**) and (**193b**) have been reported as (log) 5.07 and 5.10.[514] The X-ray structure of $[MnL(H_2O)]$ (L = (**193b**)) shows that the metal has a highly distorted trigonal prismatic geometry with two carboxylate oxygens, an amide oxygen, and two tertiary nitrogens bound to the central metal ion.



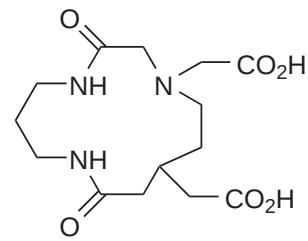
(**192a**)



(**192b**)



(**193a**)

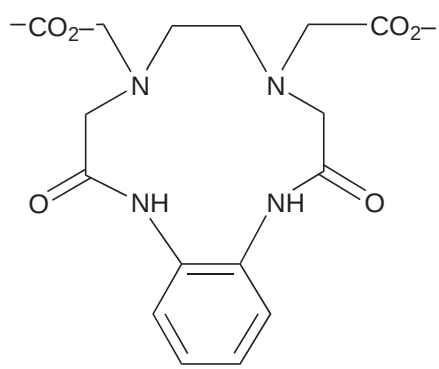


(**193b**)

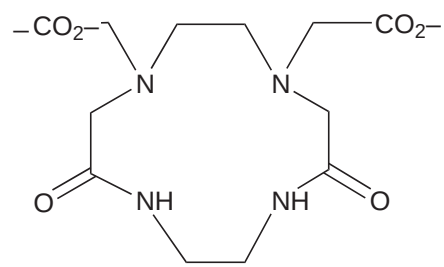
The new 13-membered macrocycle 4,7-bis(carboxymethyl)-12-hydroxy-2,9-dioxo-1,4,7,10-tetraazacyclotridecane (L) has been synthesized and shown to yield a manganese(II) complex of type $ML{\cdot}4H_2O$ which occurs as two crystallographically nonequivalent forms in the solid state.[515] The first of these has a seven-coordination geometry in which six donors from the macrocycle form a trigonal prism around the manganese, with a water oxygen forming a cap above one of the square faces of the prism. In the second form five macrocyclic donors and an oxygen atom from a water molecule coordinate to the central manganese; if an amide oxygen atom that weakly interacts at a distance of 3.188 Å from the metal is included in the coordination sphere, then the coordination geometry may be described as distorted caped trigonal prism. The ESR hyperfine structure of the above complex in a glass matrix exhibited the so-called forbidden-transition ($\Delta m_I = 1$) lines at intermediate fields between the allowed transition ($\Delta m_I = 0$) lines.

The stability constant ($I = 0.1$, 25 °C) has been reported for the 1:1 manganese(II) complex of the related amide-containing, 15-membered macrocycle 1,4,7-trimethylcarboxy-9,14-dioxo-1,4,7,10,13-pentaazacyclopentadecane as 14.7 (log value).[516]

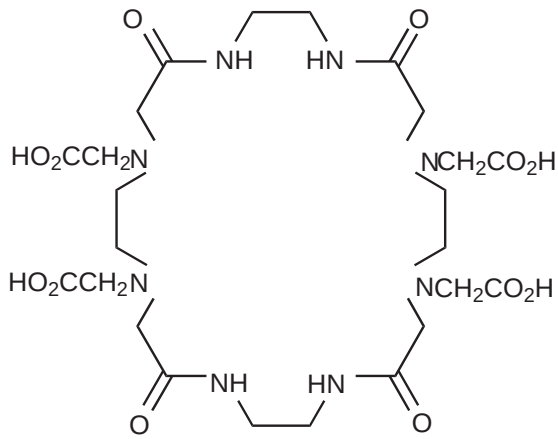
Log K values for the 1:1 manganese(II) complexes of (**194a**) and (**194b**) are 5.11 and 5.07 ($I = 0.1$, 25 °C), respectively.[517] The X-ray structure of the related dinuclear Mn^{II} complex of (**195**) shows that two crystallographic equivalent metal ions are located outside of the macrocyclic cavity with each manganese ion adopting a seven-coordinate geometry, being bound to two amine nitrogens, two pendant carboxylato oxygens, a water molecule, and two amide oxygens.[518]



(**194a**)



(**194b**)

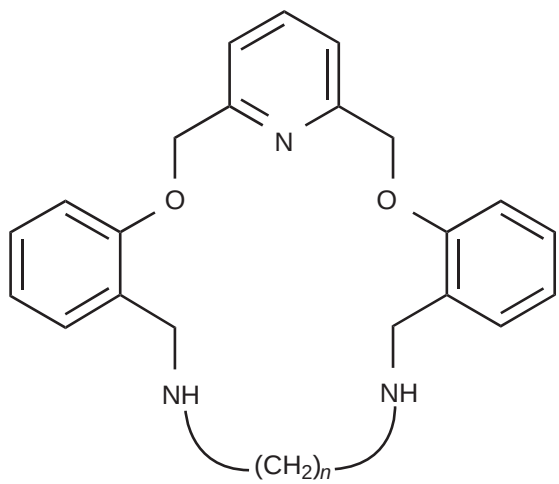


(**195**)

Solution studies involving a tetracarboxymethyl pendant arm derivative of an 18-membered, N_6 donor macrocycle incorporating two pyridyl and four tertiary amine donors demonstrated that this ligand coordinates well to a wide variety of metal ions (including manganese) in various oxidation states.[519] In part, this coordination versatility was attributed to the flexibility of the ligand framework allowing it to accommodate readily the coordination sphere preferences of the respective metals in relation to both their oxidation states and their ionic radii.

The stability constants of a series of the 1:1 complexes between divalent first-series transition metal ions (including Mn^{2+}) and the 15- to 17-membered rings 1,4-oxa-4,7,10,13-tetraazacyclopentadecane, 1,4-dioxa-7,11,13-triazacyclopentadecane, 1,4-dioxa-7,11,14-tetraazacyclopentadecane, and 1,4-dioxa-7,11,15-triazacycloheptadecane, incorporating either an N_4O or an N_3O_2 donor set, have been determined.[520] In all cases the Irving–Williams stability order was observed, with the complexes of the 15-membered ring (N_4O donor set) yielding the highest stabilities across the series. A significant drop in stability was observed for all metal complexes of the 17-membered ring; this drop was especially evident for larger metal ions such as manganese(II).

The interaction of manganese(II) with (**196**) ($n = 1$ or 2), each containing an N_3O_2 donor set, has been investigated.[521] Conductometric titrations of the 1:1 manganese(II) complexes with chloride ion indicated the formation of a 2:1 complex—presumably through bridging of a chloride ion. The stabilities of the complexes were investigated in 95% methanol; each showed a log K value of <4. The X-ray structure of $[MnLBr(EtOH)]ClO_4$ (where L = (**196**), $n = 1$) shows that the

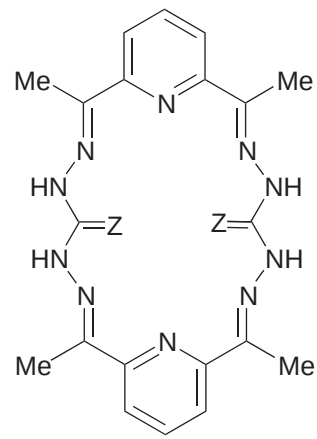


(**196**)

metal is seven-coordinate and lies within the macrocyclic cavity. The donor set comprises the five macrocyclic donor atoms, a bromide anion, and an ethanol molecule to yield a distorted pentagonal bipyramidal coordination arrangement.

The unsaturated ligands (**197**) (L, where Z = O or S), synthesized *in situ*, yielded mononuclear, high-spin complexes of type $[MnL(H_2O)]X_2$ (X = Cl, OAc) in which the metal was formulated to be six-coordinate on the basis of physical measurements.[522]

Dinuclear manganese(II) complexes of the deprotonated form of the potentially octadentate Schiff base product from the *in situ* condensation of 2,6-diformyl-4-methylphenol and 1,3,diamino-2-hydroxypropane in a 2:2 molar ratio have been synthesized.[523,524] The macrocycle employs only six of its donors for binding manganese(II), with the two alcohol functions remaining protonated and uncoordinated. Two phenoxy bridges form between adjacent metal ions in these discrete binuclear units. The complexes with chloro, bromo, nitrato, and thiocyanato counterions are five coordinate, with each metal having a distorted square pyramidal geometry in which the four basal positions are occupied by N_2O_2 donors from the macrocycle and the axial position filled by an anionic ligand. In $[Mn_2L(CH_3COO)_2]\cdot MeOH$ each manganese is six coordinate with the acetato groups present as bidentate ligands.



(**197**)

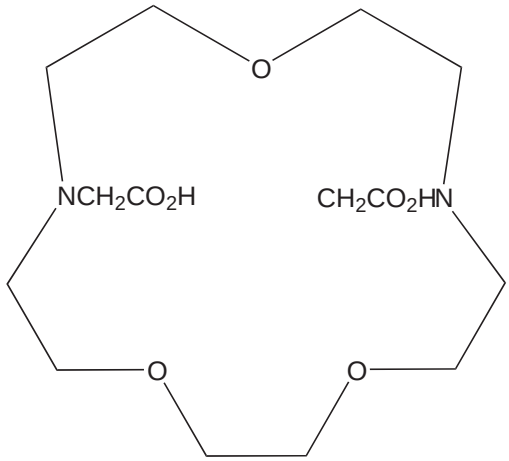
The log *K* value (25 °C, *I* = 0.10 M) for the 1:1 complex of manganese(II) of the 13-membered ring derivative 7,11-bis(carboxymethyl)-1,4-dioxa-7,11-diazacyclotridecane is 8.03. It is expected that this ligand will give rise to one six-membered chelate ring in the above complex.[525] The latter is significantly less stable than that the corresponding complex of the analogous 12-membered ring derivative 7,10-bis(carboxymethyl)-1,4-dioxa-7,10-diazacyclodecane, which will yield all five-membered rings and for which the value of log *K* is 10.72.[526]

The 14-membered oxatriaza macrocycle 4,12-bis(carboxymethyl)-1-oxa-4,8,12-triazacyclotetradecane yields nickel(II) and copper(II) complexes showing relatively high ML log *K* values of 14.7 and 17.62, respectively, while that for manganese(II), at 7.08 (*I* = 0.1, 25 °C), is only moderate, as might be expected from the position of manganese in the Irving–Williams series.[527] Such behavior is also typical of the other pendant-arm derivatives just discussed. Appending a third carboxymethyl arm to the above system to yield 4,8,12-tris(carboxymethyl)-1-oxa-4,8,12-triazacyclotetradecane results in the expected increase in the log *K* value—in this case to 9.18.[528]

The thermodynamic stabilities of the manganese(II) complexes of the O_3N_2 donor (**198a**) and O_4N_2 donor (**198b**) macrocyclic rings incorporating two pendant caboxymethyl groups have been determined to be 12.11 and 8.66 (log *K* values), respectively.[529,530] As also occurs with other metal ions, (**198a**) thus gives more stable complexes than (**198b**) and this has been shown to be a reflection of more favorable heats of reaction for the complexes of the former ligand.

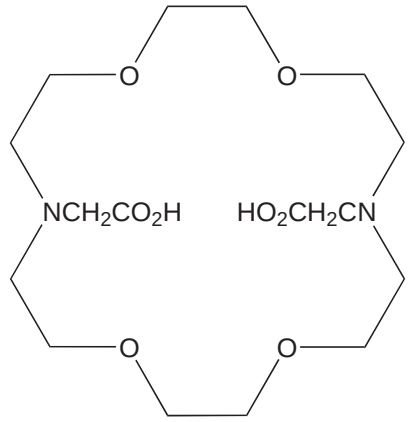
Log *K* values for a number of tricarboxymethyl pendant arm derivatives of mixed oxygen–nitrogen donor macrocycles have been reported. These include values of 16.09,[531] 12.11,[532] 14.44,[533] and 9.47[533] for the ring systems (**199**), (**200**), (**201a**), and (**201b**), respectively.

In other work, solution complex formation of the pendant-arm ligands 1,4,10,13-tetraoxoa-7,16-diazacyclooctadecane-7-malonate and 1,4,10,13-tetraoxoa-7,16-diazacyclooctadecane-7,16-bis(malonate) has been investigated with a range of both transition and nontransition metal ions;[534] the 1:1 manganese(II) complexes of these species have been reported to show stabilities (log *K* values) of 7.41 and 5.60, respectively, in water (*I* = 0.15, 25 °C).



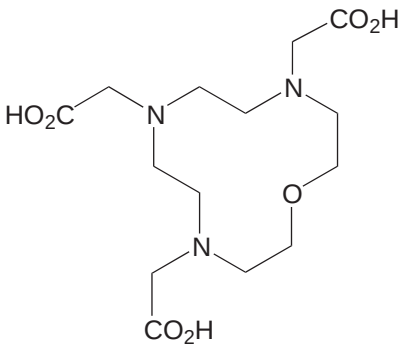
L^1

(**198a**)

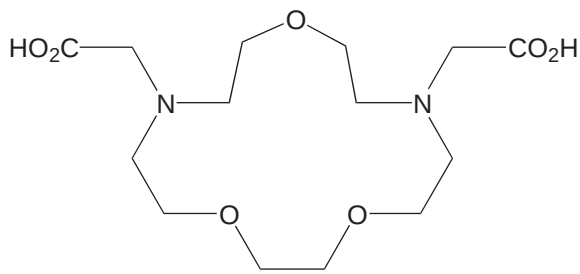


L^2

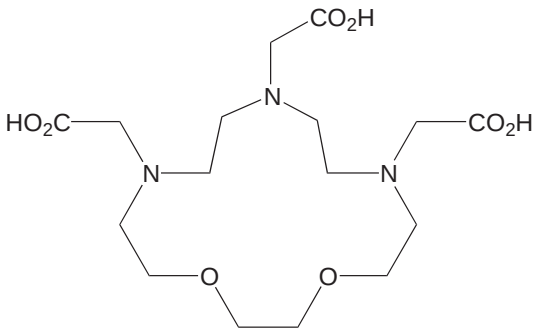
(**198b**)



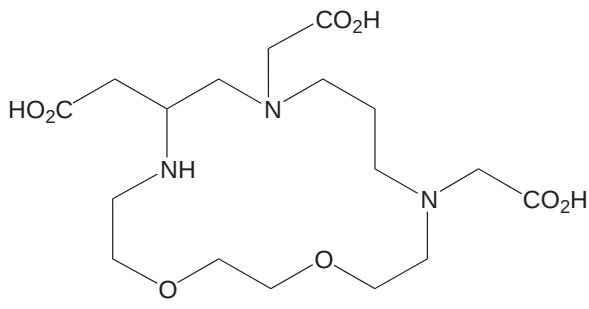
(**199**)



(**200**)



(**201a**)



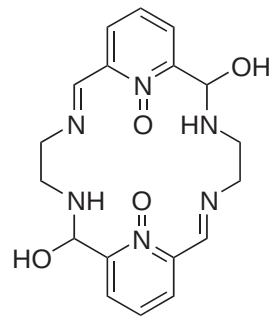
(**201b**)

The potentially sexadentate macrocyclic ligands 1,4,7-tris(3,5-dimethyl-2-hydroxybenzyl)-1,4,7-triazacyclononane ($L'H_3$), 1,4,7-tris(3,5-di-*t*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane ($L''H_3$), and 1,4,7-tris(3-*t*-butyl-5-methoxy-2-hydroxybenzyl)-1,4,7-triazacyclononane ($L'''H_3$) form the stable complexes of type $[Mn^{IV}L'']PF_6$, $[Mn^{IV}L''']PF_6$; $[M^{III}L''']$; $[Mn^{IV}L']_2(ClO_4)_3$-$(H_3O)(H_2O)_3$.[535] These complexes were investigated by spectroelectrochemistry and were shown to undergo metal- and ligand-centered redox processes; a phenoxyl radical Mn^{IV} complex, $[Mn^{IV}L''']^{2+}$, was found to be accessible.

Reaction of a methanol solution of 4,7-bis(2-hydroxybenzyl)-1-oxa-4,7-diazacyclononane (LH_2) with manganese(II) perchlorate yields colorless crystals of $[Mn_2(LH)_2(\mu\text{-}OH)]ClO_4$.[536] Variable-temperature magnetic susceptibility and ESR measurements indicate that the corresponding tetraphenylborate salt exhibits intermolecular antiferromagnetism with a J value of $-2.65\,cm^{-1}$. Deprotonation of the above dinuclear species using $N(Et)_3$ in acetonitrile yields the monomeric five-coordinate $[Mn^{II}L]$ species. The related manganese(III) species $[MnL^{III}X]$ ($X = Cl$, NCS or N_3) have also been synthesized by heating a solution of manganese(III) acetate with LH_2 in methanol then adding the respective X anions as their lithium or sodium salts.

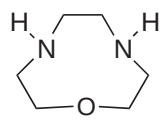
Other high-spin, mononuclear manganese(II) complexes of mixed oxygen–nitrogen macrocycles have been reported.[537,538]

A dinuclear complex of type $Mn_2L(NO_3)_4 \cdot 2MeOH \cdot H_2O$ has been isolated incorporating the bis-pyridine-*N*-oxide derivative (**202**) which shows weak antiferromagnetic coupling.[539]

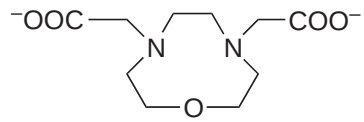


(**202**)

The solution complexation properties of a range of pendant arm derivatives of mixed oxygen–nitrogen donor macrocycles have been investigated. A comparison of the log K values of the ML complexes of manganese(II) with (**203a**) and (**203b**) yielded values of 3.0 and 7.73 ($I = 0.1$, 25 °C), respectively, clearly demonstrating that the pendant caboxymethyl groups play a very significant role in stabilizing each resulting complex.[540] The values for the latter systems were compared with those obtained for the triaza macrocycle 1,4,7-triazacyclononane (log $K = 5.8$) and its *N*,*N*′-dicaboxymethyl derivative (log $K = 14.3$). A parallel comparison was also carried out between the manganese complexes of the corresponding 12-membered N_4 and N_3O ring derivatives. As might be predicted, the replacement of one nitrogen atom by an oxygen in the macrocyclic backbone was shown to have a pronounced effect on both the kinetics of complex formation (faster equilibration) as well as on the thermodynamic stability of the resulting complexes (lower stability).



(**203a**)



(**203b**)

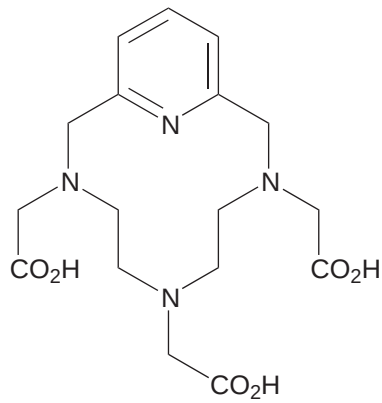
The solution complexation behavior of manganese(II) and selected other transition and post-transition metal ions with 1-carboxymethyl-1,4,7-triazacyclononane has been investigated by potentiometric titration, with the stabilities of the 1:1 complexes found to follow the usual Irving–Williams stability order.[541]

Relative to the behavior of the 1,4,7-tris(carboxymethyl)-1,4,7-triazacyclononane ring, the contribution to K_{ML} values of the 1,4,7-triazacyclononane fragment in the corresponding 1,4-bis(carboxymethyl)-1,4,7-triazacyclononane macrocycle is greater towards softer metal ions than towards harder ones such as manganese(II).[542]

The *N*,*N*′*N*″-tris(carboxymethyl) derivative of the 12-membered macrocycle 1,5,9-triazacyclododecane yields a complex of type $[MnL]^-$ in aqueous solution which is approximately two orders of magnitude less stable than the corresponding complex of 1,4,7-tris(carboxymethyl)-1,4,7-triazacyclononane, as might be expected for the substitution of three six-membered chelate rings in the former for three five-membered chelate rings in the latter.[543]

N,*N*′*N*″-tris[(2S)-2-hydroxypropyl]-1,4,7-triazacyclononane (LH_3) forms the air-stable manganese(II) species $[MnLH_3][MnCl_4]$ when conditions are such that the ligand remains fully protonated. The X-ray structure indicates the presence of a trigonal prismatic coordination geometry.[401]

The stability of the complex of the triply deprotonated form of the tetraaza macrocyclic ligand (**204**) (LH_3), incorporating three *N*-methylcarboxy pendant groups, has been reported. The log *K* value for the $[Mn^{II}L]^-$ complex is 18.59 (25 °C, $I = 0.10$).[544]

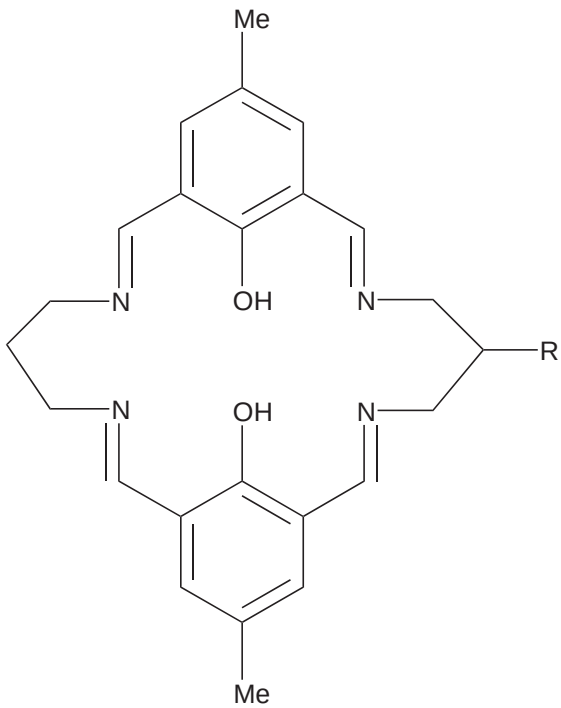


(**204**)

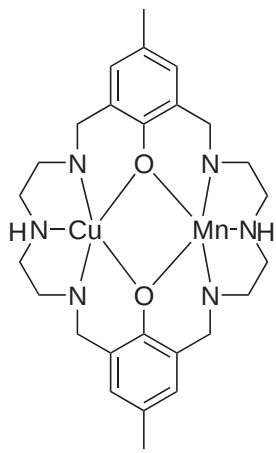
Manganese(II) complexes of triazamacrocyclic ligands bearing L-lactate-like functions were prepared for testing as model compounds able to disproportionate the superoxide radical.[545] The capacity of the macrocyclic ligands *N*,*N*′,*N*″-tris[2(S)-hydroxybutyric acid]-1,4,7-triazacyclononane and *N*,*N*′,*N*″-tris[2(S)-hydroxybutyric acid]-1,5,9-triazacyclododecane to bind the manganese(II) ion was determined potentiometrically. The first of these ligands binds most strongly to this ion and the superoxide-scavenging activity of the corresponding manganese(II) complex was investigated using a cytochrome *c* assay. This system was demonstrated to be a potent SOD mimic.

In part motivated by the desire to model biological redox processes, there have been many studies in which Robson-type macrocycles (**205**) (R = H)[532] have been employed to form dinuclear manganese species.[497,547,548] For example, a novel macrocyclic heterodinuclear catalase-like model complex of type (**206**) has been reported.[549] This complex can dismute hydrogen peroxide to dioxygen in basic aqueous solution.

In one study of this type a range of high-spin complexes given by $[Mn_2LX_2]$, (H_2L = (**205**), R = H, OH; X = Cl, Br), $[Mn_2L(CH_3COO)]ClO_4$ (H_2L = (**205**), R = H, OH), and $[Mn_2L^-]ClO_4$



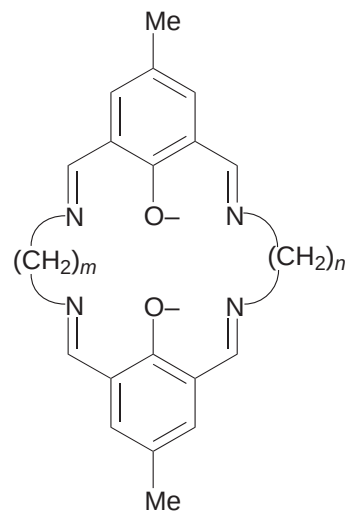
(**205**)



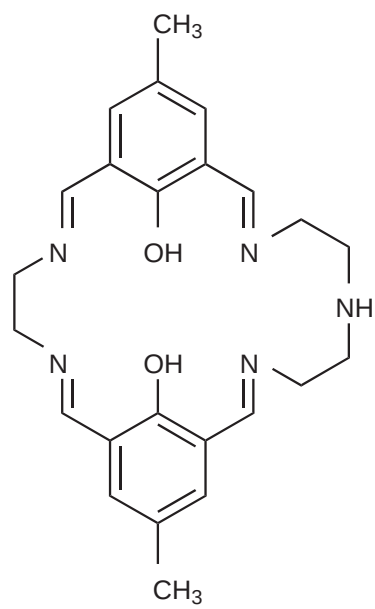
(**206**)

(H_2L = (**205**), R = O^-) were prepared and characterized using infrared and ESR spectra as well as variable-temperature magnetic susceptibility measurements.[548] The complexes of the first type are composed of isolated binuclear units in which each manganese ion attains a distorted square pyramidal geometry, with the manganese ion displaced from the macrocyclic plane towards an apical halide ligand. The second group of complexes contain binuclear units that are bridged by acetato groups into infinite chains. The metal ions are displaced from the macrocyclic ligand plane towards an acetato oxygen such that the coordination geometry of each metal is essentially square pyramidal. A weak intramolecular antiferromagnetic exchange is present in both complexes. The final complex appears to consist of tetranuclear species made up of two binuclear units bridged through alcoholate anions. Once again the high-spin manganese ions are involved in an antiferromagnetic exchange interaction.

The mononuclear species $[Mn(LH_2)](ClO_4)_2$ and the heterodinuclear species $[Mn(H_2O)LCuCl](ClO_4)$ (where L = (**207**), $n = 2$, $m = 3$), have been synthesized and investigated.[550] The latter species exhibits antiferromagnetic spin exchange between the heterometals with $J = -31\,cm^{-1}$. Related to the above, the heterodinuclear di(μ-phenoxo) $Co^{II}Mn^{II}$ complexes $[CoMnL(CH_3COO)]ClO_4$ and $[CoMnL(NCS)]ClO_4$, where L is the dianionic form of (**208**),



(**207**)

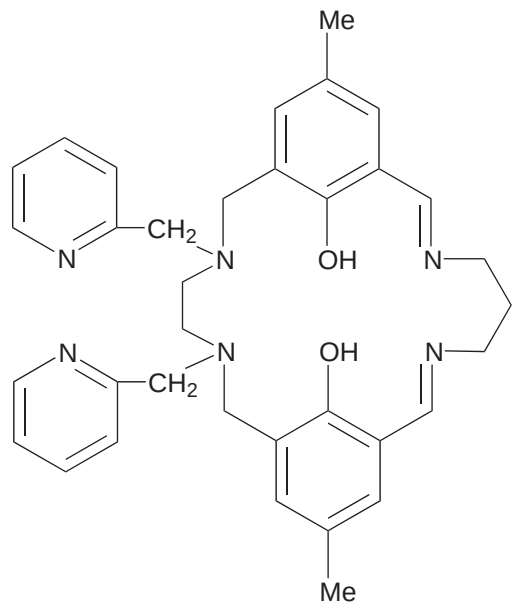


(**208**)

have been synthesized.[551] The first of these species undergoes reversible oxygenation at 0 °C in dimethylformamide. An X-ray structure of the product, $[\{CoMnL(CH_3COO)\}_2(O_2)][ClO_4]_2 \cdot 4MeCN$, confirms that the cobalt resides in the "salen" site while the manganese occupies the "saldien" site. The peroxo group bridges two $\{CoMnL(CH_3COO)\}$ units at their cobalt centers. Each cobalt site has a pseudooctahedral coordination geometry, while the manganese sites are best described as distorted six-coordinated.

The structure, properties, and catalase-like activity of $[Mn_2L(CH_3COO)_2]$, (where L = (**207**), $n = m = 4$) have been investigated.[552] This complex incorporates two manganese(II) ions bridged by two phenolic oxygens in the equatorial plane and two acetate groups via the axial sites. A pseudooctahedral geometry is assumed for each manganese ion. A strong antiferromagnetic interaction is present in this complex. The catalytic function was postulated to occur through a process involving interconversion between $Mn^{II}Mn^{III}(OH)$ and $Mn^{II}Mn^{IV}(=O)$ species.

The binucleating macrocycle (**209**) incorporating six- and four-coordination sites has been synthesized.[553] The doubly deprotonated form L of this ligand gives rise to the following mononuclear and binuclear complexes: $[MnLZnCl]PF_6$, $[ZnLMnCl]PF_6$, $[MnLMnCl]PF_6$, and the mixed-valence species $[MnL(\mu\text{-}Cl)MnCl]PF_6$. X-ray structures of the latter two complexes reveal that each six-coordinate site has an unsymmetrical arrangement of the donors that appears to reflect the presence of macrocyclic ligand strain. All of the complexes are effective catalysts for the epoxidation of styrene using iodosobenzene. In subsequent studies[554] the work has been extended to include an investigation of a related binucleating chiral macrocyclic ligand formed by employing a chiral diamine, (1S,2S)-*trans*-1,2-bis(aminomethyl)cyclopentane, for the macrocycle ring-closing Schiff base reaction; this induces topological chirality about the six-coordinate site. A range of complexes related to those mentioned above have been isolated and characterized. The presence of the chiral diamine induces the formation of a single diastereoisomer in the C_2-symmetric complexes.

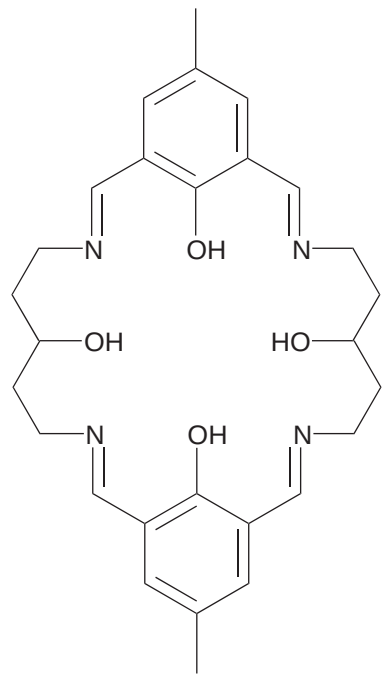


(**209**)

Transmetallation of $[Ba(LH_2)(H_2O)_2](ClO_4)_2$ with manganese acetate in methanol yields either the pentamanganese(II) complex $[Mn_5L_2(CH_3COO)_2(ClO_4)_2](ClO_4)_2$ or the tetramanganese(II) complex $[Mn_2(L)(CH_3COO)]_2(ClO_4)_2$ (2), where H_2L is a macrocyclic ligand formed by a [2 + 2] condensation of 2,6-diacetylpyridine and 1,3-diaminopropan-2-ol.[555] The complex obtained appears to depend on the pretreatment of the methanol solution of manganese(II) acetate before addition to the barium precursor complex. The X-ray structure of the pentamanganese complex contains two folded binuclear macrocyclic units, which are bridged by a six-coordinated manganese ion and two acetato groups. The structure is centrosymmetric with one of the manganese ions being located on an inversion center. This manganese is bonded to two deprotonated alkoxide oxygens from each macrocycle as well as to both acetato groups. The latter each bridge three manganese ions, one from each macrocyclic unit and the one located at the inversion center.

Transmetallation reactions using manganese(II) formate yielded only the tetramanganese complex $[Mn_2(L)(HCO_2)]_2(ClO_4)_2$. X-ray diffraction studies show that both this and the other tetramanganese complex incorporate bridging carboxylate groups as well as $Mn_4(alkoxide)_4$ cubane cores.

The localized mixed-valent $Mn^{II}_2Mn^{III}_2$ complexes of the tetranucleating macrocycle (**210**) (LH_4), formed by the [2 + 2] Schiff-base condensation of diformyl-4-methylphenol and 1,5-diaminopentan-3-ol, have been reported.[556] The X-ray structures of $[Mn_4(L)O(CH_3COO)_3Cl(MeOH)]$ and $[Mn_4(L)O(CH_3COO)_4(H_2O)]$ have been determined. The observed redox states for the individual metal centers have been rationalized in terms of the transmission of geometric constraints between metal centers through the ligand framework. Such geometric control of redox levels has been proposed to proceed via the overlapping of coordination spheres—a process that appears likely to occur for polynuclear redox-active sites in metalloenzymes.

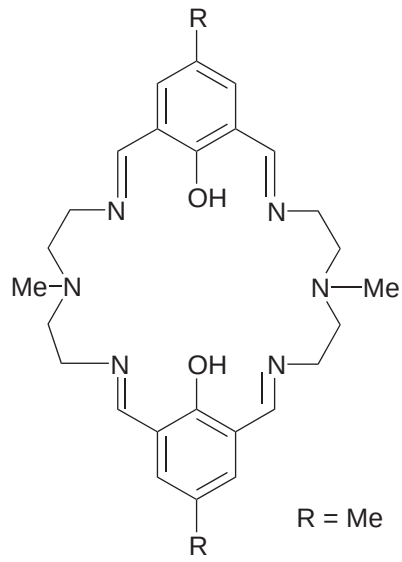


(**210**)

Dinuclear manganese(II) complexes of type $[Mn_2L(R'COO)]ClO_4$ (where L is the deprotonated form of (**211**) (R = Me) and R′ is a substituted aryl ring) have been synthesized.[557] The crystal structure of the species with R equal to $2\text{-}O_2NC_6H_4$ showed the existence of two crystallographic independant complex cations with slightly different conformations—attributed to crystal packing differences. The complexes were observed to catalyze the disproportionation of hydrogen peroxide. Interestingly, the activities showed a characteristic V-shaped dependence on the pK_a of the carboxylic acid that is in accordance with protonation occurring prior to dissociation of RCO_2^-.

A series of complexes have been reported of type $[Mn_2L(R'CO_2)]ClO_4$, where LH_2 is (**211**) (with R = OMe, H, F, Br for R′ = Me and R = Br for R = CF_3).[558] The electrochemical redox chemistry of these species was shown to be effectively controlled by the nature of R and R′. The X-ray structure of the derivative with R = R′ = Me shows that each manganese(II) ion has a highly distorted octahedral geometry.

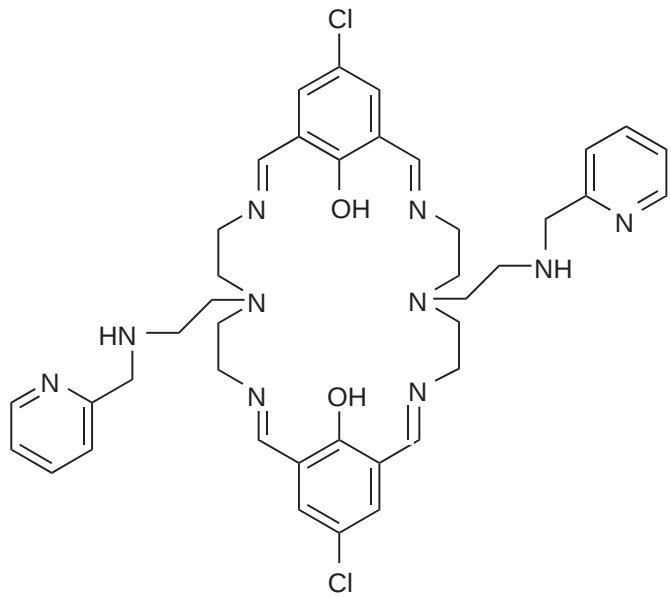
Template reaction of 2,6-diformyl-4-methylphenol, 1,8-diamino-3,6-dialkyl-3,6-diazaoctane (alkyl = Me, Et), and manganese benzoate in a 1:1:2 molar ratio gives complexes of type $[Mn_4L(BzO)_6]$ where LH_2 is the [2 + 2] condensation product between 2,6-diformyl-4-methylphenol and 1,8-diamino-3,6-dialkyl-3,6-diazaoctane (alkyl = Me or Et).[559] The structure of $[Mn_4L(BzO)_6(Me_2CHOH)_2]\cdot 2CH_2Cl_2$ (for alkyl = Et) shows that it contains two pairs of six-coordinated manganese(II) ions that are bridged by a phenolic oxygen and two benzoate groups. The manganese ions in each pair are nonequivalent. One is bound to a phenolic oxygen, an imine nitrogen, two oxygens of two bridging benzoate ligands, and two amine nitrogens. The other is bound to a phenolic oxygen, an imine nitrogen, two oxygens from two bridging benzoate ions and a monodentate benzoate ion, as well as an oxygen from a propan-2-ol molecule. A weak antiferromagnetic interaction exists between the manganese ions. Dinuclear manganese(II)



(**211**)

complexes of type $[Mn_2L(Z)](ClO_4)$, where L is one of a series of variously substituted derivatives of the above type and Z is a monodentate anionic ligand, have been reported.[560] The effect of the ligating anion on the catalase activity of these Schiff base manganese(II) complexes was shown to depend on the nature of the ligand Z^-.

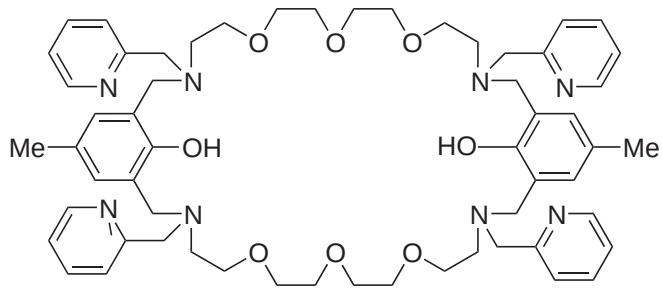
The pendant arm ligand (**212**) (LH_2), formed by a metal template reaction, gives rise to a dinuclear species of type $[Mn_2L](ClO_4)_2$.[561] An X-ray study has revealed an unusual structural arrangement in which each manganese ion is bound to the donors of a pendant arm as well as to four donors from the macrocycle—two (bridging) phenoxy oxygens and two imine nitrogens. Both pendant arms are orientated on the same side of the macrocycle. Each metal ion is essentially high spin, with only a very weak antiferromagnetic interaction between ions being evident. This complex shows moderate activity as a catalyst for the decomposition of hydrogen peroxide.



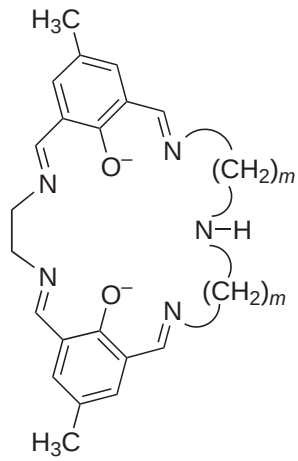
(**212**)

The large ring diphenol macrocycle (**213**) incorporating four pyridylmethyl groups yields the tetranuclear species $[Mn_4L(CH_3COO)_4](ClO_4)_2 \cdot 3H_2O$ (where L is the doubly deprotonated form of (**213**)) which shows antiferromagnetic interactions between the ligand-encapsulated metal centers.[562]

Complexes incorporating copper(II) or nickel(II) and manganese(II) in heterodinucleating macrocycles have been reported.[563–566] For example, a complex of type $[Cu^{II}Mn^{II}L](CH_3COO)(BPh_4)$, where L = (**214**), has been prepared and its X-ray structure determined.[563] The Cu^{II} and Mn^{II} ions lie in the four- and five-coordinate sites of the ligand, respectively. Once again, antiferromagnetic spin exchange occurs between the metal centers.

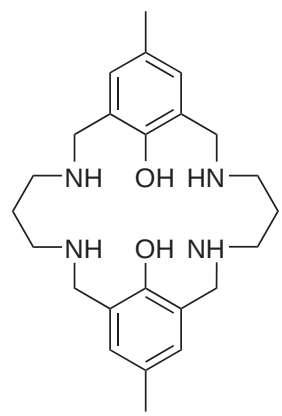


(**213**)



(**214**)

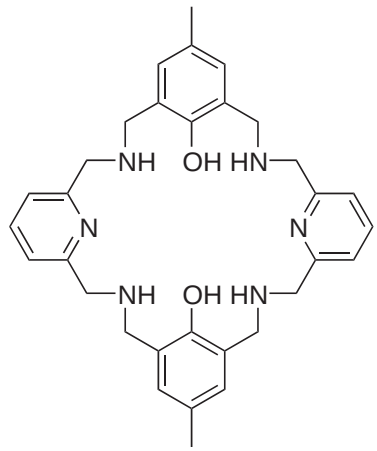
In addition to the systems mentioned already, a range of other heterobimetallic complexes in which manganese(II) occupies one of the macrocyclic ligand sites has been reported.[566] For example, spin exchange coupling in $[(V^{IV}O)LMn^{II}(\mu\text{-}CH_3COO)(H_2O)](ClO_4)\cdot H_2O$, where LH_2 = (**215**), has been investigated. The observed magnetic behavior is characteristic of an antiferromagnetically coupled system (with $J = -14.2\,cm^{-1}$). In a further example, solution studies involving potentiometric titrations showed that (**216**) interacts with manganese(II) in a stepwise fashion to form the



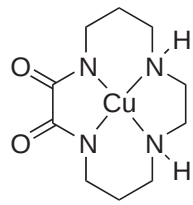
(**215**)

corresponding dinuclear complex.[567] In a an extension of this study, the presence of a 1:1:1 ratio of (**216**):Mn^{II}:Zn^{II} in the solution was demonstrated to result in the formation of the corresponding species of stoichiometry $[MnZnL]^{2+}$ (where L is the doubly deprotonated form of (**216**)).

Oxamidato-bridged $Cu^{II}{}_3Mn^{II}$ tetranuclear complexes have been reported.[568,569] For example, $[Cu^{II}{}_3Mn^{II}(\mu\text{-}L)_3](N_3)_2 \cdot EtOH$, incorporating the macrocyclic oxamide (**217**), has been synthesized.[569] The X-ray structure shows tetranuclear units in which the central Mn^{II} atom lies on a twofold axis and is linked to each external Cu^{II} atom ion via exo-*cis*-arranged O atoms of the oxamidato ligands.

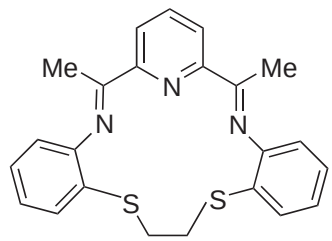


(**216**)



(**217**)

A high-spin manganese(II) complex of the sulfur containing, potentially pentadentate Schiff base derivative (**218**) has been reported.[570]

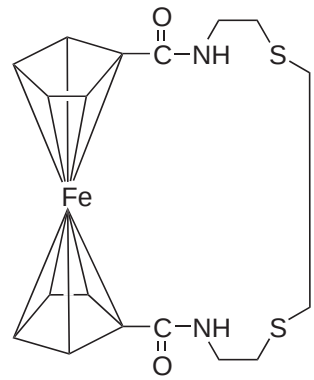


(**218**)

Mixed donor macrocycles have been employed in a number of applications involving the separation or analysis of manganese(II). These include examples of use of such a ligand as the extractant in solvent extraction processes[571,572] and as the ionophore in membrane transport studies.[573,574]

The stability constants ($I = 0.1$, 25 °C) of the deprotonated forms of the pendant arm macrocyclic species 1-thia-4,7-diazacyclononane-*N*,*N*′-diacetic acid and 1-thia-4,8-diazacyclodecane-*N*,*N*′-diacetic acid, have been reported for a wide range of divalent metal ions.[575] The ML $\log K$ values for manganese(II) with these ligand species do not differ greatly at 9.25, and 8.97; as expected, both are significantly higher than the value (8.48) for the related open-chain derivative 2,5-diazahexane-*N*,*N*′-diacetic acid.

The host–guest interaction of manganese(II) with a range of ferrocene-containing species, which included the dithia derivative (**219**), has been investigated in acetonitrile.[576] Complexation gave rise to a bathochromic shift of the lowest-energy ferrocene-centered *d–d* transitions.



(**219**)

5.1.7.4 Oxidation State I

5.1.7.4.1 Nitrogen donor macrocycles

Reaction of 1,4,7-triazacyclononane with $Mn(CO)_5Br$ has been reported to yield orange-yellow $[MnL(CO)_3]Br$.[577]

5.1.7.4.2 Phosphorus donor macrocycles

The synthesis of a manganese(I) complex of the macrocyclic phosphine ligand 1,5,9-triethyl-1,5,9-triphosphacyclododecane (L) has been reported.[578] Thus, reaction of L with $Mn(CO)_5Br$ yields $MnL(CO)_2Br$ whose six-coordinate structure was confirmed by X-ray diffraction.

5.1.7.4.3 Sulfur donor macrocycles

The reaction of $[Mn(CO)_5X]$ (X = Cl, Br, I) with 1,4,7-trithiacyclononane (L) in DMF yielded products of type $[MnL(CO)_3]X$ in which the manganese is present in a pseudooctahedral environment with three facially coordinated thioether donors and the three carbonyl groups frilling the remaining positions.[579] Reaction of this species with hydrazine hydrate gives rise to $[MnL(CO)_2(NCO)]$ which reacts further with 5 M HCl to form $[MnL(CO)_2Cl]$. With $NOBF_4$, the $[MnL(CO)_3]^+$ entity generates $[MnL(CO)_2(H_2O)]^+$ as its tetrafluoroborate salt.

The related manganese(I) complexes of type *fac*-$[MnL(CO)_3]$ (where L is one of the tetrathia macrocycles 1,4,7,10-tetrathiacyclododecane, 1,4,8-11-tetrathiacyclotetradecane, or 1,4,7,10,13-pentathiacyclopentadecane) were obtained by reaction of *fac*-$[Mn(CO)_3(CH_3COO)_3]^+$ with L in acetonitrile.[580] These species are readily decarbonylated with Me_3NO to yield the corresponding *cis*-$[Mn(CO)_2(L)]^+$ species. The facial arrangements in the products containing the 12- and 15-membered ring macrocycles were confirmed by X-ray structure determinations.

5.1.8 BIOINORGANIC CHEMISTRY

5.1.8.1 Introduction

Manganese is an essential metal cofactor in enzymes that cover the entire range of enzyme functionality. It is only possible to include some of the more important and better-characterized

examples of manganese ions in biological systems in this section. In many cases the references given are to reviews and not to the original literature. The reader who desires greater detail is referred to the review articles, to two handbooks,[581,582] to a volume in the series *Metal Ions in Biological Systems* devoted to manganese,[583] and to reviews of manganese-containing enzymes[584–591] that provide much greater detail than is possible here.

Manganese is an essential element with a recommended daily intake by humans of between 2 and 5 mg. A 70 kg human contains about 20 mg of manganese distributed approximately equally between the soft tissue and bone. The distribution of manganese within the body is not uniform; the concentration within the central nervous system is orders of magnitude greater than in most other organs. Dietary manganese deficiency is rare in humans; in animals it results in impairment in oxidant defences, cardiovascular and insulin production systems, altered lipoprotein metabolism, arteriosclerosis, and diabetes. If the deficiency occurs during early development, there are pronounced skeletal abnormalities and an irreversible ataxia. Manganese toxicity in humans occurs in individuals with exposure to high levels of airborne manganese or where manganese excretory pathways are compromised.[592] The levels of manganese intake associated with adverse effects are uncertain.

5.1.8.1.1 Manganese coordination spheres in proteins

Mn^{2+} is usually six-coordinate in proteins but examples of four- and five-coordinate Mn^{2+} have been reported. The coordination environments of Mn^{2+} and Mn^{3+} in all structurally characterized proteins contain oxygen donor atoms and frequently oxygen is the only donor to Mn^{2+}. In addition to protein side chain donor groups Mn^{2+} is frequently bound to one or more phosphate oxygens of enzyme substrates such as ATP. Mn^{3+} in all structurally characterized examples is bound to at least one histidine residue. There are only two structurally characterized examples of Mn^{2+} bound to the sulfur of a cysteine or a methionine side chain. Both examples are described below. Mn porphyrin complexes exhibit biological activity; however, there are no examples of Mn being bound to a heme or a corrin ring in any proteins.[593]

5.1.8.1.2 Acquisition of Mn

Studies on how metal cofactors are transported into a cell, distributed to diverse locations within the cell, and subsequently supplied to the correct metalloenzymes are very active areas of research. A family of metal receptor proteins known as "metallochaperones" that acts in the intracellular trafficking of metal ions has been recognized.[594] The proteins responsible for the influx of Mn^{2+} into bacterial cells, bacterial permeases, are members of the "ABC" (ATP binding cassette) superfamily of transporter proteins.[595,596] A cell surface protein of the pathogenic bacterium *Streptococcus pneumoniae* involved in the uptake of Mn^{2+} and possibly Zn^{2+} has been structurally characterized. The protein consists of two $(\beta/\alpha)_4$ domains linked by a single helix. The metal binding site is four-coordinate, formed by the side chains of two histidines, a glutamate, and an aspartate. In this structure the metal present is probably Zn^{2+} and when Mn^{2+} binds to this protein the coordination geometry may well be different.[597]

Studies with *Saccharomyces cerevisiae* have shown that the uptake of any one metal ion is often mediated by two or more specific transport systems.[598] High-affinity systems are active in metal-limited cells, whereas low-affinity systems operate when the metal ion is more abundant. These systems are tightly controlled, and both transcriptional and posttranscriptional regulatory mechanisms have been identified.[599] Within the cell our knowledge of what happens to the metal ions is sparse but it is known that in *S. cerevisiae*, a cell surface protein, Smf2p, is involved in transport of Mn^{2+} to manganese superoxide dismutase and other manganese dependant enzymes in the Golgi.[600] Transport of Mn^{2+} into the secretory pathway of *S. cerevisiae* is accomplished by an ATPase known as Pmr1p.[601] Another protein, Atx2p, is a manganese homeostasis factor in intracellular vesicles[602] and uptake of both Fe^{2+} and Mn^{2+} into intracellular vesicles is accomplished by a protein Ccc1p.[603]

The uptake of manganese by plants and its transport within plants has been reviewed.[604,605] Reviews describing Mn speciation in the blood and the transport kinetics of Mn into the central nervous system of mammals have appeared.[606,607] Manganese has a unique capacity to be taken up via the olfactory pathways and pass trans-neuronally to other parts of the brain.[608,609]

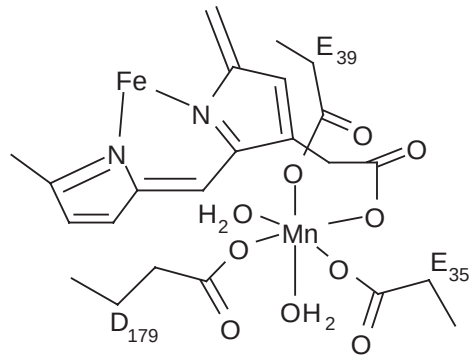


Figure 23 Schematic representation of the active site in Manganese peroxidase.

5.1.8.2 Enzymes with Mononuclear Active Sites

A listing of the enzymes and proteins believed to be Mn activated has been published but undoubtedly other examples exist.[589] Structurally characterized, Mn-activated enzymes and proteins which are not included here include dioxygenases,[610] integrins,[611] muconate cycloisomerase,[612] and isocitrate dehydrogenase.[613]

5.1.8.2.1 Manganese peroxidase

Peroxidases are heme proteins that are able to catalyze the oxidation of a large variety of substrates through a reaction with hydrogen peroxide. A general review of the structural properties of peroxidases has been published[614] and a review specific to manganese peroxidase (MnP) has also appeared.[615] The intense interest in these enzymes is due to their ability to degrade lignin and recalcitrant pollutants.[616–618] Each molecule of MnP contains about 360 amino acids, one iron protoporphyrin IX prosthetic group, and two Ca^{2+} ions and is able to bind one Mn^{2+}. MnP occurs in the extra cellular medium of a wide variety of white rot fungi. It oxidizes Mn^{II} to a Mn^{III} complex using H_2O_2 and the Mn^{III} complex oxidizes the lignin or other compounds. The ligands bound to the Mn^{III} *in vivo* are not known. The crystal structure of MnP from the white rot fungus, *Phanerochaete chrysosporium*, has been determined.[619] The overall polypeptide fold is similar to other peroxidases. The Mn^{2+} binding site is six-coordinate with two water molecules, and four carboxylate ligands, Glu-35, Glu-39, Asp-179, and a propionate residue attached to the heme (Figure 23). Electron transfer is assumed to take place via the propionate ligand although Glu-35 and Asp-179 residues influence the electron transfer from Mn^{2+} to the enzyme.[620]

5.1.8.2.2 Superoxide dismutase

Superoxide dismutase (SOD) catalyzes the reaction shown in Equation (1):

$$2O_2^- + 2H^+ \longrightarrow H_2O_2 + O_2 \tag{1}$$

It is believed that MnSOD plays a pivotal role in many diseases.[621,622] There have been many reviews of the biochemistry of MnSOD[623,624] and focusing on the structural aspects of the enzyme.[625] Four different types of SOD are known, a Cu/Zn-containing SOD, a FeSOD, a NiSOD, and MnSOD. MnSODs, which are structurally related to the FeSODs, have a M_r of ~23,000 (~200 amino acids) and function as a dimer or as a tetramer. MnSOD catalyzes the dismutation reaction by cycling between the +2 and +3 oxidation states. One proton is taken up by the system in each step (Equation (2)):

$$\begin{aligned} Mn^{III}SOD + O_2^- + H^+ &\longrightarrow Mn^{II}SOD_{H+} + O_2 \\ Mn^{II}SOD_{H+} + H^+ + O_2^- &\longrightarrow Mn^{III}SOD + H_2O_2 \end{aligned} \tag{2}$$

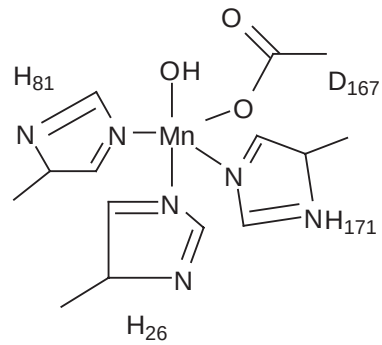


Figure 24 Active site of the MnSOD molecule. Active site residues are numbered in accordance with the *E. coli* enzyme.

Crystal structure determinations of MnSODs from organisms ranging from *E. coli* to humans have been reported. Structural determinations of note include those by Jameson *et al.* on the *E. coli* enzyme and mutant forms of this enzyme with atomic resolution,[626–628] a cambialistic superoxide dismutase from *Porphyromonas gingivalis*,[629] and mutant forms of the human enzyme; the Y34F,[630,631] Q143N,[632] and Q143A mutants.[633] The coordination sphere of the Mn in the active site of these MnSODs is illustrated in Figure 24. Glu-143 in human manganese superoxide dismutase forms a hydrogen bond with the coordinated water (or OH) molecule. Crystal structures reveal that the Q143A mutation makes no significant change in the overall structure of the enzyme. Two water molecules in this MnSOD are situated at positions nearly identical with the O and N groups of the replaced Gln-143 side chain and maintained the hydrogen-bonded network connecting the manganese-bound solvent molecule to other residues in the active site.[633]

One area of research interest has been the metal ion specificity of the MnSOD and FeSOD molecules. The tertiary structures of these molecules are very similar and the ligands coordinated to the metal ions are identical. Many organisms contain both forms of the enzyme and each form has an absolute specificity for its metal ion, the enzyme is completely inactive if the wrong metal ion is present. Cambialistic enzymes that occur in some organisms are active with either metal ion present in the active site. Comparisons of the structures of the MnSOD, FeSOD, and the cambialistic enzymes have not revealed any single obvious structural differences that could explain this phenomenon.[634]

Vance and Miller *et al.* have shown that the inactivity of enzyme is due to changes in the redox potentials of the enzyme. In order to dismute O_2^- the redox potential of the enzyme must lie between the E° values for the reactions shown in Equation (3). The E° value of the *E. coli* MnSOD enzyme is 0.290 V and that for the FeSOD is 0.220 V. The Fe-substituted form of the Mn enzyme has $E^\circ = -0.240\,V$[635] and Mn-substituted FeSOD has $E^\circ > 0.960V$.[636] These values are outside the required range and the changes in redox potentials are not due to changes in the metal ligands. Mutations of His-30 and Tyr-34, two conserved residues in the immediate vicinity of the metal binding site, do not alter the redox potential of the enzyme either:[637]

$$\begin{aligned} O_2^- + 2H^+ + e^- &\longrightarrow H_2O_2 \quad E^\circ = 0.89\,V \\ O_2 + e^- &\longrightarrow O_2^- \quad E^\circ = -0.16\,V \end{aligned} \tag{3}$$

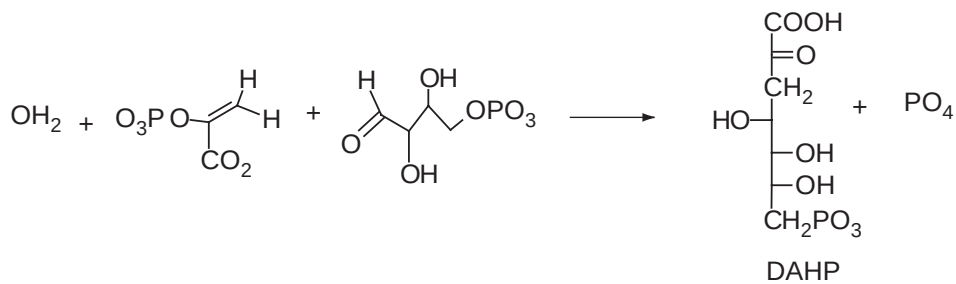
Wild type *E. coli* MnSOD has a glycine at position 77, and a glutamine at position 146. Gln-146 is hydrogen bonded to the coordinated water molecule or OH^- group. Most FeSOD molecules have a glutamine at a position equivalent to 77 of the *E. coli* enzyme and this glutamine is hydrogen bonded to the coordinated solvent. A (G77Q, Q146A) double mutant of *E. coli* MnSOD with the active site Gln in the location characteristic of Fe-specific SODs has an active site that is spectroscopically similar to that of MnSOD. The Fe-supported activity of this mutant is at least 7% that of FeSOD, in contrast to wild type Fe-substituted MnSOD, which has no activity. Thus, this mutation has converted the Mn-specific SOD into a cambialistic SOD and the Gln residue is an important, but not the only, determinant of metal ion

specificity. The active site of Fe^{3+}-substiturted MnSOD differs from that of Fe^{3+}-SOD with respect to the EPR signals produced at both neutral and high pH, suggesting different coordination environments for Fe^{3+}.[638] A ^{15}N NMR study of the Fe^{2+} forms of the enzymes has drawn similar conclusions.[639]

Other mutagenesis studies of *E. coli* MnSOD have shown that the highly conserved Tyr-34, which is hydrogen bonded to Gln-146, is not essential for catalysis.[631] In *E. coli* MnSOD, Glu-170 of one monomer is hydrogen bonded to the Mn ligand, His-171, of the other monomer, forming a double bridge at the dimer interface. The E170A mutant protein was found to occur as a mixture of dimer and monomer species, to be devoid of SOD activity, and to contain exclusively iron as the metal cofactor. The manganese-containing form of this mutant is also inactive.[640] In human MnSOD His-30 is partially exposed to solvent, and its side chain participates in a hydrogen-bonded network that includes the active-site residues Tyr-166 and Tyr-34, and extends to the Mn-bound water molecule. Other position 30 mutants and the mutant containing Phe-166 showed a 10–40-fold decrease in k_{cat}. This is the same magnitude of decrease in k_{cat} obtained by replacing Tyr-34 by Phe, suggesting that interrupting the active-site hydrogen bond network at any of the sites of these three participants (His-30, Tyr-34, and Tyr-166) leads to an equivalent decrease in k_{cat} and probably less efficient proton transfer to product peroxide.[641]

5.1.8.2.3 3-Deoxy-D-arabino-heptulosonate-7-phosphate synthetase

3-Deoxy-D-*arabino*-heptulosonate-7-phosphate synthetase (DAHPS) is the initial enzyme in the pathway responsible for the synthesis of aromatic compounds in microorganisms and plants. It catalyses the reaction shown in Equation (4):



(4)

The structure DAHPS from *E. coli* with Mn^{2+} and the substrate analogue, 2-phosphoglycolate (PGL), in the active site has been determined. Mn^{2+}, the most efficient metal activator of DAHPS, is coordinated by four amino acid side chains; the PGL and a water molecule complete the octahedral coordination (Figure 25).[642] This structure is notable for the fact that it contains a rare example of a Mn—S bond in a protein. The Mn—S bond is quite long, 2.74 Å, and spectroscopic evidence for the formation of this bond is lacking.[643]

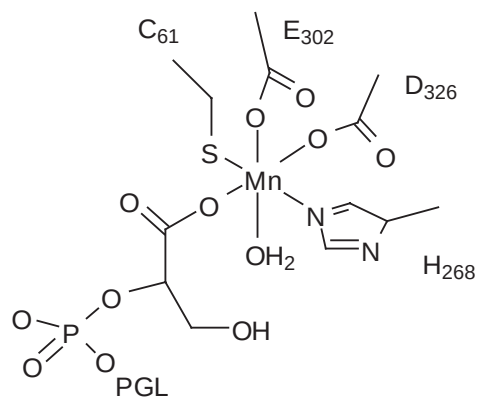


Figure 25 Schematic of the active site of DAHPS with the substrate analogue PGL bound to Mn^{2+}.

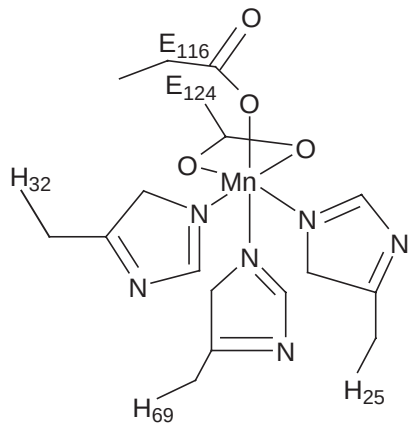


Figure 26 Schematic of the Mn^{2+} coordination sphere in manganese inorganic pyrophosphatase.

5.1.8.2.4 Inorganic pyrophosphatase

Inorganic pyrophosphatases (PP_iase) are found in almost all living cells, where they catalyze the hydrolysis of $P_2O_7^{4-}$ to phosphate. All known PP_iases require a divalent metal ion for catalysis, Mg^{2+} usually has the highest activity. Crystal structures of the Mg^{2+}-activated enzymes from a number of organisms, *Sulfolobus acidocaldarius*,[644] *S. cerevisiae*[645–647] and *E. coli*[648–650] have been determined with Mn^{2+} bound in the active site and these structural studies have been reviewed.[651] The active site structure formed by ~15 amino acid residues and the three or four metal ions are highly conserved in these different enzymes. The ligands to the metal ions in these structures are aspartate and glutamate side chains, water molecules, and phosphate oxygens.

In 1998 the long-known *Bacillus subtilis* inorganic pyrophosphatase was characterized and found to have much greater activity than the above enzymes, to have a completely different amino acid sequence, not to be inhibited by F^- and to be activated by Mn^{2+}.[652–656] This form of the enzyme has since been recognized as being present in many more bacterial species. Crystal structures of the enzymes from *Streptococcus mutans*[657] and from *Streptococcus gordonii*[658] have been determined. The active site geometry is shown in Figure 26. The preference for Mn^{2+} over Mg^{2+} is explained by the histidine ligands.

5.1.8.2.5 Oxalate decarboxylase

Oxalate decarboxylase converts oxalate to formate and CO_2 and requires dioxygen and Mn^{2+} for activity.[659] Structurally the enzyme from *Bacillus subtilis* belongs to the cupin superfamily of enzymes, having a β-sandwich domain with one seven-stranded β-sheet and one five-stranded β-sheet within a β-barrel structure. The molecule has two domains, each domain contains one Mn^{2+} binding site, the two sites are separated by 26 Å. A schematic diagram of the metal binding site is shown in Figure 27. Both Mn ions are coordinated to four protein residues, three histidines, and a glutamate carboxylate. One metal completes its octahedral coordination with two water molecules and the other completes its coordination with a water molecule and a formate ion.[660] The metal coordination sphere is almost identical to that in oxalate oxidase discussed below and very similar to the five-coordinate manganese in superoxide dismutase.

5.1.8.2.6 Oxalate oxidase

Oxalate oxidase catalyzes the reaction shown in Equation (5):

$$C_2O_4^{2-} + O_2 + 2H^+ \longrightarrow H_2O_2 + 2CO_2 \qquad (5)$$

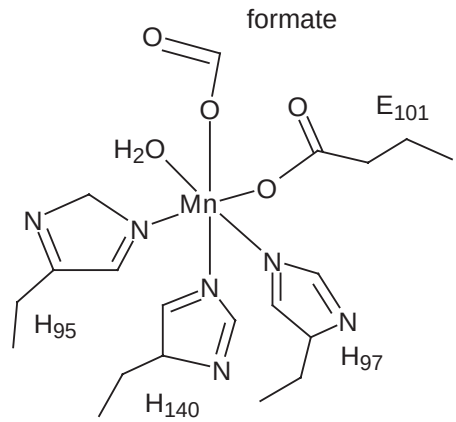


Figure 27 Schematic of one active site of oxalate decarboxylase from *Bacillus subtilis*. The other active site is similar but a water molecule replaces the formate.

Germin, a plant protein involved in seed germination, is an oxalate oxidase. Germin isolated from *Hordeum vulgare* has both an oxalate oxidase and a superoxide dismutase activity.[661] In contrast, a germin-like protein isolated from the moss *Barbula unguiculata* has superoxide dismutase activity but no oxalate oxidase activity.[662] The structure of the enzyme from *Hordeum vulgare* revealed the same Mn^{2+} coordination sphere as the Mn^{2+} in oxalate decarboxylase described above.[661] Reasons for the different activities of oxalate oxidase and oxalate decarboxylase given their structural similarity have been discussed.[660] One appealing explanation is that the active site of oxalate oxidase lacks a proton donor whereas oxalate decarboxylase has several possible residues able to donate protons.

5.1.8.2.7 Isopentenyl diphosphate isomerase

Isopentenyl diphosphate isomerase catalyzes the isomerization of isopentenyl diphosphate to dimethylallyl diphosphate (Equation (6)):[663,664]

(6)

These two compounds constitute the basic building blocks of isoprenoids, a family of compounds that is extraordinarily diverse in structure and function. The enzyme requires one Mn^{2+} or Mg^{2+} ion to fold into its active conformation. Crystal structures of the enzyme from *E. coli* have been reported and the active site is shown in Figure 28.[665,666] Two critical residues, Cys-67

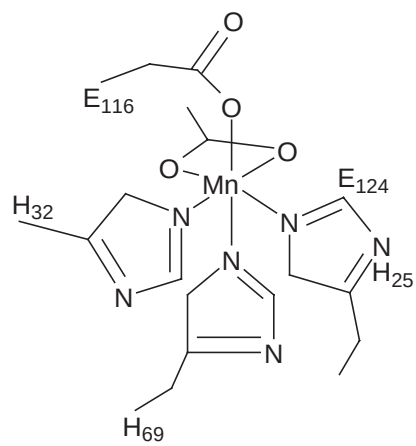


Figure 28 Active site of the isopentenyl diphosphate isomerase enzyme from *E. coli*. In the crystals studied by Bonanno *et al.*[666] the bidentate glutamate is monodentate and the Mn^{2+} has a distorted square pyramidal geometry.

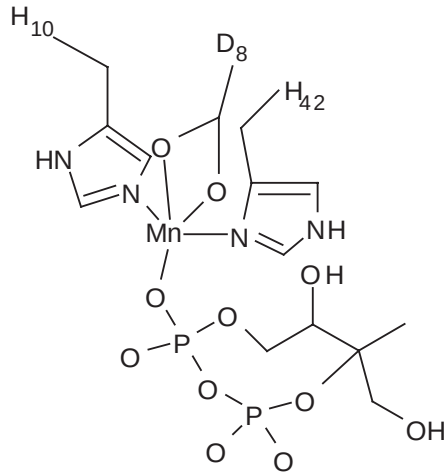
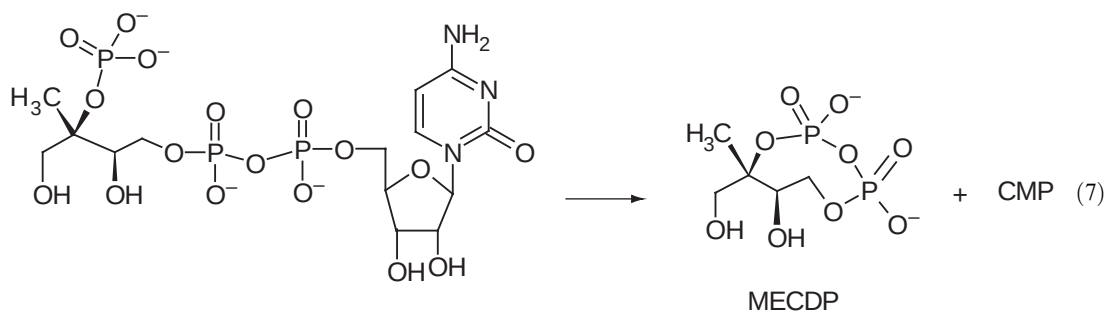


Figure 29 Schematic view of the metal binding site of MECDP synthase.

and Glu-116, face each other within the active site, close to the metal binding site. The mechanism is believed to involve protonation of the carbon–carbon double by the cysteine, with the antarafacial rearrangement ultimately achieved by one of the glutamates involved in the metal coordination sphere.

5.1.8.2.8 2-C-methyl-D-erythritol 2,4-cyclodiphosphate synthase

2-C-methyl-D-erythritol 2,4-cyclodiphosphate synthase catalyses the conversion of 4-diphosphocytidyl-2-C-methyl-D-erythritol 2-phosphate to 2-C-methyl-D-erythritol 2,4-cyclodiphosphate (MECDP) (Equation (7)). This reaction is part of the isoprenoid biosynthesis pathway in many plants and bacteria. The structure of the *E. coli* enzyme bound to Mn^{2+}, cytosine monophosphate, and 2-C-methyl-D-erythritol 2,4-cyclodiphosphate has been determined.[667] The enzyme in the crystal and probably in solution is trimeric, three monomers are packed in a circular assembly with three-fold symmetry. The active site is at the interface of two adjacent monomers; all the ligands bound to the Mn^{2+} come from one monomer and a MECDP molecule. The structure of this active site is shown in Figure 29:



(7)

5.1.8.3 Enzymes with Binuclear Active Sites

Enzymes with binuclear Mn^{2+} active sites that have not yet been structurally characterized include a glycohydrolase responsible for regulating the activity of the nitrogenase enzyme;[668,669] γ-glutamylcysteine synthetase which catalyzes the first and rate-limiting step in glutathione biosynthesis;[670] the major sperm protein of *Ascaris suum*;[671] many sugar transferases;[589] a thiosulfate oxidizing enzyme;[672] a Mn^{2+} activated alkaline phosphatase;[673] amidohydrolases related to arginase,[674] arginine deaminase;[675] agmatinase;[676] formiminoglutamase;[677] the MutT enzyme that catalyses the hydrolysis of nucleoside triphosphates to yield nucleoside monophosphate and

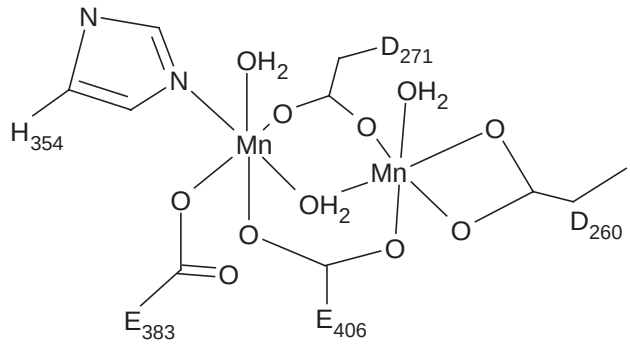


Figure 30 Schematic view of the active site of the aminopeptidase P from *E. coli*.

pyrophosphate;[678,679] ribonucleotide reductase from *Corynebacterium ammoniagenes*;[680] and the enzymes responsible for the cleavage of peptide bonds in proline-containing dipeptides and tripeptides, prolinase and prolidase.[681,682] Structurally characterized examples not included in the discussion below include endonucleases;[683–685] a phosphotriesterase from *Pseudomonas diminuta* that catalyzes the hydrolysis of organophosphate nerve agents;[686] and lectins.[687,688]

5.1.8.3.1 Aminopeptidases

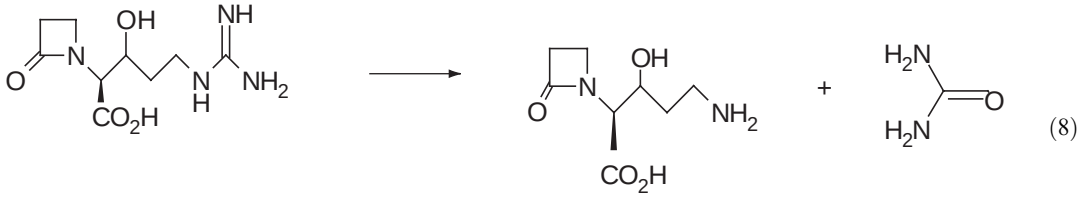
Aminopeptidases catalyze the hydrolysis of the amino end of polypeptides and proteins.[689] The cyclic structure of proline imposes conformational constraints on proline-containing polypeptides. These constraints provide protection against nonspecific proteolytic cleavage but proline-containing polypeptides can be sequentially degraded by two Mn^{2+}-dependant aminopeptidases.[681] Human clostridial aminopeptidase cleaves any N-terminal amino acid residue including proline from polypeptide chains, but does not cleave the N-terminal peptide bonds involving a prolyl nitrogen. Aminopeptidase P cleaves such prolyl nitrogen bonds.[690–692] A form of the human enzyme apparently contains only a single Mn^{2+} ion.[693] The binuclear enzyme has been structurally characterized and studied using EPR, EXAFS, and XANES.[694] The active site, in the C-terminal domain, contains a binuclear manganese center (the Mn—Mn distance is 3.3 Å). A representation of the structure of the active site is shown in Figure 30. The bridging H_2O or OH^- apparently acts as the nucleophile in the attack on the scissile peptide bond of the substrate.

5.1.8.3.2 Arginase

Arginase is a binuclear Mn^{2+}-activated enzyme that catalyzes the hydrolysis of L-arginine to L-ornithine and urea. A number of reviews of the behavior and structure of arginase have appeared.[585,695–697] Structures of arginase from *B. caldovelox*[698] and the rat liver enzyme[699–703] have been determined. Both forms contain a binuclear active site and forms of the enzyme that contain only one Mn^{2+} have very low activity.[704] The Mn^{2+} ions are located at the bottom of a 15 Å deep cleft in the monomer, separated by 3.3 Å, and are bridged by a OH^- ion and two aspartate residues. Figure 31 shows the metal coordination sphere. The mechanism for the hydrolysis reaction is believed to involve the arginine substrate hydrogen bonding to four amino acid side chains via the guanidine group. This places the carbon atom of the guanidine group directly over the bridging OH group at a distance of 2.25 Å and ideally placed for nucleophilic attack.

5.1.8.3.3 Proclavaminate amidino hydrolase

Proclavaminate amidino hydrolase (PAH) is one of a number of enzymes that are Mn^{2+} activated and whose amino acid sequence shows strong homology with arginase.[677] PAH catalyzes the hydrolysis of a guanidino group to give proclavaminate and urea (Equation (8)):



(8)

Proclavaminic acid

Arginine is capable of binding in the active site of PAH but it is not an enzyme substrate. Crystal structures of PAH from *Streptomyces clavuligerus* show that the metal binding site is very similar to that of arginase and the Mn—Mn distance is 3.3 Å The main difference between arginase and PAH is in the binding pocket at the "α-amino-terminus" of the substrate.[705]

5.1.8.3.4 Catalase

Catalases catalyze the conversion of hydrogen peroxide to dioxygen and water. Two families of catalases are known, one having a heme cofactor and the second a structurally distinct family, found in thermophilic and lactic acid bacteria.[706] The manganese enzymes contain a binuclear active site and the functional form of the enzyme cycles between the $(Mn^{II})_2$ and the $(Mn^{III})_2$ oxidation states. When isolated, the enzyme is in a mixture of oxidation states including the Mn^{III}/Mn^{IV} superoxidized state and this form of the enzyme has been extensively studied using XAS, UV–visible, EPR, and ESEEM spectroscopies.[707] Multifrequency EPR and microwave polarization studies of the $(Mn^{II})_2$ catalytically active enzyme from *L. plantarum* have also been reported.[708]

Crystal structures of manganese catalases (in the $(III)_2$ oxidation state) from *Lactobacillus plantarum*,[709] its azide-inhibited complex,[624] and from *Thermus thermophilus*[710] have been determined. There are differences between the structures that may reflect distinct biological functions for the two enzymes, the *L. plantarum* enzyme functions only as a catalase, while the *T. thermophilus* enzyme may function as a catalase/peroxidase.[709] The active sites are conserved in the two enzymes and are shown schematically in Figure 32. Each subunit contains an Mn_2 active site,

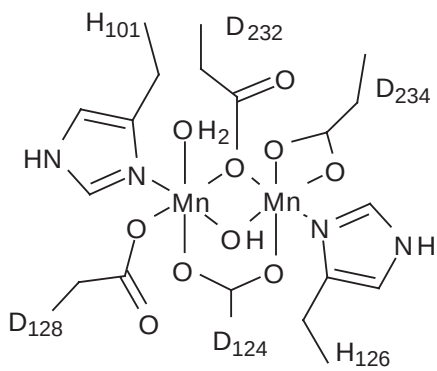


Figure 31 Schematic view of the manganese binding in arginase.

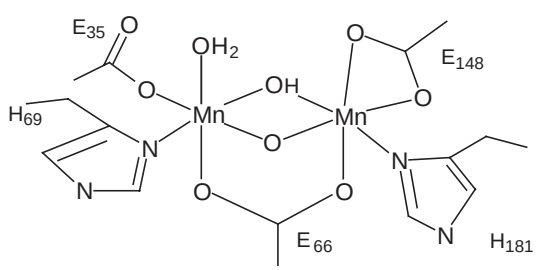


Figure 32 Schematic of the active site of the catalase from *L. plantarum*.

accessed by a single substrate channel lined by charged residues. The active site is enclosed within a web of hydrogen bonds that radiates out from the metal centers. The Mn_2O_2 core is not planar, the oxygen bridging atoms arch about 12° above the Mn—Mn vector. The Mn—Mn separation is 3.03 Å and the Mn—O bonds to the bridging oxygens *trans* to the histidines are longer, consistent with an OH^- bridge. In the $(II)_2$ form of the enzyme it is known from EXAFS studies that the Mn—Mn separation is significantly longer (3.53 Å) so that the groups bridging the Mn atoms may change with oxidation state.[709]

5.1.8.3.5 Protein phosphatases

Phosphorylation of serine, threonine, and tyrosine side-chain OH groups of proteins by kinases and their dephosphorylation by protein phosphatases provides an important mechanism for biological regulation. Tyrosine phosphatases are not metalloenzymes but the serine/threonine phosphatases contain a bimetallic site.

(i) Purple acid phosphatase

Purple acid phosphatase (PAP) or tartrate-resistant phosphatase is not thought to be a protein phosphatase but it has a very similar dimetallic active site structure to that found in protein phosphatases.[711,712] PAPs have been identified in bacteria, plants, mammals, and fungi.[713] The molecular weights (animal ~35 kDa, plant ~55 kDa) are different and they exhibit low sequence homology between kingdoms but the residues involved in coordination of the metal ions are invariant.[714] There has been considerable debate as to the identity of the metal ions in PAPs *in vivo*. Sweet potato, *Ipomoea batatas,* has been shown to possess two different PAP enzymes[715] and the active site of one of them has been shown to contain one Fe^{3+} and one Zn^{2+} ion.[716,717] Another report has established that the active site of a PAP from sweet potato contains one Fe^{3+} and one Mn^{2+}.[718] The well-characterized red kidney bean enzyme and the soybean enzyme contain Fe^{3+} and Zn^{2+}.[719] Claims that PAP from sweet potato has 2Fe ions or 2Mn ions have been discussed elsewhere.[584] One explanation is that these are different forms of the enzyme, another is that because the metal ions are labile and are rapidly incorporated into the active site, the enzyme contains a mixture of metal ions *in vivo* and the form isolated depends on the conditions of isolation.

Crystal structures of PAP from red kidney beans,[720] rat,[721] and pig[722] are available. A crystal structure determination of the Fe/Mn sweet potato enzyme has been carried out.[723] The structures of the active sites are shown in Figure 33.

(ii) Protein phosphatases

In mammalian tissues four different types of protein phosphatases, known as PP1, PP2A, PP2B (or calcineurin), and PP2C, have been identified. Except for PP2C, these enzymes are evolutionary

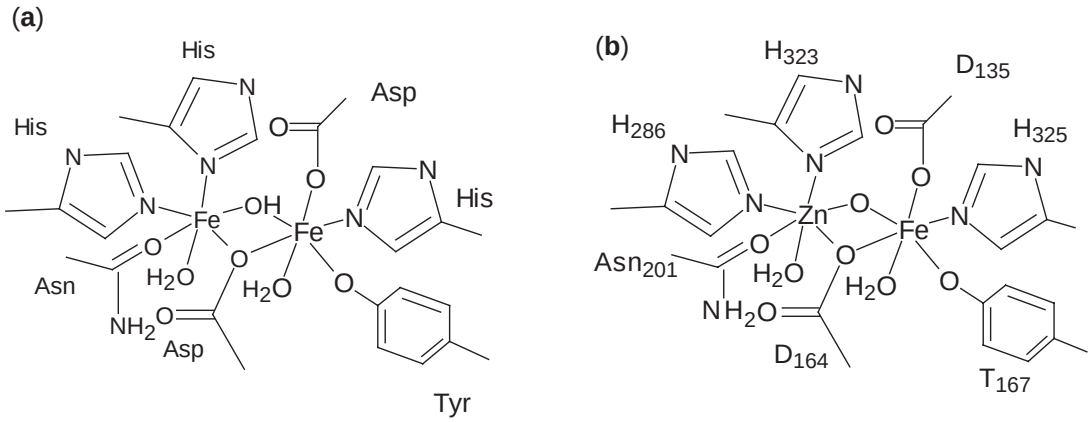


Figure 33 Structures of the active sites in (a) mammalian PAP and (b) kidney bean PAP.

related. These protein phosphatases are responsible for the hydrolysis of serine and threonine esters; they have two active site metal ions and many are activated by Mn^{2+}.[586,712,724–727] Mn^{2+} is probably not the native metal in most PP1 and PP2B enzymes but it is a potent activator of both enzymes and may be the *in vivo* metal ion in some species.[728] The rabbit muscle PP1 becomes Mn^{2+} dependant upon long storage and when expressed in *E. coli*.[729] In many organisms the native metals are probably Fe/Zn but the crystals used in the crystal structure determination of the human PP1 enzyme contained manganese and the metals were modeled as one Mn and one Fe atom in the refinement. Both metal ions are five coordinate, one has a square pyramidal geometry and the other has trigonal bipyramidal coordination. A later determination of the structure of human PP1 modeled the metal ions as manganese.[730] Human PP2A occurs in a number of forms, a Fe/Zn-activated form and a Mn-activated form,[731,732] but a crystal structure is not yet available. The sole structure of P2B was modeled with Zn^{2+}/Fe^{3+} in the active site.[733] PP2C enzymes exist in at least five different forms (α, β, γ, δ, and ζ) and all appear to be Mn dependant. Human PP2C contains a binuclear Mn^{2+} active site. The metal ion coordination differs considerably from the other protein phosphatases. Protein architecture is similar in the PP1, PP2A, PP2B, and PP2C enzymes despite the lack of sequence similarity. The active sites of the PP1, PP2B, and PP2C enzymes are shown in Figure 34. The metal binding sites in PP1 and PP2B are similar, both metal ions are five-coordinate, one metal ion is bound to two histidines and a glutamine residue, the other is bound to a histidine, an aspartate, and a water molecule. A bridging monodentate aspartate joins the two metal ions and there is another bridging group, the identity of which may be dependant on the isolation conditions of the crystal. The metal-binding site in PP2C is quite different, the metal ions are six-coordinate and the ligands are all oxygen atoms.

A protein phosphatase from bacteriophage λ is also Mn^{2+} dependant with a high- and low-affinity binding site for Mn. Analysis of mutant forms has shown that the high-affinity site has His-186 and Asn-75 as ligands and His-22 is a ligand to the lower-affinity binding site.[734] This phosphatase has been structurally characterized.[735] There are three molecules in the asymmetric unit and the active site is very similar to the active sites of PP1. There are two differences in the coordination sphere of the metals; both Mn ions are six-coordinate, the low-affinity binding site Mn has two coordinated water molecules and there is a sulfate ion coordinated to the high-affinity metal center. In two of the molecules in the asymmetric unit the sulfate is coordinated as a monodentate ligand to the Mn ion in the high-affinity binding site; in the third molecule the sulfate acts as a tridentate bridging ligand between the Mn atoms.

5.1.8.3.6 Phosphoglycerate mutase

There are two types of phosphoglycerate mutase, one form from plants and some bacteria is Mn^{2+} dependant, the other form, from mammals, yeast, and some bacteria, is not activated by metal ions. These enzymes catalyze the interconversion of 3-phosphoglycerate and 2-phosphoglycerate. The enzyme from *Bacillus stearothermophilus* has been structurally characterized and has a globular shape containing two domains with similar folds. The two metal ions are located in a cleft between the two domains. One Mn ion is bound to the protein via Asp-403, His-409, and His-462 and bound to two phosphate oxygens from 2-phosphoglycerate present in the active site. The other Mn ion is bound to Asp-12 (bidentate), Ser-62, His-444, and His-445. Both metal ions have a distorted square pyramidal geometry. There is a weak interaction (3.33 Å) from the second Mn to one of the phosphate oxygens bound to the other Mn^{2+}.[737–739] A schematic view of this active site is shown in Figure 35. The Mn—Mn distance is 4.92 Å. The mechanism of the reaction suggested by these structures has one domain that participates in a phosphatase reaction and the formation of a phosphoserine enzyme intermediate. The other domain is involved in the phosphotransferase reaction regenerating phosphoglycerate.[738]

5.1.8.3.7 Glutamine synthetase

Glutamine synthetase catalyzes the conversion of L-glutamate, ATP, and ammonia into L-glutamine, ADP, and PO_4^{3-}. Divalent metal ions are required for activity and Mn^{2+} or Mg^{2+} are the *in vivo* activators. Two different types of glutamine synthetase have been identified in the cyanobacterium *Synechocystis sp*. PCC 6803. The second type has a different amino acid sequence from the prokaryotic and the eukaryotic glutamine synthetases. This enzyme is composed of six identical subunits with an apparent molecular mass of 80 kDa and is strongly stabilized in the presence of Mn^{2+} but not by other divalent cations and its structure is unknown.[740]

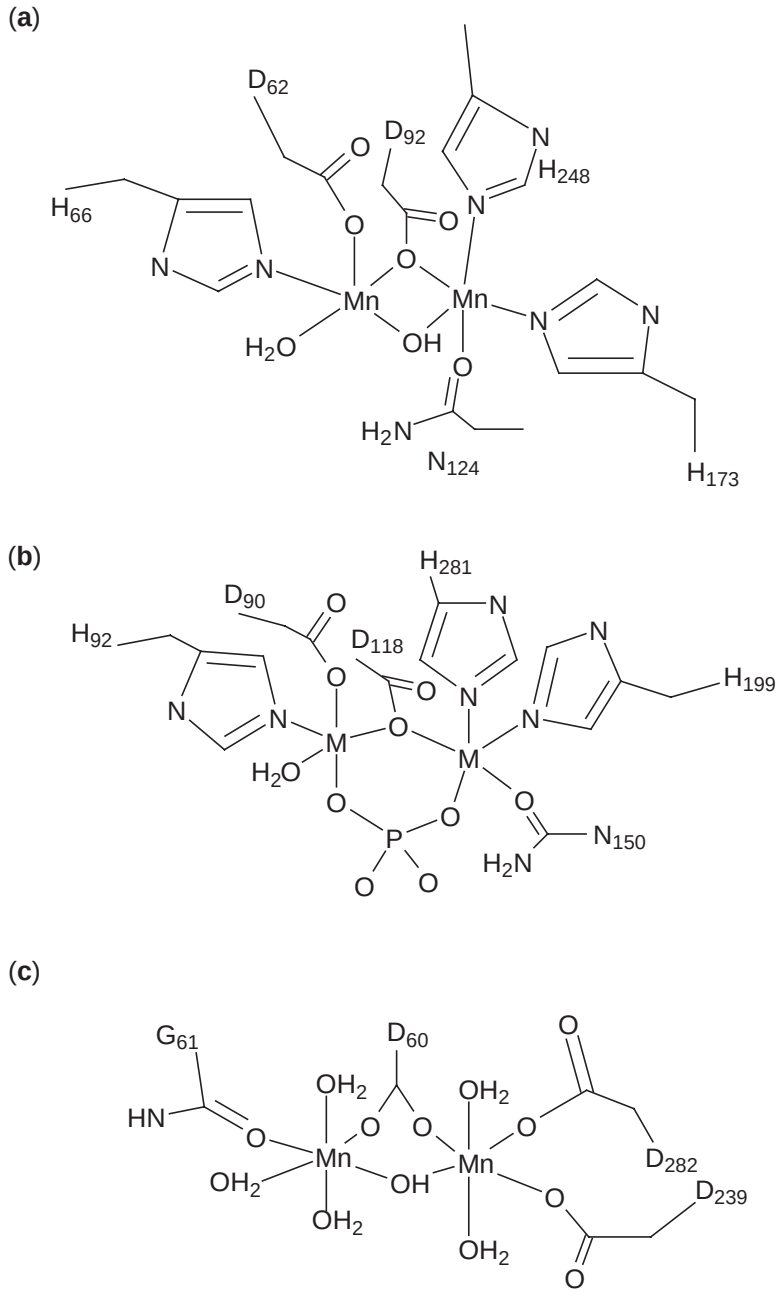


Figure 34 Active sites of human protein phosphatases: (a) PP1[720]; (b) PP2B, the metal ions are Fe^{3+} and Zn^{2+};[733] (c) PP2C.[736]

X-ray crystal structures of glutamine synthetase from both *Salmonella typhimurium*[741] and *Mycobacterium tuberculosis*[742] are very similar. Structures of wild type enzymes and of active site mutants have been determined. All structures have been solved with Mn^{2+} in the active site. There are twelve identical subunits arranged in two face-to-face symmetrical hexamers. The active sites are in funnel-shaped open-ended cavities located between adjacent subunits of the hexamer. These cavities are ~45 Å long, 30 Å wide at the outer end, and 10 Å wide at the inner end and the active site with the two Mn^{2+} ions is approximately halfway down the cavity. The metal–metal distance is 5.8 Å. The more tightly bound Mn^{2+} is coordinated to the side chains of Glu-131, Glu-212, Glu-220, and two water molecules, one of which is shared by both metal ions. Glu-129, Glu-357, His-269, and two additional water molecules are bound to the Mn^{2+} at the lower affinity site. A schematic view of the active site metal coordination is shown in Figure 36.

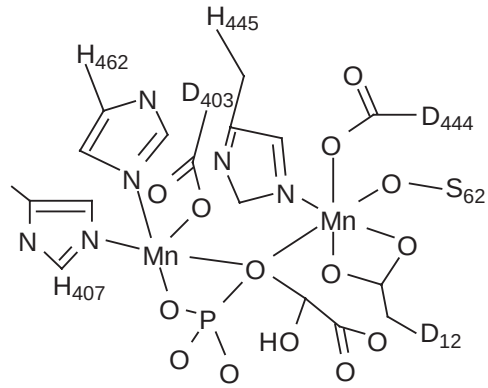


Figure 35 Schematic view of the active site of *Bacillus stearothermophilus* phosphoglycerate mutase.

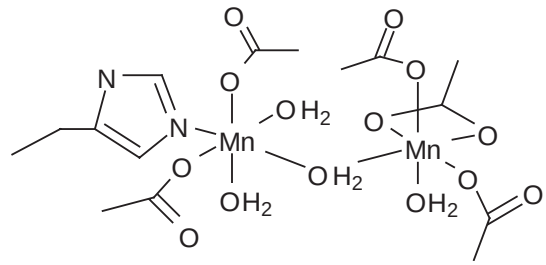
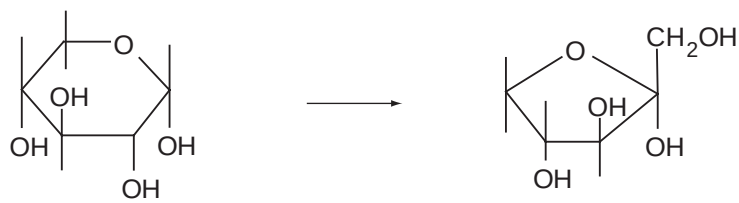


Figure 36 Schematic view of the binuclear metal binding site in glutamine synthetase.

The proposed mechanism involves the binding of ATP adjacent to one Mn^{2+} and glutamate adjacent to the other Mn^{2+} followed by glutamate attack on the γ-phosphorus atom of ATP, producing a γ-glutamyl phosphate intermediate and releasing ADP. Ammonia then attacks the γ-glutamyl phosphate intermediate, forming another intermediate from which inorganic phosphate and glutamine are released.

5.1.8.3.8 Isomerases

Many sugar isomerases are activated by Mn^{2+}.[589] Three Mn^{2+} activated sugar isomerases have been structurally characterized, xylose isomerase, fucose isomerase, and rhamnose isomerase. Xylose isomerase catalyzes the interconversion of D-xylose and D-xylulose (Equation (9)) and also the interconversion of D-glucose and D-fructose. This latter activity is the basis of the important commercial application of this enzyme.[743] Xylose isomerase is widely distributed in bacteria and plants and the catalytic and metal binding sites are conserved. Mg^{2+}, Co^{2+}, and Mn^{2+} are the activating cations. Mn^{2+} gives the highest activity in *Escherichia*, *Bacillus*, and *Lactobacillus* species, in *Paenibacillus sp.*, and in barley.[744,745] EPR studies of the Mn^{2+} forms of the enzyme have been reviewed.[746] The generally agreed mechanism involves ring opening as the first step followed by a proton shuttle involving a structural water molecule, and then a rate-determining hydride shift step. The role of metal ions in the catalytic process has been discussed in detail.[747]



(9)

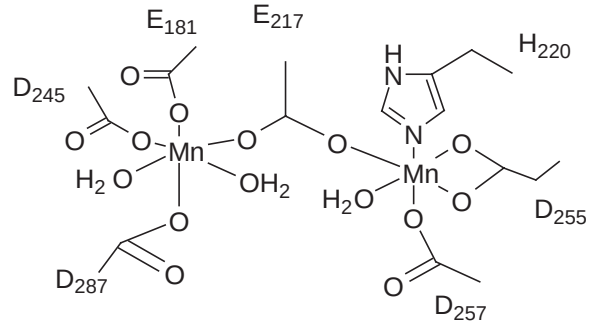


Figure 37 Schematic view of the active site of xylose isomerase in the absence of substrate.

Crystal structure determinations of xylose isomerases with Mn^{2+} in the active site have been reported from many different bacteria.[748] The structures from different bacterial species are similar, each monomer consists of an eight-stranded β/α barrel and a C-terminal domain which loops around the barrel of a neighboring molecule. The active site, located near the center of the barrel, contains two metal ions and the metal-binding ligands are conserved in all species investigated. The metal ions are bridged by a glutamate residue and are 4.9 Å apart in the substrate-free form of the enzyme. A schematic view of the active site is shown in Figure 37.

L-Rhamnose isomerase catalyzes the interconversion of L-rhamnose and L-rhamnulose. L-Rhamnose, a deoxy sugar, is found in bacteria and plants and it plays an essential role in many pathogenic bacteria. The pathway for the metabolism of this sugar does not exist in humans, and this makes enzymes of this pathway attractive targets for therapeutic intervention.[749] Rhamnose isomerase from *E. coli* is a tetramer of $(\beta/\alpha)_8$-barrels similar to xylose isomerase.[750] The binuclear metal center in rhamnose isomerase appears to bind one Zn^{2+} and one Mn^{2+}. The metal-mediated hydride-shift mechanism outlined above is also feasible for L-rhamnose isomerase.

L-Fucose isomerase catalyzes the interconversion of L-fucose to L-fuculose and D-arabinose to D-ribulose. It has neither sequence nor structural similarity with the other aldose–ketose isomerases. A crystal structure of the *E. coli* enzyme with an L-fucitol bound in the active site shows that the active site is located in a 20 Å deep pocket, at the bottom of which is a single Mn^{2+} ion. Mn^{2+} is bound to O_1 and O_2 of L-fucitol; the side chains of a monodentate Glu-337, a bidentate Asp-361 (with long bonds to both oxygens), His-528; and a water molecule.[751]

5.1.8.3.9 Transferases

Proteins and lipids are frequently modified by attachment of carbohydrate groups and additional sugar residues can then be added to the attached sugars to form complex oligosaccharide structures. These glysolated molecules have a wide range of roles including the determination of protein structure and folding, the determination of membrane and cell wall structures, and they can provide recognition elements in cell–cell interactions. Many different enzymes catalyze these glysolation reactions; 12 different groups and 5 families of galactosyltransferases and 27 families of glycosyltransferases have been recognized on the basis of sequence comparisons. In most cases these enzymes catalyze the transfer of a nucleotide sugar residue to a hydroxyl group on the target protein, lipid, or carbohydrate although some use lipid-based dolichol phosphate sugars. Many glycosyltransferases require divalent metal ions for activity. The concentration of Mn^{2+} required *in vitro* to give maximum activity with these enzymes is usually >1 mM and such a high concentration would normally exclude them from consideration as Mn^{2+}-activated enzymes. However, Mn^{2+} is often the only divalent metal ion that shows activity. Our understanding of the behavior of these enzymes has advanced rapidly since the late 1990s as a result of a number of crystal structure determinations. In many of the determined structures the Mn^{2+} is bound to the substrate (often in a bidentate fashion) and is attached to the protein by only one carboxylate side chain.

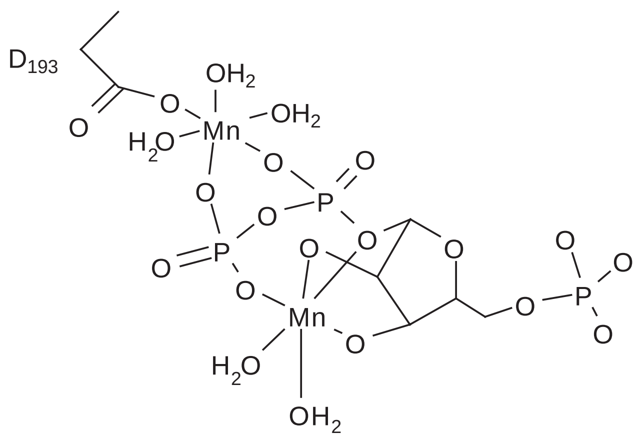


Figure 38 Schematic of the active site of hypoxanthine phosphoribosyltransferase[753] with bound phosphoribosylpyrpphosphate.

(i) Ribosyltransferases

Structures of Mn^{2+}-activated ribose sugar transferases, hypoxanthineguanidine phosphoribosyltransferase from *Trypanosoma cruzi*[752,753] and *Toxoplasma gondii*,[754–756] and quinolinic acid phosphoribosyltransferase from *Mycobacterium tuberculosis*,[757] are available. The binuclear Mn^{2+} binding sites in the hypoxanthineguanidine phosphoribosyltransferases are almost identical and are illustrated in Figure 38. One Mn^{2+} is coordinated by two ribose hydroxyl groups, two α- and β-pyrophosphate oxygens, and two water molecules, while the other Mn^{2+} is bound to four water molecules and to α- and β-pyrophosphate oxygens. The active site in the quinolinic acid phosphoribosyltransferase[757] is similar except that Asp-193 is replaced by a water molecule.

(ii) Galactosyltransferases

UDP-galactose:β-galactosyl-α-1,3-galactosyltransferase catalyzes the transfer of galactose from UDPα-D-galactose to an acceptor having LacNAc(Galβ1,4GlcNAc) as the terminal disaccharide. This enzyme, which requires two Mn^{2+} ions for activity, is expressed in most mammals, but is absent from humans. Natural antibodies are directed at its product, the α-galactose epitope and these antibodies present a major barrier to the use of nonhuman organs for xenotransplantation in humans. The structure of the bovine enzyme has been solved and the active site is in a deep tunnel inside the molecule.[758–760] Only one Mn^{2+} ion could be identified in the crystals studied. The metal ion coordination is shown in Figure 39. Mn^{2+} is bound to the α- and

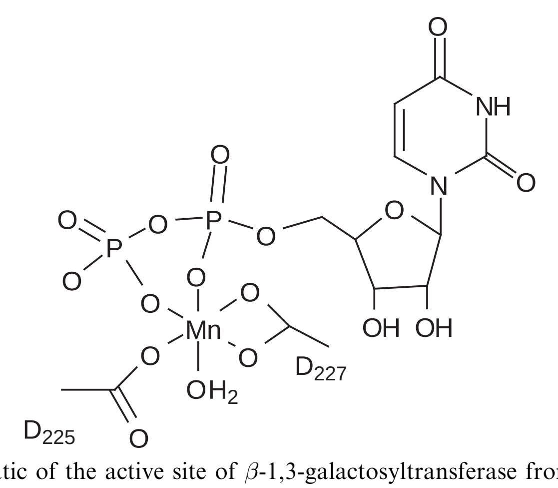


Figure 39 Schematic of the active site of β-1,3-galactosyltransferase from *Bos taurus*.[759,760]

β-phosphates of UDP, two aspartate residues, one monodentate and the other bidentate, and a water molecule. These aspartates form part of the DVD sequence motif known from mutagenesis studies to be essential for enzymatic activity. The other Mn^{2+} binding site has not been identified.

Bacterial pathogens, such as *Neisseria meningitides*, can express lipooligosaccharides that mimic human cell surface glycoconjugates, enabling the bacteria to attach to host receptors and to evade the immune response. A key enzyme in this process catalyzes the transfer of α-D-galactose from UDP-galactose to a terminal lactose. Crystal structures of the complex of this enzyme with Mn^{2+} and UDP 2-deoxy-2-fluoro-galactose (a donor sugar analogue) in the presence and absence of the acceptor sugar analogue 4′-deoxylactose have been determined.[761] In these structures Mn^{2+} is six-coordinate with a monodentate and bidentate aspartate, a histidine, and two phosphate oxygens as ligands.

β-1,4-Galactosyltransferase I (β4Gal-T1) is a bifunctional enzyme. It transfers galactose (Gal) from UDP-galactose (UDP-Gal) to *N*-acetylglucosamine (GlcNAc). In the presence of α-lactalbumin (LA), β4Gal-T1 transfers Gal to glucose (Glc), so that it is both a galactosyltransferase and a lactose synthase. Crystal structures of the Gal-T1LA complex with UDP-GlcMn^{2+} have been determined. The Mn^{2+} is five-coordinate with two phosphate oxygen donors from the UDP; a carboxylate oxygen from an aspartate, nitrogen from a histidine, and sulfur from a methionine residue making up the coordination sphere.[762,763]

(iii) Glucosyltransferases

X-ray crystal structures of bacteriophage T4 β-glucosyltransferase,[764] *Bacillus subtilis* SpsA,[765,766] and rabbit *N*-acetylglucosaminyltransferase I[767] have been solved and a commentary on these structures has appeared.[768] SpsA is a glycosyltransferase implicated in the synthesis of the spore coat of *Bacillus subtilis*, whose homologues include cellulose synthase and many lipopolysaccharide and bacterial O-antigen synthases. Structures of uncomplexed SpsA and in complex with both M-UDP and M-dTDP ($M = Mg^{2+}$ and Mn^{2+}) have been determined.[765,766] In the Mn-UDP complex the Mn binding is very similar to the coordination sphere of the Mn^{2+} in β-1,3- galactosylytransferase (Figure 39), The UDP is a bidentate ligand binding via α- and β-phosphate oxygens. The only point of attachment of the metal ion to the protein is a monodentate aspartate, as opposed to a bidentate attachment in β-1,3-galactosylytransferase. There is a water molecule in the vacated coordination site. Another point of difference is that there is an Mg^{2+} ion in the active site; it is bound to an α-phosphate oxygen of UDP, four water molecules, and an OH of a glycerol molecule. A schematic view of the active site is shown in Figure 40.

Two other structurally characterized transferases have the same or almost the same mode of Mn^{2+} coordination as Mn^{2+} in *Bacillus subtilis* glycosyltransferase SpsA described above. *N*-acetylglucosaminyltransferase I which serves as the gateway from oligomannose to hybrid and complex *N*-glycans and plays a critical role in mammalian development, has the same active site structure except the Mg^{2+} ion and the glycerol are not present.[767] β 1,3-Glucuronyltransferase I

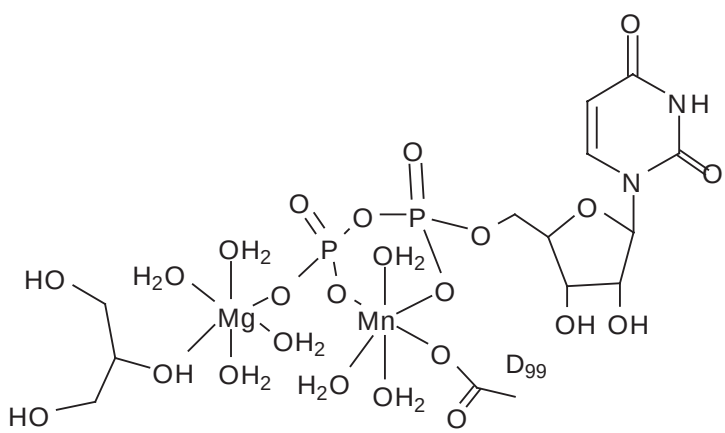


Figure 40 Active site of the Mn-UDP complex of SpsA.

is the transferase responsible for the formation of the β 1,3-glycosidic bond in the first step in the formation of proteoglycans with side chains such as heparan sulfate and chondroitin sulphate. The Mn^{2+} has octahedral coordination, the α- and β-phosphates of UDP, a bidentate aspartate (Asp-196), and two water molecules. A second unidentified metal ion, with tetrahedral coordination geometry, is bound to a different α-phosphate oxygen, His-308, and two water molecules.[769]

5.1.8.4 Enzymes with Trinuclear Active Sites

Enzymes that probably require three metal ions for full activity include the *Tetrahymena* group I ribozyme,[770,771] a Mn^{2+}-activated bifunctional enzyme with inositol monophosphatase and fructose 1,6-bisphosphatase activities described below,[772] and some endonucleases.[773,774] Inorganic pyrophosphatases from *E. coli* and *S. cerevisiae* are well characterized both structurally and mechanistically. Both Mg^{2+} and Mn^{2+} are activating metal ions and the enzyme from *E. coli* is most active with just three metal ions in the active site.[775] These enzymes have been described in Section 5.1.8.2.4.

5.1.8.4.1 Bifunctional inositol monophosphatase/fructose 1,6-bisphosphatase

The bifunctional inositol monophosphatase (IMPase)/fructose 1,6-bisphosphatase (FBPase) from the thermophilic microorganism *Methanococcus jannaschii* MJ109 has been structurally characterized at relatively low resolution. The structure of this enzyme is very similar to that of the pig kidney fructose 1,6-bisphosphatase while the amino acid sequence is similar to that of human IMPase. These latter enzymes are inactive with the alternative substrates, whereas the bifunctional enzyme has similar activity with either inositol monophosphate or fructose 1,6-bisphosphate. The active site of this enzyme is much more open and contains more charged residues than the human IMPase or the porcine FBPase and this probably explains the variety of enzyme substrates. Three structures have been determined, two with inhibitory Ca^{2+} and Zn^{2+} and one with activating Mn^{2+} in the active site. The Ca^{2+}-containing crystals have two Ca^{2+} ions present, the other two forms contain three M^{2+} ions and, in the case of Mn^{2+}, a PO_4^{3-} and a *myo*-inositol. The active site of the Mn^{2+} form is shown in Figure 41. Mn_1 and Mn_2 are bound close to the positions occupied by Ca^{2+} in that form of the enzyme; Mn_1 is tetrahedrally bound to two oxygens from the phosphate ion and two aspartate residues. Mn_2 is six-coordinate with six oxygen donors, a phosphate oxygen, two aspartate oxygens, a glutamate oxygen, an amide oxygen from Ile-83, and a water molecule. Some of these bonds are apparently quite long. Mn_3 has only one well-defined ligand, a phosphate oxygen, longer and less well-defined bonds are made to a water molecule and an aspartate oxygen and a second water ligand is possible. The Zn^{2+} ions are bound close to the Mn^{2+} binding sites.

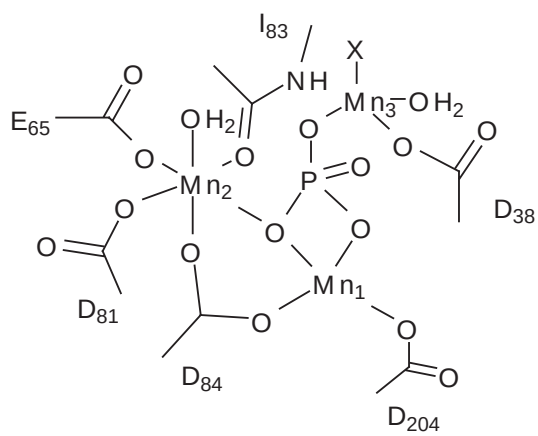


Figure 41 Schematic of the active site in the bifunctional inositol monophosphatase/fructose 1,6-bisphosphatase from *Methanococcus jannaschii* MJ109.

5.1.8.5 Enzymes with Tetranuclear Active Sites

5.1.8.5.1 The oxygen-evolving complex of photosystem II

The oxygen-evolving complex of the thylakoid membrane of plant cells and of photosynthetic bacteria catalyzes the reaction shown in Equation (10):

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{10}$$

This membrane-bound, multi-subunit complex contains more than 14 membrane spanning subunits, three hydrophilic peripheral subunits, organic cofactors that include chlorophylls, carotenoids, and plastoquinones, and the essential inorganic cofactors Fe^{2+}, a cluster of four Mn^{n+} ions, Ca^{2+}, Cl^-, and HCO_3^-. Not all the proteins are necessary for O_2 evolution; those that are essential include the membrane-bound proteins called CP_{47}, CP_{43}, D_1, D_2, cyt b_{559}, and the three extrinsic proteins 33 kDa, 24 kDa, and 17 kDa. The extrinsic proteins probably assist in the binding of the Mn^{n+}, Cl^-, and Ca^{2+} ions. The function of D_2 is not clear. D_1 and D_2 contain redox active tyrosine residues, Y_z and Y_D, respectively. Y_z is part of the electron transfer pathway of the water oxidation reaction; it reduces the PSII reaction centre P_{680}, a special pair of chlorophyll molecules at the heart of the photochemical system This electron pathway is from the water molecule, to the manganese cluster, to Y_z, and then to P_{680}. Y_D is apparently not part of this process and its function remains mysterious although it can donate an electron to P_{680}.[776] Spectroscopic evidence suggests that Y_z is 5–8 Å from the manganese cluster and 10–15 Å from CP_{47}.

Understanding the behavior and the structure of the OEC has proved to be something of a "holy grail" for biophysicists, biochemists, and bioinorganic chemists alike. Many reviews have been published. The structure of the OEC complex and the proteins involved,[777–782] the use of X-ray spectroscopies to study the OEC complex,[783,784] the role of the carotenoids,[785] the mechanism of oxygen evolution,[786–791] the requirement for HCO_3^-[792,793] and calcium,[794] the coordination of the iron atoms,[789] the redox active tyrosine residues,[795,796] the coupling of electron transfer and proton release,[797] the photochemistry of the process,[798] the nature of the manganese cluster,[783,787] the manganese ligands,[799–801] and the oxidation state of the Mn ions,[802] have all been separately reviewed and in many cases continue to be the subject of intense debate.

How the OEC functions became apparent from experiments in which dark-adapted PSII preparations were subjected to intense short flashes of light. O_2 evolution began on the third flash and then peaks of oxygen evolution were observed every fourth flash. An interpretation of these results is that the dark-adapted PSII preparations exist in a stable state called S_1. Each of the first three flashes removes one electron from the manganese cluster to produce new states called S_2, S_3, and S_4 which have increasing oxidizing ability. S_4 oxidizes water to O_2, gaining four electrons and forming the most reduced S_0 state. The fourth flash oxidizes S_0 to the dark-stable S_1 state.

In the absence of suitable crystals for an X-ray structural study, combinations of FTIR, RR, XAS, EPR, ENDOR, XANES, and ESEEM spectroscopies were used to characterize the manganese site in the OEC. Vibrational spectroscopy, particularly low-frequency FT infrared[803] and Raman,[804] has been used to study hydrogen bonding to the Y_z radical,[805–807] structural changes in the different S states,[808] and Mn–ligand vibrational bands.[804] Three major well-resolved peaks are observed in the EXAFS spectrum of the S_1 state of PSII. They are best fitted by about two O (or N) atoms per Mn at ~1.82 Å, by 2–4 oxygen or nitrogen atoms located 1.95–2.15 Å from the Mn centres, by ~1.25 Mn atoms at 2.72 Å, and 0.5 Mn or Ca^{2+} at about 3.30 Å.[809,810] Another study at room temperature has suggested Mn—Mn or Mn—Ca distances of ~3.1 Å.[811] Four Ca^{2+} ions are bound with high affinity to PSII in plants. EXAFS investigations of the Ca^{2+} ions have generated some controversy but unperturbed samples gave a Mn^{2+}—Ca^{2+} distance of 3.5 Å, which is consistent with the results from the Sr^{2+}-substituted enzyme and the Mn EXAFS.[812,813]

Whether the manganese atoms are oxidized in each of the S state advances is controversial. XANES experiments suggest that the Mn oxidation state increases on going from S_0 to S_1 and from S_1 to S_2.[814,815] An oxidation state decrease is observed on going from S_3 to S_0 (the S_4 state cannot be observed). Some groups observed no apparent change to the XANES spectrum in going from S_2 to S_3[816] and so proposed that radical formation of histidine, tyrosine, or the manganese μ-oxo bridge may occur. The actual oxidation state of Mn in the manganese cluster in the different S states is uncertain. The question is complicated by the uncertainty as to whether Mn is oxidized in the S_2 to S_3 transition. Various proposals have been made; one review concluded that the S_2 state is $3Mn^{III}Mn^{IV}$.[817]

EPR has played an important role in understanding of the OEC, and four of the five S states in the catalytic cycle can be characterized by EPR.[812,817–819] Three EPR signals can arise from the S_2 state of the OEC, a multiline signal at $g = 2$ ($S = 1/2$), a $g = 5.1$ state ($S = 5/2$), and a state with $g = 4$ to $g = 9$ ($S = 5/2$ ($S > 5/2$ is possible)). Stability of these states differs between plants and cyanobacteria.[820] The multiline $g = 2$ signal of the S_2 state consists of at least 18 lines, separated by ~80 G (8×10^{-3} T), and it arises from the ground state of the Mn_4 unit. A multiline EPR signal from the S_0 state has been observed which is wider than the S_2 signal with structure over more than 2500 G (0.25 T), and at least 20 peaks on each side of $g = 2$. The S_0 state has a ground, $S = 1/2$ state, with no thermally accessible excited state. The S_1 state of spinach OEC has been studied using parallel polarization EPR. The signal arises from an $S = 1$ excited state with $g = 4.9$ and a width of 600 G (0.06 T). In *Synechocystis* sp. PCC 6803 an 18-line signal is observed in the S_1 state centered on $g = 12$ with a splitting of 32 G (3.2% 10^{-3} T). EPR signals from the S_3 state are observed in a variety of PSII samples in which the OEC has been inhibited. These signals are thought to arise from interactions between the manganese cluster in an oxidation state equivalent to S_2 and a radical.[821]

Much of the impetus for the investigation of polynuclear manganese complexes has come from a desire to produce structural and/or functional models of the manganese cluster of the OEC. Many of the results of these studies have been described in Section 5.1.2 and in reviews.[590,591,822] Manganese complexes capable of oxidizing water have been prepared and investigated.[823–827]

A 3D image of PSII at 8 Å resolution was first obtained by electron cryomicroscopy of 2D crystals obtained from plants.[828] Three-dimensional crystals have been obtained from two species of thermophilic cyanobacteria, *Thermosynechococcus elongatus* (formerly *Synechococcus elongatus*)[829,830] and *Thermosynechococcus vulcans*.[831] A crystal structure of the complex from *Thermosynechococcus elongatus* at 3.8 Å resolution has been reported.[832] Rutherford has provided a commentary on, and critique of, this structure.[833] The crystallized complex contains the proteins CP_{47}, CP_{43}, D_1, D_2, cyt b_{559}, the extrinsic proteins cyt c_{550}, and the 33 kDa protein and some low-molecular-weight subunits. The locations of some of the cofactors and the manganese cluster were identified. The D_1/D_2 proteins each bind six chlorophylls and two phenophytins; CP_{47} binds 16 chlorophylls and CP_{43} 13 chlorophylls. The manganese cluster is clearly visible in the structure as a triangular blob of electron density with three Mn atoms at the corners of the triangle and the fourth Mn at the center of the triangle but out of the plane of the other three Mn atoms. The resolution of the structure is insufficient to enable the ligands to the cluster to be identified but they come fro the D_1 protein. There is no Ca^{2+} (or Cl^-) in the structure of this cyanobacterial protein and Ca^{2+} is required for O_2 evolution from plant enzymes.

ACKNOWLEDGEMENTS

The diagrams in Section 5.1.2 were produced using ORTEP-3 for Windows XXX[834] using cif files from the Cambridge Crystallographic Data Centre.[835]

5.1.9 REFERENCES

1. Herbstein, F. H.; Kapon, M.; Weissman, A. *J. Therm. Anal.* **1994**, *41*, 303–322.
2. Oku, M. *J. Elect. Spectrosc. Relat. Phenom.* **1995**, *74*, 135–148.
3. Firouzabadi, H.; Mottghinejad, E.; Seddighi, M. *Tetrahedron* **1989**, *46*, 6869–6878.
4. Holba, V.; Kosicka, R. *Coll. Czech. Chem. Commun.* **1997**, *62*, 849–854.
5. Barakat, S. A. *Anal. Chim. Acta* **1999**, *393*, 223–226.
6. Vincent, J. B.; Christmas, C.; Chang, H. R.; Li, Q.; Boyd, P. D. W.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1989**, *111*, 2086–2097.
7. Wang, S.; Huffman, J. C.; Folting, K.; Streib, W. E.; Lobkovsky, E. B.; Christou, G. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 1672–1684.
8. Saadeh, S. M.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991**, *30*, 8–15.
9. Corbella, M.; Costa, R.; Ribas, J.; Fries, P. H.; Latour, J. M.; Ohrstrom, L.; Solans, X.; Rodriguez, V. *Inorg. Chem.* **1996**, *35*, 1857–1865.
10. Jaeger, H.; Luetolf, J.; Meyer, M. W. *Angew. Chem., Int. Ed.* **1979**, *18*, 786–787.
11. Morris, J. A.; Mills, D. C. *Chem. Br.* **1978**, *14*, 326.
12. Dash, S.; Mishra, B. K. *Int. J. Chem. Kinet.* **1995**, *27*, 627–635.
13. Radtke, R.; Heesing, A. *Chem. Ber.* **1990**, *123*, 621–626.
14. Zhang, Z.; Wu, J.; Deng, R.; Xing, Y. *Huaxue Xuebao* **1988**, *46*, 364–366.
15. Simon, A.; Dronskowski, R.; Krebs, B.; Hettich, B. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 139–140.
16. Dronskowski, R.; Krebs, B.; Simon, A.; Miller, G.; Hettich, B. *Z. Anorg. Allg. Chem.* **1988**, *558*, 7–20.

17. Baran, E. J. *Z. Natur. A Phys. Sci.* **1987**, *42*, 307–309.
18. Amado, A. M.; Ribeiro-Claro, P. J. A. *Theochem* **1999**, *469*, 191–200.
19. Brisdon, A. K.; Holloway, J. H.; Hope, E. G. *J. Fluor. Chem.* **1998**, *89*, 35–37.
20. Levason, W.; Ogden, J. S.; Saad, A. K.; Young, N. A.; Brisdon, A. K.; Holliman, P. J.; Holloway, J. H.; Hope, E. G. *J. Fluor. Chem.* **1991**, *53*, 43–51.
21. Brisdon, A. K.; Holloway, J. H.; Hope, E. G.; Townson, P. J.; Levason, W.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1991**, 3127–3132.
22. Burger, H.; Weinrath, P.; Dressler, S.; Hansen, T.; Thiel, W. *J. Mol. Spectrosc.* **1997**, *183*, 139–150.
23. Varetti, E. L. *J. Raman Spectrosc.* **1991**, *22*, 307–309.
24. Bytheway, I.; Wong, M. W. *Chem. Phys. Lett.* **1998**, *282*, 219–226.
25. Rettrup, S.; Bo, S.; Ballhausen, C. J. *Acta Chem. Scand.* **1990**, *44*, 853–854.
26. Wistuba, T.; Limberg, C. *Chem. Eur. J.* **2001**, *7*, 4674–4685.
27. Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–422.
28. Rosseinsky, D. R.; Quillin, K. C. *NATO ASI Ser. Ser.C: Math. Phys. Sci.* **1991**, *343*, 401–406.
29. Hursthouse, M. B.; Quillin, K. C.; Rosseinsky, D. R. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 3071–3077.
30. Cannon, R. D.; Jayasooriya, U. A.; Anson, C. E.; White, R. P.; Tasset, F.; Ballou, R.; Rosseinsky, D. R. *J. Chem. Soc., Chem. Commun.* **1992**, 1445–1446.
31. Stride, J. A.; Jayasooriya, U. A.; Cannon, R. D.; Bourke, J. P.; Rosseinsky, D. R.; Ballou, R.; Cottrell, S. P. *Chem. Phys. Chem.* **2001**, *2*, 683–688.
32. Etheredge, K. M. S.; Gardberg, A. S.; Hwu, S.-J. *Inorg. Chem.* **1996**, *35*, 6358–6361.
33. Danopoulos, A. A.; Green, J. C.; Hursthouse, M. B. *J. Organomet. Chem.* **1999**, *591*, 36–44.
34. Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1994**, 1037–1049.
35. Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1995**, 205–216.
36. Kopelev, N. S.; Val'kovskii, M. D.; Popov, A. I.; Chumaevskii, N. A. *Zh. Neorg. Khim.* **1991**, *36*, 2210–2216.
37. Zhang, Z. *Wujiyan Gongye* **2001**, *33*, 31–32.
38. Berka, A.; Zavesky, Z.; Velasevic, K.; Nikolic, K. *Arhiv za Farmaciju* **1990**, *40*, 89–94.
39. Zahonyi-Budo, E.; Simandi, L. I. *Inorg. Chim. Acta* **1995**, *237*, 173–175.
40. Rush, J. D.; Bielski, B. H. J. *Inorg. Chem.* **1995**, *34*, 5832–5838.
41. Fiedler, D. A.; Albering, J. H.; Besenhard, J. O. *J. Solid State Electrochem.* **1998**, *2*, 413–419.
42. Hazenkamp, M. F.; Brunold, T. C.; Güdel, H.-U. *J. Luminesc.* **1997**, *72–74*, 675–676.
43. Brunold, T. C.; Güdel, H. U.; Riley, M. J. *J. Chem. Phys.* **1996**, *105*, 7931–7941.
44. Schenker, R. P.; Brunold, T. C.; Güdel, H. U. *Inorg. Chem.* **1998**, *37*, 918–927.
45. Brunold, T. C.; Güdel, H. U. *Chem. Phys. Lett.* **1996**, *257*, 123–129.
46. Brunold, T. C.; Güdel, H. U. *Chem. Phys. Lett.* **1996**, *249*, 77–80.
47. Brunold, T. C.; Güdel, H. U. *Inorg. Chem.* **1997**, *36*, 1946–1954.
48. Noda, L. K.; Ribeiro, M. C. C.; Goncalves, N. S. *J. Raman Spectrosc.* **1999**, *30*, 697–704.
49. Deeth, R. J. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3745–3749.
50. Atanasov, M. *Z. Phys. Chem. (Munich)* **1997**, *200*, 57–68.
51. Atanasov, M.; Brunold, T. C.; Güdel, H. U.; Daul, C. *Inorg. Chem.* **1998**, *37*, 4589–4602.
52. Choy, J. H.; Demazeau, G.; Dance, J. M. *J. Solid State Chem.* **1990**, *84*, 1–9.
53. Choy, J.-H.; Hong, S.-T.; Park, N.-G.; Byeon, S.-H.; Demazeau, G. *Bull. Korean Chem. Soc.* **1995**, *16*, 105–110.
54. Demazeau, G.; Oh-Kim, E. O.; Choy, J. H.; Hagenmuller, P. *J. Solid State Chem.* **1992**, *101*, 221–228.
55. Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1995**, 937–950.
56. Mukhopadhyay, R.; Chatterjee, A. B.; Bhattacharyya, R. *Polyhedron* **1992**, *11*, 1353–1358.
57. Bendix, J.; Meyer, K.; Weyhermueller, T.; Bill, E.; Metzler-Nolte, N.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 1767–1775.
58. Weller, M. T.; Skinner, S. J. *Acta Crystallogr. C: Cryst. Struct. Commun.* **1999**, *C55*, 154–156.
59. Uchida, M.; Tanaka, H.; Bartashevich, M. I.; Goto, T. *J. Phys. Soc. Jpn.* **2001**, *70*, 1790–1793.
60. Firouzabadi, H.; Etemadi, S.; Karimi, B.; Jarrahpour, A. A. *Phosphorus, Sulfur, Silicon Related Elements* **1999**, *152*, 141–151.
61. Srivastava, R. G.; Venkataramani, P. S. *Synth. Commun.* **1992**, *22*, 35–45.
62. Zahonyi-Budo, E.; Simandi, L. I. *Stud. Surf. Sci. Catal.* **1994**, *82*, 623–628.
63. Reinen, D.; Rauw, W.; Kesper, U.; Atanasov, M.; Güdel, H. U.; Hazenkamp, M.; Oetliker, U. *J. Alloys Comp.* **1997**, *246*, 193–208.
64. Güdel, H. U.; Brunold, T.; Hazenkamp, M.; Herren, M.; Oetliker, U.; Schenker, R. *Proc. Electrochem. Soc.* **1998**, *97–29*, 225–234.
65. Moncorge, R.; Manaa, H. *Ann. Chimie (Paris)* **1995**, *20*, 241–248.
66. Herren, M.; Riedener, T.; Güdel, H. U.; Albrecht, C.; Kaschuba, U.; Reinen, D. *J. Luminesc.* **1992**, *53*, 452–456.
67. Oetliker, U.; Herren, M.; Güdel, HansU.; Kesper, U.; Albrecht, C.; Reinen, D. *J. Chem. Phys.* **1994**, *100*, 8656–8665.
68. Atanasov, M.; Adamsky, H.; Reinen, D. *Chem. Phys.* **1996**, *202*, 155–165.
69. Verdun, H. R. *OSA Proc. Adv. Solid-State Lasers, Proc. Top. Meet.* **1993**, 315–319.
70. Manaa, H.; Guyot, Y.; Deghoul, F.; Moncorge, R.; Merkle, L. D. *Chem. Phys. Lett.* **1995**, *238*, 333–337.
71. Merkle, L. D.; Chai, B. H. T.; Guyot, Y. *Mater. Res. Soc. Symp. Proc.* **1994**, *329*, 239–244.
72. Merkle, L. D.; Guyot, Y.; Chai, B. H. T. *J. Appl. Phys.* **1995**, *77*, 474–480.
73. Misra, S. K.; Misiak, L. E.; Capobianco, J. A. *J. Phys. Condens. Matter* **1994**, *6*, 3955–3963.
74. Buijsse, B.; Schmidt, J.; Chan, I. Y.; Singel, D. J. *Phys. Rev. B Condens. Matter* **1995**, *51*, 6215–6220.
75. Capobianco, J. A.; Cormier, G.; Morrison, C. A.; Moncorge, R. *Optical Mat. (Amsterdam, Netherlands)* **1992**, *1*, 209–216.
76. Capobianco, J. A.; Cormier, G.; Bettinelli, M.; Moncorge, R.; Manaa, H. *J. Luminesc.* **1992**, *54*, 1–11.
77. Capobianco, J. A.; Cormier, G.; Moncorge, R.; Manaa, H.; Bettinelli, M. *Appl. Phys. Lett.* **1992**, *60*, 163–165.
78. Scott, M. A.; Han, T. P. J.; Gallagher, H. G.; Henderson, B. *J. Luminescence* **1997**, *72–74*, 260–262.
79. Reinen, D.; Lachwa, H.; Allmann, R. *Z. Anorg. Allg. Chem.* **1986**, *542*, 71–88.
80. Kueck, S.; Schepler, K. L.; Chai, B. H. T. *J. Optical Soc. Am. B Optical Phys.* **1997**, *14*, 957–963.

81. Albrecht, C.; Cohen, S.; Mayer, I.; Reinen, D. *J. Solid State Chem.* **1993**, *107*, 218–228.
82. Scott, M. A.; Henderson, B.; Gallagher, H. G.; Han, T. P. J. *J. Phys. Condens. Matter* **1997**, *9*, 9893–9908.
83. Dardenne, K.; Vivien, D.; Ribot, F.; Chottard, G.; Huguenin, D. *Eur. J. Solid State Inorg. Chem.* **1998**, *35*, 419–431.
84. Dardenne, K.; Vivien, D.; Huguenin, D. *J. Solid State Chem.* **1999**, *146*, 464–472.
85. Lachwa, H.; Reinen, D. *Inorg. Chem.* **1989**, *28*, 1044–1053.
86. Misra, S.; Misiak, L.; Capobianco, J. A.; Bettinelli, M. *J. Magn. Reson. Ser. A* **1994**, *109*, 216–220.
87. Riedener, T.; Shen, Y.; Smith, R. J.; Bray, K. L. *Chem. Phys. Lett.* **2000**, *321*, 445–451.
88. Merkle, L. D.; Pinto, A.; Verdun, H. R.; McIntosh, B. *Appl. Phys. Lett.* **1992**, *61*, 2386–2388.
89. Whitmore, M. H.; Verdun, H. R.; Singel, D. J. *Phys. Rev. B Condens. Matter Mater. Phys.* **1993**, *47*, 11479–11482.
90. Whitmore, M. H.; Farrar, C. T.; Singel, D. J.; Buysse, B.; Coremans, J.; Schmidt, J. *OSA Proc. Adv. Solid-State Lasers, Proc. Top. Meet.* **1994**, 219–221.
91. Xu, J.; Deng, P.; Gan, F.; Sun, P.; Xu, Z. *Cailiao Yanjiu Xuebao* **1996**, *10*, 517–520.
92. Xu, J.; Deng, P.; Chen, W.; Gan, F. *Proc. SPIE* **1996**, *2778*, 648–649.
93. Hazenkamp, M. F.; Güdel, H. U.; Kueck, S.; Huber, G.; Rauw, W.; Reinen, D. *Chem. Phys. Lett.* **1997**, *265*, 264–270.
94. Wang, Y.-P.; Lei, Y.-H.; Wang, R.-M. *Indian J. Chem. Sect. B Org. Chem.* **1998**, *37B*, 1034–1036.
95. Noginov, M. A.; Noginova, N.; Loutts, G. B.; Babalola, K.; Rakhimov, R. R. *Mater. Res. Soc. Symp. Proc.* **2001**, *602*, 107–112.
96. Reinen, D.; Brunold, T. C.; Güdel, H. U.; Yordanov, N. D. *Z. Anorg. Allg. Chem.* **1998**, *624*, 438–442.
97. Noginov, M. A.; Loutts, G. B.; Noginova, N.; Hurling, S.; Kuck, S. *Phys. Rev. B Condens. Matter Mater. Phys.* **2000**, *61*, 1884–1891.
98. Senuliene, D.; Babonas, G.; Sileika, A.; Leonov, E. I.; Orlov, V. M. *Lietuvos Fizikos Rinkinys* **1987**, *27*, 71–78.
99. Capelletti, R.; Beneventi, P.; Kovacs, L.; Ruffini, A. *Ber. Bunsen-Ges.* **1997**, *101*, 1282–1285.
100. Xu, L.; Liu, J.; Shu, B.; Xiao, B. *Wuji Cailiao Xuebao* **1992**, *7*, 137–144.
101. Beneventi, P.; Briat, B.; Capelletti, R.; Gospodinov, M.; Kovacs, L.; Mazzocchi, E.; Ruffini, A. *Radiat. Effects Defects Solids* **1999**, *150*, 635–639.
102. Hoemmerich, U.; Eilers, H.; Yen, W. M.; Verdun, H. R. *Chem. Phys. Lett.* **1993**, *213*, 163–167.
103. Shen, Y.; Riedener, T.; Bray, K. L. *Phys. Rev. B Condens. Matter Mater. Phys.* **2000**, *61*, 9277–9286.
104. Barba, M. F.; Callejas, P.; Ajo, D.; Pozza, G.; Bettinelli, M. *Ceramic Eng. Sci. Proc.* **1997**, *18*, 22–27.
105. Choy, J. H.; Demazeau, G.; Hong, S. T. *Jpn. J. Appl. Phys. 1* **1992**, *31*, 3649–3654.
106. Atanasov, M.; Adamsky, H.; Eifert, K. *J. Solid State Chem.* **1997**, *128*, 1–16.
107. Wexler, D.; Zink, J. I. *Inorg. Chem.* **1995**, *34*, 1500–1506.
108. Deghoul, F.; Chermette, H.; Rogemond, F.; Moncorge, R.; Stuckl, C.; Daul, C. *Phys. Rev. B Condens. Matter Mater. Phys.* **1999**, *60*, 2404–2409.
109. Salagram, M.; Madhukar, K.; Jayatyagaraju, V. *Spectrochim. Acta A* **1995**, *51A*, 65–69.
110. Fokkens, R. H.; Gregor, I. K.; Nibbering, N. M. M. *Org. Mass Spectrosc.* **1992**, *27*, 1013–1018.
111. Fokkens, R. H.; Gregor, I. K.; Nibbering, N. M. M. *Rapid Commun. Mass Spect.* **1991**, *5*, 368–370.
112. Cheng, Y. X.; Hu, M. L.; Yuan, J. X.; Wang, Y. C. *Chinese Chem. Lett.* **2000**, *11*, 645–648.
113. MacDonnell, F. M.; Fackler, N. L. P.; Stern, C.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1994**, *116*, 7431–7432.
114. Collins, T. J.; Gordon-Wylie, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 4511–4513.
115. Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M. *Acc. Chem. Res.* **1997**, *30*, 364–372.
116. Zhang, W.; Jacobsen, E. N. *J. Org. Chem.* **1991**, *56*, 2296–2298.
117. Das, D.; Cheng, C. P. *J. Chem. Soc. Dalton Trans.* **2000**, *7*, 1081–1086.
118. Senanayake, C. H.; Jacobsen, E. N. *Proc. Chem. Pharm. Indust.* **1999**, 347–368.
119. Jacobsen, E. N.; Wu, M. H. *Comprehen. Asymm. Catal. (IIII)* **1999**, *2*, 649–677.
120. Bansal, V.; Sharma, P. K.; Banerji, K. K. *Indian J. Chem. Sect. A Inorg. Bio-inorg. Phys. Theor. Anal. Chem.* **2000**, *39A*, 654–659.
121. Kumbhat, V.; Sharma, P. K.; Banerji, K. K. *J. Chem. Res. Synop.* **2001**, 179–181562-585.
122. Bansal, V.; Sharma, P. K.; Banerji, K. K. *J. Chem. Res. S* **1999**, 480–481.
123. Chellamani, A.; Alhaji, N. I.; Rajagopal, S.; Sevvel, R.; Srinivasan, C. *Tetrahedron* **1995**, *51*, 12677–12698.
124. Chellamani, A.; Alhaji, N. M. I.; Rajagopal, S. *J. Chem. Soc., Perkin Trans. 2* **1997**, 299–302.
125. Chellamani, A.; Kulanthaipandi, P.; Rajagopal, S. *J. Org. Chem.* **1999**, *64*, 2232–2239.
126. Chellamani, A.; Alhaji, N. M. I. *Indian J. Chem. Sect. A Inorg. Bio-Inorg. Phys. Theor. Anal. Chem.* **1999**, *38A*, 888–894.
127. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801–2803.
128. Jacobsen, E. N.; Zhang, W.; Guler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703–6704.
129. Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063–7064.
130. Pospisil, P. J.; Carsten, D. H.; Jacobsen, E. N. *Chem. Eur. J.* **1996**, *2*, 974–980.
131. Feichtinger, D.; Plattner, D. A. *Angew. Chem., Int. Ed.* **1997**, *36*, 1718–1719.
132. Feichtinger, D.; Plattner, D. A. *J. Chem. Soc., Perkin Trans. II* **2000**, *5*, 1023–1028.
133. Feichtinger, D.; Plattner, D. A. *Chem. Eur. J.* **2001**, *7*, 591–599.
134. Jepsen, A. S.; Roberson, M.; Hazell, R. G.; Jorgensen, K. A. *Chem. Commun.* **1998**, 1599–1600.
135. Chatterjee, D.; Mukherjee, S.; Roy, B. C. *J. Mol. Catal. A: Chem.* **2001**, *169*, 41–45.
136. Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 7318–7319.
137. Buchler, J. W.; Dreher, C.; Lay, K. L. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1982**, *37B*, 1155–1162.
138. Buchler, J. W.; Dreher, C.; Lay, K.-L.; Lee, Y. J. A.; Scheidt, W. R. *Inorg. Chem.* **1983**, *22*, 888–891.
139. Du Bois, J.; Hong, J.; Carreira, E. M.; Day, M. W. *J. Am. Chem. Soc.* **1996**, *118*, 915–916.
140. Svenstrup, N.; Bogevig, A.; Hazell, R. G.; Jorgensen, K. A. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1559–1566.
141. Iwamoto, H.; Tsuchimoto, M.; Ohba, S. *Acta Crystallogr. C: Cryst. Struct. Commun.* **2000**, *56*, E187.
142. Du Bois, J.; Tomooka, C. S.; Hong, J.; Carreira, E. M.; Day, M. W. *Angew. Chem., Int. Ed.* **1997**, *36*, 1645–1647.
143. Ho, C.-M.; Lau, T.-C.; Kwong, H.-L.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **1999**, 2411–2413.
144. Boulineau, F. P.; Wei, A. *Carbohydrate Res.* **2001**, *334*, 271–279.
145. Chang, C. J.; Low, D. W.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 270–271.

146. Eikey, R. A.; Abu-Omar, M. *Abstr. Pap. Am. Chem. Soc.* **2001**, *221*, INOR-212.
147. Formentin, P.; Folgado, J. V.; Fornes, V.; Garcia, H.; Marquez, F.; Sabater, M. J. *J. Phys. Chem. B* **2000**, *104*, 8361–8365.
148. Grapperhaus, C. A.; Bill, E.; Weyhermuller, T.; Neese, F.; Wieghardt, K. *Inorg. Chem.* **2001**, *40*, 4191–4198.
149. Chang, C. J.; Connick, W. B.; Low, D. W.; Day, M. W.; Gray, H. B. *Inorg. Chem.* **1998**, *37*, 3107–3110.
150. Tsuchimoto, M.; Iwamoto, H.; Kojima, M.; Ohba, S. *Chem. Lett.* **2000**, 1156–1157.
151. Bendix, J.; Weyhermuller, T.; Bill, E.; Wieghardt, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 2766–2768.
152. Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem.* **1988**, *27*, 967.
153. Hagen, K. S.; Westmoreland, T. D.; Scott, M. J.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 1907.
154. Dave, B. C.; Czernuszewicz, R. S.; Bond, M. R.; Carrano, C. J. *Inorg. Chem.* **1993**, *32*, 3593.
155. Low, D. W.; Eichhorn, D. M.; Draganescu, A.; Armstrong, W. H. *Inorg. Chem.* **1991**, *30*, 877.
156. Mukhopadhyay, S.; Staples, R. J.; Armstrong, W. H. *Chem. Commun.* **2002**, 864.
157. Wemple, M. W.; Adams, D. M.; Hagen, K. S.; Folting, K.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1995**, 1591.
158. Hendrickson, D. N.; Christou, G.; Schmitt, E. A.; Libby, E.; Bashkin, J. S.; Wang, S.; Tsai, H. L.; Vincent, J. B.; Boyd, P. D. W. *et al. J. Am. Chem. Soc.* **1992**, *114*, 2455.
159. Lis, T. *Acta Crystallogr. B* **1980**, *36*, 2042.
160. Pal, S.; Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1992**, *114*, 6398.
161. Dubé, C. E.; Wright, D. W.; Bonitatebus, P. J. Jr.; Pal, S.; Armstrong, W. H. *J. Am. Chem. Soc.* **1998**, *120*, 3704.
162. Bhaduri, S.; Pink, M.; Christou, G. *Chem. Commun.* **2002**, 2352.
163. Horner, O.; Anxolabéhére-Mallart, E.; Charlot, M. F.; Tchertanov, L.; Guilhem, J.; Mattioli, T. A.; Boussac, A.; Girerd, J. J. *Inorg. Chem.* **1999**, *38*, 1222.
164. Nyholm, R. S.; Turco, A. *Chem. Ind.* **1960**, 74.
165. Plaksin, P. M.; Stoufer, R. C.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc.* **1972**, *94*, 2121.
166. Limburg, J.; Vrettos, J. S.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H.; Brudvig, G. W. *Science (Washington, DC)* **1999**, *283*, 1524.
167. Collomb, M. N.; Deronzier, A.; Richardot, A.; Pecaut, J. *New J. Chem.* **1999**, *23*, 351.
168. Baffert, C.; Collomb, M.-N.; Deronzier, A.; Pecaut, J.; Limburg, J.; Crabtree, R. H.; Brudvig, G. W. *Inorg. Chem.* **2002**, *41*, 1404.
169. Pal, S.; Gohdes, J. W.; Wilisch, W. C. A.; Armstrong, W. H. *Inorg. Chem.* **1992**, *31*, 713.
170. Schaefer, K.-O. Bittl R.; Zweygart, W.; Lendzian, F.; Haselhorst, G.; Weyhermueller, T.; Wieghardt, K.; Lubitz, W. *J. Am. Chem. Soc.* **1998**, *120*, 13104.
171. Bossek, U.; Saher, M.; Weyhermueller, T.; Wieghardt, K. *J. Chem. Soc., Chem. Commun.* **1992**, 1780.
172. Wieghardt, K.; Beauvillain, P.; Bonvoisin, J.; Bossek, U.; Girerd, J.-J.; Heinze, J.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed.* **1986**, *25*, 1030.
173. Bashkin, J. S.; Schake, A. R.; Vincent, J. B.; Chang, H. R.; Li, Q.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1988**, 700.
174. Larson, E.; Haddy, A.; Kirk, M. L.; Sands, R. H.; Hatfield, W. E.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1992**, *114*, 6263.
175. Rajendiran, T. M.; Kirk, M. L.; Setyawati, I. A.; Caudle, M. T.; Kampf, J. W.; Pecoraro, V. L. *Chem. Commun. (Cambridge, UK)* **2003**, 824.
176. Goodin, D. B.; Yachandra, V. K.; Britt, R. D.; Sauer, K.; Klein, M. P. *Biochim. Biophys. Acta* **1984**, *767*, 209.
177. Yachandra, V. K.; Guiles, R. D.; McDermott, A.; Britt, R. D.; Dexheimer, S. L.; Sauer, K.; Klein, M. P. *Biochim. Biophys. Acta* **1986**, *850*, 324.
178. Yachandra, V. K.; Sauer, K.; Klein, M. P. *Chem. Rev.* **1996**, *96*, 2927.
179. Manchanda, R.; Brudvig, G. W.; Crabtree, R. H. *Coord. Chem. Rev.* **1995**, *144*, 1.
180. Ananyev, G. M.; Zaltsman, L.; Vasko, C.; Dismukes, G. C. *Biochim. Biophys. Acta* **2001**, *1503*, 52.
181. Peloquin, J. M.; Campbell, K. A.; Randall, D. W.; Evanchik, M. A.; Pecoraro, V. L.; Armstrong, W. H.; Britt, R. D. *J. Am. Chem. Soc.* **2000**, *122*, 10926.
182. Debus, R. J.; Campbell, K. A.; Gregor, W.; Li, Z.-L.; Burnap, R. L.; Britt, R. D. *Biochemistry* **2001**, *40*, 3690.
183. Diner, B. A. *Biochim. Biophys. Acta* **2001**, *1503*, 147.
184. Debus, R. J. *Biochim. Biophys. Acta* **2001**, *1503*, 164.
185. Yachandra, V. K.; DeRose, V. J.; Latimer, M. J.; Mukerji, I.; Sauer, K.; Klein, M. P. *Science* **1993**, *260*, 675.
186. Zouni, A.; Witt, H. T.; Kern, J.; Fromme, P.; Krauss, N.; Saenger, W.; Orth, P. *Nature* **2001**, *409*, 739.
187. Kamiya, N.; Shen, J.-R. *Proc. Natl. Acad. Sci. USA* **2003**, *100*, 98.
188. Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1990**, *112*, 4985.
189. Suzuki, M.; Senda, H.; Suenaga, M.; Sugisawa, T.; Uehara, A. *Chem. Lett.* **1990**, 923.
190. Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1991**, *113*, 5055.
191. Suzuki, M.; Hayashi, Y.; Munezawa, K.; Suenaga, M.; Senda, H.; Uehara, A. *Chem. Lett.* **1991**, 1929.
192. Dubé, C. E.; Sessoli, R.; Hendrich, M. P.; Gatteschi, D.; Armstrong, W. H. *J. Am. Chem. Soc.* **1999**, *121*, 3537.
193. Canada-Vilalta, C.; Huffman, J. C.; Streib, W. E.; Davidson, E. R.; Christou, G. *Polyhedron* **2001**, *20*, 1375.
194. Tasiopoulos, A. J.; Abboud, K. A.; Christou, G. *Chem. Commun. (Cambridge, UK)* **2003**, 580.
195. Brechin, E. K.; Soler, M.; Davidson, J.; Hendrickson, D. N.; Parsons, S.; Christou, G. *Chem. Commun. (Cambridge, UK)* **2002**, 2252.
196. Hagen, K. S.; Armstrong, W. H.; Olmstead, M. M. *J. Am. Chem. Soc.* **1989**, *111*, 774.
197. Geisselmann, A.; Klufers, P.; Pilawa, B. *Angew. Chem., Int. Ed.* **1998**, *37*, 1119.
198. Wemple, M. W.; Adams, D. M.; Folting, K.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1995**, *117*, 7275.
199. Wang, S.; Wemple, M. S.; Yoo, J.; Folting, K.; Huffman, J. C.; Hagen, K. S.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **2000**, *39*, 1501.
200. Aromi, G.; Wemple, M. W.; Aubin, S. J.; Folting, K.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1998**, *120*, 5850.
201. Aromi, G.; Bhaduri, S.; Artus, P.; Folting, K.; Christou, G. *Inorg. Chem.* **2002**, *41*, 805.
202. Aubin, S. M. J.; Dilley, N. R.; Wemple, M. W.; Maple, M. B.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1998**, *120*, 839.

203. Aromi, G.; Bhaduri, S.; Artus, P.; Folting, K.; Christou, G. *Inorg. Chem.* **2002**, *41*, 805.
204. Aliaga, N.; Folting, K.; Hendrickson, D. N.; Christou, G. *Polyhedron* **2001**, *20*, 1273.
205. Ruettinger, W. F.; Campana, C.; Dismukes, G. C. *J. Am. Chem. Soc.* **1997**, *119*, 6670.
206. Ruettinger, W. F.; Ho, D. M.; Dismukes, G. C. *Inorg. Chem.* **1999**, *38*, 1036.
207. Ruettinger, W. F.; Dismukes, G. C. *Inorg. Chem.* **2000**, *39*, 1021.
208. Boyd, P. D. W.; Li, Q.; Vincent, J. B.; Folting, K.; Chang, H. R.; Streib, W. E.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 8537.
209. Aubin, S. M. J.; Spagna, S.; Eppley, H. J.; Sager, R. E.; Folting, K.; Christou, G.; Hendrickson, D. N. *Mol. Cryst. Liq. Cryst. Sci. Technol. A* **1997**, *305*, 181.
210. Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature (London)* **1993**, *365*, 141.
211. Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S. Y.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804.
212. Cornia, A.; Affronte, M.; Jansen, A. G. M.; Gatteschi, D.; Caneschi, A.; Sessoli, R. *Chem. Phys. Lett.* **2000**, *322*, 477.
213. Christou, G.; Gatteschi, D.; Hendrickson, D. N.; Sessoli, R. *MRS Bull.* **2000**, *25*, 66.
214. Sessoli, R.; Caneschi, A.; Gatteschi, D.; Sangregorio, C.; Cornia, A.; Wernsdorfer, W. In *Clusters and Nanostructure Interfaces*, Proceedings the International Symposium, Richmond, VA, Oct. 25–28, 1999; 2000, pp 149.
215. Sun, Z.; Ruiz, D.; Hendrickson, D. N.; Dilley, N. R.; Maple, M. B.; Soler, M.; Folting, K.; Christou, G.; Ribas, J. *Chem. Commun.* **1999**, 1973.
216. Soler, M.; Artus, P.; Folting, K.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **2001**, *40*, 4902.
217. Aubin, S. M. J.; Sun, Z. M.; Pardi, L.; Krzystek, J.; Folting, K.; Brunel, L. C.; Rheingold, A. L.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1999**, *38*, 5329.
218. Aubin, S. M. J.; Spagna, S.; Eppley, H. J.; Sager, R. E.; Christou, G.; Hendrickson, D. N. *Chem. Commun.* **1998**, 803.
219. Soler, M.; Chandra, S. K.; Davidson, E. R.; Christou, G.; Ruiz, D.; Hendrickson, D. N. *Chem. Commun.* **2000**, 2417.
220. Soler, M.; Wernsdorfer, W.; Abboud, K. A.; Huffman, J. C.; Davidson, E. R.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **2003**, *125*, 3576.
221. Schake, A. R.; Tsai, H. L.; De Vries, N.; Webb, R. J.; Folting, K.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1992**, 181.
222. Artus, P.; Boskovic, C.; Yoo, J.; Streib, W. E.; Brunel, L.-C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **2001**, *40*, 4199.
223. Boskovic, C.; Pink, M.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **2001**, *123*, 9914.
224. Price, D. J.; Batten, S. R.; Moubaraki, B.; Murray, K. S. *Chem. Commun.* **2002**, 762.
225. Brockman, J. T.; Huffman, J. C.; Christou, G. *Angew. Chem., Int. Ed.* **2002**, *41*, 2506.
226. Soler, M.; Rumberger, E.; Folting, K.; Hendrickson, D. N.; Christou, G. *Polyhedron* **2001**, *20*, 1365.
227. Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328.
228. Bashkin, J. S.; Chang, H. R.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1987**, *109*, 6502.
229. Li, Q.; Vincent, J. B.; Libby, E.; Chang, H. R.; Huffman, J. C.; Boyd, P. D. W.; Christou, G.; Hendrickson, D. N. *Angew. Chem.* **1988**, *100*, 1799.
230. Wemple, M. W.; Tsai, H. L.; Folting, K.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1993**, *32*, 2025.
231. Wernmsdorfer, W.; Aliaga-Alcalde, N.; Hendrickson, D. N.; Christou, G. *Nature (London)* **2002**, *416*, 406.
232. Wang, S.; Tsai, H. L.; Streib, W. E.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1992**, 1427.
233. Perlepes, S. P.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1657.
234. Collins, M. A.; Hodgson, D. J.; Michelsen, K.; Towle, D. K. *J. Chem. Soc., Chem. Commun.* **1987**, 1659.
235. Brewer, K. J.; Calvin, M.; Lumpkin, R. S.; Otvos, J. W.; Spreer, L. O. *Inorg. Chem.* **1989**, *28*, 4446.
236. Oki, A. R.; Glerup, J.; Hodgson, D. J. *Inorg. Chem.* **1990**, *29*, 2435.
237. Suzuki, M.; Senda, H.; Kobayashi, Y.; Oshio, H.; Uehara, A. *Chem. Lett.* **1988**, 1763.
238. Stebler, M.; Ludi, A.; Bürgi, H.-B. *Inorg. Chem.* **1986**, *25*, 4743.
239. Towle, D. K.; Botsford, C. A.; Hodgson, D. J. *Inorg. Chim. Acta* **1988**, *141*, 167.
240. Glerup, J.; Goodson, P. A.; Hazell, A.; Hazell, R.; Hodgson, D. J.; McKenzie, C. J.; Michelsen, K.; Rychlewska, U.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 4105.
241. Schindler, S.; Walter, O.; Pedersen, J. Z.; Toftlund, H. *Inorg. Chim. Acta* **2000**, *303*, 215.
242. Goodson, P. A.; Hodgson, D. J.; Glerup, J.; Michelsen, K.; Weihe, H. *Inorg. Chem. Acta* **1992**, *197*, 141.
243. Frapart, Y. M.; Boussac, A.; Albach, R.; Anxolabéhére-Mallart, E.; Delroisse, M.; Verlhac, J. B.; Blondin, G.; Girerd, J.-J.; Guilhem, J.; Cesario, M.; Lexa, R. A. W. D. *J. Am. Chem. Soc.* **1996**, *118*, 2669.
244. Dave, B. C.; Czernuszewicz, R. S. *Inorg. Chim. Acta* **1994**, *227*, 33.
245. Wieghardt, K.; Bossek, U.; Zsolnai, L.; Huttner, G.; Blondin, G.; Girerd, J. J.; Babonneau, F. *J. Chem. Soc., Chem. Commun.* **1987**, 651.
246. Wieghardt, K.; Bossek, U.; Nuber, B.; Weiss, J.; Bonvoisin, J.; Corbella, M.; Vitols, S. E.; Girerd, J. J. *J. Am. Chem. Soc.* **1988**, *110*, 7398.
247. Osawa, M.; Fujisawa, K.; Kitajima, N.; Moro-oka, Y. *Chem. Lett.* **1997**, 919.
248. Lal, T. K.; Mukherjee, R. *Inorg. Chem.* **1998**, *37*, 2373.
249. Matzapetakis, M.; Karligiano, N.; Bino, A.; Dakanali, M.; Raptopoulou, C. P.; Tangoulis, V.; Terzis, A.; Giapintzakis, J.; Salifoglou, A. *Inorg. Chem.* **2000**, *39*, 4044.
250. Saadeh, S. M.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1991**, *30*, 8.
251. Mikuriya, M.; Kida, S.; Murase, I. *Chem. Lett.* **1988**, 35.
252. Nishida, Y.; Oshino, N.; Tokii, T. *Z. Naturforsch. B* **1988**, *43*, 472.
253. Mikuriya, M.; Yamato, Y.; Tokii, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2624.
254. Palopoli, C.; Chansou, B.; Tuchagues, J. P.; Signorella, S. *Inorg. Chem.* **2000**, *39*, 1458.
255. Chiswell, B.; McKenzie, E. D.; Lindoy, L. F. Manganese. In *Comprehensive Coordination Chemistry*; Wilkinson, G., GIllard, R. D., McCleverty, J. A. Eds.; Pergamon, Oxford, **1987**.
256. Zhang, C. G.; Janiak, C. *Acta Crystallogr. C* **2001**, *57*, 719.
257. Oberhausen, K. J.; O'Brien, R. J.; Richardson, J. F.; Buchanan, R. M.; Costa, R.; Latour, J. M.; Tsai, H. L.; Hendrickson, D. N. *Inorg. Chem.* **1993**, *32*, 4561.

258. Arulsamy, N.; Glerup, J.; Hazell, A.; Hodgson, D. J.; McKenzie, C. J.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 3023.
259. Triller, M. U.; Hsieh, W. Y.; Pecoraro, V. L.; Rompel, A.; Krebs, B. *Inorg. Chem.* **2002**, *41*, 5544.
260. Wieghardt, K.; Bossek, U.; Ventur, D.; Weiss, J. *J. Chem. Soc., Chem. Commun.* **1985**, 347.
261. Sheats, J. E.; Czernuszewicz, R. S.; Dismukes, G. C.; Rheingold, A. L.; Petrouleas, V.; Armstrong, W. H.; Beer, R. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 1435.
262. Bossek, U.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chim. Acta* **1989**, *165*, 123.
263. Ménage, S.; Girerd, J. J.; Gleizes, A. *J. Chem. Soc., Chem. Commun.* **1988**, 431.
264. Nishida, Y.; Oshino, N.; Tokii, T. *Z. Naturforsch. B* **1988**, *43*, 637.
265. Bossek, U.; Hummel, H.; Weyhermüller, T.; Wieghardt, K.; Russell, S.; Vanderwolf, L.; Kolb, U. *Angew. Chem., Int. Ed.* **1996**, *35*, 1552.
266. Blackman, A. G.; Huffman, J. C.; Lobkovsky, E. B.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1991**, 989.
267. Vincent, J. B.; Tsai, H. L.; Blackman, A. G.; Wang, S. Y.; Boyd, P. D. W.; Folting, K.; Huffman, J. C.; Lobkovsky, E. B.; Henderickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1993**, *115*, 12353.
268. Vincent, J. B.; Folting, K.; Huffman, J. C.; Christou, G. *Biochem. Soc. Trans.* **1988**, *16*, 822.
269. Hotzelmann, R.; Wieghardt, K.; Ensling, J.; Romstedt, H.; Gütlich, P.; Bill, E.; Flörke, U.; Haupt, H.-J. *J. Am. Chem. Soc.* **1992**, *114*, 9470.
270. Wu, F. J.; Kurtz, D. M., Jr.; Hagen, K. S.; Nyman, P. D.; Debrunner, P. G.; Vankai, V. A. *Inorg. Chem.* **1990**, *29*, 5174.
271. Toftlund, H.; Markiewicz, A.; Murray, K. S. *Acta Chem. Scand.* **1990**, *44*, 443.
272. Mandal, S. K.; Armstrong, W. H. *Inorg. Chim. Acta* **1995**, *229*, 261.
273. Mok, H. J.; Davis, J. A.; Pal, S.; Mandal, S. K.; Armstrong, W. H. *Inorg. Chim. Acta* **1997**, *263*, 385.
274. Gultneh, Y.; Ahvazi, B.; Khan, A. R.; Butcher, R. J.; Tuchagues, J. P. *Inorg. Chem.* **1995**, *34*, 3633.
275. Tanase, T.; Lippard, S. J. *Inorg Chem* **1995**, *34*, 4682.
276. Reddy, K. R.; Rajesekharan, M. V.; Sukumar, S. *Polyhedron* **1996**, *15*, 4161.
277. Corbella, M.; Costa, R.; Ribas, J.; Fries, P. H.; Latour, J. M.; Ohrstrom, L.; Solans, X.; Rodriguez, V. *Inorg. Chem.* **1996**, *35*, 1857.
278. Dave, B. C.; Czernuszewicz, R. S. *Inorg. Chim. Acta* **1998**, *281*, 25.
279. Hage, R.; Gunnewegh, E. A.; Niel, J.; Tjan, F. S. B.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chim. Acta* **1998**, *268*, 43.
280. Ruiz, R.; Sangregorio, C.; Caneschi, A.; Rossi, P.; Gaspar, A. B.; Real, J. A.; Munoz, M. C. *Inorg. Chem. Commun.* **2000**, *3*, 361.
281. Bolm, C.; Meyer, N.; Raabe, G.; Weyhermüller, T.; Bothe, E. *Chem. Commun.* **2000**, 2435.
282. Canada-Vilalta, C.; Huffman, J. C.; Streib, W. E.; Davidson, E. R.; Christou, G. *Polyhedron* **2001**, *20*, 1375.
283. Chen, C.; Zhu, H.; Huang, D.; Wen, T.; Liu, Q.; Liao, D.; Cui, J. *Inorg. Chim. Acta* **2001**, *320*, 159.
284. Li, J.; Yang, S.; Zhang, F.; Tang, Z.; Ma, S.; Shi, Q.; Wu, Q.; Huang, Z. *Inorg. Chim. Acta* **1999**, *294*, 109.
285. An, J.; Chen, Z.-D.; Bian, J.; Jin, X.-L.; Wang, S.-X.; Xu, G.-X. *Inorg. Chim. Acta* **1999**, *287*, 82.
286. Vincent, J. B.; Chang, H. R.; Folting, K.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 5703.
287. Wu, R.; Poyraz, M.; Sowery, F. E.; Anson, C. E.; Wocadlo, S.; Powell, A. K.; Jayasooriya, U. A.; Cannon, R. D.; Nakamoto, T.; Katada, M.; Sano, H. *Inorg. Chem.* **1998**, *37*, 1913.
288. Bhula, R.; Gainsford, G. J.; Weatherburn, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7550.
289. Mikuriya, M.; Yamato, Y.; Tokii, T. *Chem. Lett.* **1991**, 1429.
290. Wang, S.; Folting, K.; Streib, W. E.; Schmitt, E. A.; McCusker, J. K.; Hendrickson, D. N.; Christou, G. *Angew. Chem.* **1991**, *103*, 314.
291. Libby, E.; Folting, K.; Huffman, C. J.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1993**, *32*, 2549.
292. Wang, S.; Tsai, H. L.; Folting, K.; Martin, J. D.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1994**, 671.
293. Wemple, M. W.; Coggin, D. K.; Vincent, J. B.; McCusker, J. K.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Chem. Soc., Dalton Trans.* **1998**, 719.
294. Wang, S. Y.; Wemple, M. S.; Yoo, J.; Folting, K.; Huffman, J. C.; Hagen, K. S.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **2000**, *39*, 1501.
295. Aromi, G.; Bhaduri, S.; Artus, P.; Folting, K.; Christou, G. *Inorg. Chem.* **2002**, *41*, 805.
296. Canada-Vilalta, C.; Huffman, J. C.; Christou, G. *Polyhedron* **2001**, *20*, 1785.
297. Vincent, J. B.; Christmas, C.; Chang, H. R.; Li, Q.; Boyd, P. D. W.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1989**, *111*, 2086.
298. Bouwman, E.; Bolcar, M. A.; Libby, E.; Huffman, J. C.; Folting, K.; Christou, G. *Inorg. Chem.* **1992**, *31*, 5185.
299. Libby, E.; McCusker, J. K.; Schmitt, E. A.; Folting, K.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1991**, *30*, 3486.
300. Boskovic, C.; Folting, K.; Christou, G. *Polyhedron* **2000**, *19*, 2111.
301. Pistilli, J.; Beer, R. H. *Inorg. Chem. Commun.* **2002**, *5*, 206.
302. Gerbeleu, N. V.; Batsanov, A. S.; Timko, G. A.; Struchkov, Y. T.; Indrichan, K. M.; Popovich, G. A. *Dokl. Akad. Nauk SSSR* **1987**, *294*, 878.
303. Xia, X. P.; Verelst, M.; Daran, J. C.; Tuchagues, J. P. *J. Chem. Soc., Chem. Commun.* **1995**, 2155.
304. Brechin, E. K.; Coxall, R. A.; Parkin, A.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2700.
305. Wang, S.; Tsai, H. L.; Streib, W. E.; Christou, G.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1992**, 677.
306. Wang, S.; Huffman, J. C.; Folting, K.; Streib, W. E.; Lobkovsky, E. B.; Christou, G. *Angew. Chem.* **1991**, *103*, 1681.
307. Tsai, H. L.; Wang, S. Y.; Folting, K.; Streib, W. E.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1995**, *117*, 2503.
308. Libby, E.; Folting, K.; Huffman, J. C.; Christou, G. *J. Am. Chem. Soc.* **1990**, *112*, 5354.
309. Grillo, V. A.; Knapp, M. J.; Bollinger, J. C.; Hendrickson, D. N.; Christou, G. *Angew. Chem., Int. Ed.* **1996**, *35*, 1818.
310. Low, D. W.; Eichhorn, D. M.; Draganescu, A.; Armstrong, W. H. *Inorg. Chem.* **1991**, *30*, 877.
311. Murrie, M.; Parsons, S.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **1998**, 1423.
312. Eppley, H. J.; Aubin, S. M. J.; Streib, W. E.; Bollinger, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1997**, *36*, 109.

313. Squire, R. C.; Aubin, S. M. J.; Folting, K.; Streib, W. E.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1995**, *34*, 6463.
314. Eppley, H. J.; deVries, N.; Wang, S.; Aubin, S. M.; Tsai, H.-L.; Folting, K.; Hendrickson, D. N.; Christou, G. *Inorg. Chim. Acta* **1997**, *263*, 323.
315. Schake, A. R.; Schmitt, E. A.; Conti, A. J.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1991**, *30*, 3192.
316. Geisselmann, A.; Klufers, P.; Pilawa, B. *Angew. Chem., Int. Ed.* **1998**, *37*, 1119.
317. Bouwman, E.; Caulton, K. G.; Christou, G.; Folting, K.; Gasser, C.; Hendrickson, D. N.; Huffman, J. C.; Lobkovsky, E. B.; Martin, J. D. *et al. Inorg. Chem.* **1993**, *32*, 3463.
318. Swarnabala, G.; Reddy, K. R.; Tirunagar, J.; Rajasekharan, M. V. *Transition Met. Chem.* **1994**, *19*, 506.
319. Wieghardt, K.; Pohl, K.; Bossek, U.; Nuber, B.; Weiss, J. *Z. Naturforsch. B* **1988**, *43*, 1184.
320. Barra, A.-L.; Gatteschi, D.; Sessoli, R.; Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Uytterhoeven, M. G. *Angew. Chem., Int. Ed.* **1997**, *36*, 2329.
321. Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Caneschi, A.; Gatteschi, D. *Inorg. Chem.* **1998**, *37*, 3759.
322. Abbati, G. L.; Cornia, A.; Fabretti, A. C.; Caneschi, A.; Gatteschi, D. *Inorg. Chem.* **1998**, *37*, 1430.
323. Sabat, M.; Cini, R.; Haromy, T.; Sundaralingam, M. *Biochemistry* **1985**, *24*, 7827.
324. Zuniga-Villareal, N.; Lezama, M. R.; Hernandez-Ortega, S.; Silvestru, C. *Polyhedron* **1998**, *17*, 2679.
325. Henkel, G.; Greiwe, K.; Krebs, B. *Angew. Chem., Int. Ed.* **1985**, *24*, 117.
326. Seela, J. L.; Knapp, M. J.; Kolack, K. S.; Chang, H.-R.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1998**, *37*, 516.
327. Bashkin, J. S.; Huffman, J. C.; Christou, G. *J. Am. Chem. Soc.* **1986**, *108*, 5038.
328. Gohdes, J. W.; Armstrong, W. H. *Inorg. Chem.* **1988**, *27*, 1841.
329. Ellison, J. J.; Power, P. P.; Shoner, S. C. *J. Am. Chem. Soc.* **1989**, *111*, 8044.
330. Wieghardt, K.; Bossek, U.; Nuber, B.; Weiss, J. *Inorg. Chim. Acta* **1987**, *126*, 39.
331. Limburg, J.; Vrettos, J. S.; Crabtree, R. H.; Brudvig, G. W.; de Paula, J. C.; Hassan, A.; Barra, A.-L.; Duboc-Toia, C.; Collomb, M.-N. *Inorg. Chem.* **2001**, *40*, 1698.
332. Kitajima, N.; Komatsuzaki, H.; Hikichi, S.; Osawa, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1994**, *116*, 11596.
333. Goodson, P. A.; Hodgson, D. J. *Inorg. Chem.* **1989**, *28*, 3606.
334. Goodson, P. A.; Oki, A. R.; Glerup, J.; Hodgson, D. J. *J. Am. Chem. Soc.* **1990**, *112*, 6248.
335. Kitajima, N.; Singh, U. P.; Amagai, H.; Osawa, M.; Morooka, Y. *J. Am. Chem. Soc.* **1991**, *113*, 7757.
336. Glerup, J.; Goodson, P. A.; Hazell, A.; Hazell, R.; Hodgson, D. J.; McKenzie, C. J.; Michelsen, K.; Rychlewska, U.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 4105.
337. Tan, X. S.; Tang, W. X.; Sun, J. *Polyhedron* **1996**, *15*, 2671.
338. Larson, E.; Lah, M. S.; Li, X.; Bonadies, J. A.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 373.
339. Vincent, J. B.; Folting, K.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1986**, *25*, 996.
340. Pecoraro, V. L. Butler W. M. *Acta Crystallogr. C* **1986**, *42*, 1151.
341. Nagata, T.; Imagawa, K.; Yamada, T.; Mukaiyama, T. *Inorg. Chim. Acta* **1994**, *220*, 283.
342. Nagata, T.; Imagawa, K.; Yamada, T.; Mukaiyama, T. *Chem. Lett.* **1994**, 1259.
343. Nagata, T.; Imagawa, K.; Yamada, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3241.
344. Jacobsen, E. N.; Zhang, W.; Muci, A. R.; Ecker, J. R.; Deng, L. *J. Am. Chem. Soc.* **1991**, *113*, 7063.
345. Jacobsen, H.; Cavallo, L. *Chem. Eur. J.* **2001**, *7*, 800.
346. Jacobsen, E. N.; Zhang, W.; Guler, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 6703.
347. Zhang, Z.-Y.; Brouca-Cabarrecq, C.; Hemmert, C.; Dahan, F.; Tuchagues, J.-P. *J. Chem. Soc., Dalton Trans.* **1995**, 1453.
348. Gelasco, A.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1993**, *115*, 7928.
349. Gelasco, A.; Kirk, M. L.; Kampf, J. W.; Pecoraro, V. L. *Inorg. Chem.* **1997**, *36*, 1829.
350. Larson, E. J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1991**, *113*, 3810.
351. Garcia-Deibe, A.; Sousa, A.; Bermejo, M. R.; Rory, P. P. M.; McAuliffe, C. A.; Pritchard, R. G.; Helliwell, M. *J. Chem. Soc., Chem. Commun.* **1991**, 728.
352. Matsumoto, N.; Zhuang, J. Z.; Okawa, H.; Kida, S. *Inorg. Chem. Acta* **1989**, *160*, 153.
353. Shindo, K.; Mori, Y.; Motoda, K.; Sakiyama, H.; Matsumoto, N.; Okawa, H. *Inorg. Chem.* **1992**, *31*, 4987.
354. Gallo, E.; Solari, E.; De Angelis, S.; Floriani, C.; Re, N.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1993**, *115*, 9850.
355. Eichhorn, D. M.; Armstrong, W. H. *J. Chem. Soc., Chem. Commun.* **1992**, 85.
356. Cheng, B.; Fries, P. H.; Marchon, J.-C.; Scheidt, W. R. *Inorg. Chem.* **1996**, *35*, 1024.
357. Kipke, C. A.; Scott, M. J.; Gohdes, J. W.; Armstrong, W. H. *Inorg. Chem.* **1990**, *29*, 2193.
358. Horner, O.; Anxolabéhére-Mallart, E.; Charlot, M. F.; Tchertanov, L.; Guilhem, J.; Mattioli, T. A.; Boussac, A.; Girerd, J. J. *Inorg. Chem.* **1999**, *38*, 1222.
359. Bonadies, J. A.; Kirk, M. L.; Lah, M. S.; Kessissoglou, D. P.; Hatfield, W. E.; Pecoraro, V. L. *Inorg. Chem.* **1989**, *28*, 2037.
360. Bertoncello, K.; Fallon, G. D.; Murray, K. S.; Tiekink, E. R. T. *Inorg. Chem.* **1991**, *30*, 3562.
361. Mikuriya, M.; Yamato, Y.; Tokii, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1466.
362. Mikuriya, M.; Yamato, Y.; Tokii, T. *Chem. Lett.* **1992**, 1571.
363. Yu, S. B.; Wang, C. P.; Day, E. P.; Holm, R. H. *Inorg. Chem.* **1991**, *30*, 4067.
364. Mikuriya, M.; Majima, K.; Yamato, Y. *Chem. Lett.* **1992**, 1929.
365. Kwak, B.; Rhee, H.; Lah, M. S. *Polyhedron* **2000**, *19*, 1985.
366. Kwak, B.; Rhee, H.; Park, S.; Lah, M. S. *Inorg. Chem.* **1998**, *37*, 3599.
367. Liu, S. X.; Lin, S.; Lin, B. Z.; Lin, C. C.; Huang, J. Q. *Angew. Chem., Int. Ed.* **2001**, *40*, 1084.
368. Sreerama, S. G.; Pal, S. *Inorg. Chem.* **2002**, *41*, 4843.
369. Gedye, C.; Harding, C.; McKee, V.; Nelson, J.; Patterson, J. *J. Chem. Soc., Chem. Commun.* **1992**, 392.
370. Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112*, 2801.
371. Seela, J. L.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Chem. Commun.* **1985**, 58.
372. Arulsamy, N.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 4531.

373. Reddy, K. R.; Rajasekharan, M. V. *Polyhedron* **1994**, *13*, 765.
374. Yamaguchi, K. S.; Sawyer, D. T. *Inorg. Chem.* **1985**, *24*, 971.
375. Mahapatra, S.; Lal, T. K.; Mukherjee, R. *Inorg. Chem.* **1994**, *33*, 1579.
376. Vincent, J. B.; Christmas, C.; Huffman, J. C.; Christou, G.; Chang, H. R.; Hendrickson, D. N. *J. Chem. Soc., Chem. Commun.* **1987**, 236.
377. Wang, S.; Tsai, H.-L.; Hagen, K. S.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1994**, *116*, 8376.
378. Aromi, G.; Knapp, M. J.; Claude, J. P.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *J. Am. Chem. Soc.* **1999**, *121*, 5489.
379. Waldo, G. S.; Yu, S.; Penner-Hahn, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 5869–5870and references therein.
380. Barynin, V. V.; Vagin, A. A.; Melik-Adamyan, V. R.; Grebenko, A. I.; Khangulov, S. V.; Popov, A. N.; Andrianova, M. E.; Vainstein, A. *Dokl. Akad. Nauk. SSSR* **1986**, *288*, 877–880.
381. Barynin, V. V.; Hempsted, P. D.; Vagin, V. S.; Antonyuk, S. V.; Melik-Adamyan, W. R.; Lamzin, V. S.; Harrison, P. M.; Artymiuk, P. J. *J. Inorg, Biochem.* **1997**, *67*, 196.
382. Hage, R.; Kerschner, J. *Trends Inorg. Chem.* **1998**, *5*, 145–159.
383. Collinson, S. R.; Fenton, D. E. *Coord. Chem. Rev.* **1996**, *148*, 19–40.
384. Zhang, L.; Yan, S.; Li, C.; Liao, D.; Jiang, Z.; Cheng, P.; Wang, G.; Weng, L.; Leng, X. *J. Chem. Cryst.* **2000**, *30*, 251–254.
385. Koek, J. H.; Russell, S. W.; van der Wolf, L.; Hage, R.; Warnaar, J. B.; Spek, A. L.; Kerschner, J.; DelPizzo, L. *J. Chem. Soc., Dalton Trans.* **1996**, 353–362.
386. Argouarch, G.; Gibson, C. L.; Stones, G.; Sherrington, D. C. *Tetrahedron Lett.* **2002**, *43*, 3795–3798.
387. de Vos, D. E.; Bein, T. *J. Organomet. Chem.* **1996**, *520*, 195–200.
388. Brewer, K. J.; Calvin, M.; Lumpkin, R. S.; Otvos, J. W.; Spreer, L. O. *Inorg. Chem.* **1989**, *28*, 4446–4451.
389. Meyer, K.; Bendix, J.; Metzler-Nolte, N.; Weyhermueller, T.; Wieghardt, K. *J. Am. Chem. Soc.* **1998**, *120*, 7260–7270.
390. Niemann, A.; Bossek, U.; Haselhorst, G.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1996**, *35*, 906–915.
391. Penkert, F. N.; Weyhermueller, T.; Bill, E.; Hildebrandt, P.; Lecomte, S.; Wieghardt, K. *J. Am. Chem. Soc.* **2000**, *122*, 9663–9673.
392. Srinivasan, K.; Michaud, P.; Kochi, J. K. *J. Am. Chem. Soc.* **1986**, *108*, 2309–2320.
393. Palucki, M.; Finney, N. S.; Pospisil, P. J.; Güler, M. L.; Ishida, T.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 948–954.
394. Groves, J. T.; Stern, M. K. *J. Am. Chem. Soc.* **1988**, *110*, 8628–8638.
395. Groves, J. T.; Lee, J.; Marla, S. S. *J. Am. Chem. Soc.* **1997**, *119*, 6269–6273.
396. Collins, T. J.; Powell, R. D.; Slebodnick, C; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899–901.
397. Workman, J. M.; Powell, R. D.; Procyk, Alexand, D.; Collins, T. J.; Bocian, D. F. *Inorg. Chem.* **1992**, *31*, 1548–1550.
398. Collins, T. J.; Gordon-Wylie, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 4511–4513.
399. Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899–901.
400. Miller, C. G.; Gordon-Wylie, S. W.; Horwitz, C. P.; Strazisar, S. A.; Peraino, D. K.; Clark, G. R.; Weintraub, S. T.; Collins, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 11540–11541.
401. Belal, A. A.; Chaudhuri, P.; Fallis, I.; Farrugia, L. J.; Hartung, R.; MacDonald, N. M.; Nuber, B.; Peacock, R. D.; Weiss, J.; Weighardt, K. *Inorg. Chem.* **1991**, *30*, 4397–4002.
402. Fallis, I. A.; Farrugia, L. J.; Macdonald, N. M.; Peacock, R. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2759–2763.
403. Burdinski, D.; Bothe, E.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 105–116.
404. Birkelbach, F.; Floerke, U.; Haupt, H-J; Butzlaff, C.; Trautwein, AX.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **1998**, *37*, 2000–2008.
405. Hage, R.; Gunnewegh, E. A.; Niel, J.; Tjan, F. S. B.; Weyhermuller, T.; Wieghardt, K. *Inorg. Chim. Acta* **1998**, *268*, 43–48.
406. Weighardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153–1172.
407. Hotzelmann, R.; Wieghardt, K.; Ensling, J.; Romstedt, H.; Guetlich, P.; Bill, E.; Floerke, U.; Haupt, H. J. *J. Am. Chem. Soc.* **1992**, *114*, 9470–9483.
408. Park, Y. C.; Kim, S. S.; Na, H. G. *J. Korean Chem. Soc.* **1993**, *37*, 648–54.
409. Hambley, T. W.; Lawrance, G. A.; Sangster, D. F.; Ward, C. B. *Aust. J. Chem.* **1987**, *40*, 883–893.
410. Burgess, J.; Davies, D. L.; Grist, A. J.; Hall, J. A.; Parsons, S. A. *Monatsh. Chem.* **1994**, *125*, 515–523.
411. Samnani, P. B.; Manjula, V.; Bhattacharya, P. K. *J. Chem.* **1997**, *36A*, 1078–1081.
412. Bossek, U.; Weyhermuller, T.; Wieghardt, K.; Bonvoisin, J.; Girerd, J. J. *J. Chem. Soc., Chem. Commun.* **1989**, 633–636.
413. Gao, E.-Q.; Yang, G.-M.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Wang, G.-L.; Kou, H.-Z. *Transition Met. Chem.* **1999**, *24*, 244–246.
414. Brewer, K. J.; Liegeois, A.; Otvos, J. W.; Calvin, M.; Spreer, L. O. *J. Chem. Soc., Chem. Commun.* **1988**, 1219–1220.
415. Fukuda, Y.; Hirota, M.; Kon-No, M.; Nakao, A.; Umezawa, K. *Inorg. Chim. Acta* **2002**, *339*, 322–326.
416. Auerbach, U.; Eckert, U.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1990**, *29*, 938–944.
417. Muller, J.; Kikuchi, A.; Bill, E.; Weyhermuller, T.; Hildebrandt, P.; Ould-Moussa, L.; Wieghardt, K. *Inorg. Chim. Acta* **2000**, *297*, 265–277.
418. Qian, M.; Gou, S.-H.; Ju, H.-X.; Huang, W.; Duan, C.-Y.; You, X.-Z. *Transition Met. Chem.* **2000**, *25*, 584–588.
419. Lindoy, L. F. In *Advances in Inorganic Chemistry*; Sykes, A. G., Ed., Academic Press: New York, 1998; Vol. 45, pp 75–125.
420. Diril, H.; Chang, H.-R.; Nilges, M. J.; Zhang, X.; Potenza, J. A.; Schugar, H. J.; Isied, S. S.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 5102–5114.
421. Gou, S.; Zeng, Q.; Yu, Z.; Qian, M.; Zhu, J.; Duan, C.; You, X. *Inorg. Chim. Acta* **2000**, *303*, 175–180.
422. Wada, H.; Motoda, K.-I.; Ohba, M.; Sakiyama, H.; Matsumoto, N.; Okawa, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1105–1114.
423. Chang, H. R.; Diril, H.; Nilges, M. J.; Zhang, X.; Potenza, J. A.; Schugar, H. J.; Hendrickson, D. N.; Isied, S. S. *J. Am. Chem. Soc.* **1988**, *110*, 625–627.
424. Yoshino, A.; Miyagi, T.; Asato, E.; Mikuriya, M.; Sakata, Y.; Sugiura, K.-I.; Iwasaki, K.; Hino, S. *J. Chem. Soc., Chem. Commun.* **2000**, 1475–1476.

425. Diril, H.; Chang, H. R.; Zhang, X.; Larsen, S. K.; Potenza, J. A.; Pierpont, C. G.; Schugar, H. J.; Isied, S. S.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 6207–6208.
426. Chang, H. R.; Larsen, S. K.; Boyd, P. D. W.; Pierpont, C. G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4565–4576.
427. Edwards, A. J.; Hoskins, B. F.; Robson, R.; Wilson, J. C.; Moubaraki, B.; Murray, K. S. *J. Chem. Soc., Dalton Trans.* **1994**, 1837–1842.
428. Marappan, M.; Narayanan, V.; Kandaswamy, M. *J. Chem. Soc., Dalton Trans.* **1998**, 3405–3410.
429. Brudenell, S. J.; Spiccia, L.; Bond, A. M.; Fallon, G. D.; Hockless, D. C. R.; Lazarev, G.; Mahon, P. J.; Tiekink, E. R. T. *Inorg. Chem.* **2000**, *39*, 881–892.
430. Wieghardt, K.; Schoeffmann, E.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 4877–4883.
431. Fallon, G. D.; Mclachlan, G. A.; Moubaraki, B.; Murray, K. S.; O'Brien, L.; Spiccia, L. *J. Chem. Soc., Dalton Trans.* **1997**, 2765–2769.
432. Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230–1235.
433. Chaudhuri, P.; Weighardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329–436.
434. Brudenell, S. J.; Spiccia, L.; Bond, A. M.; Fallon, G. D.; Hockless, D. C. R.; Lazarew, G.; Mahon, P. J.; Tiekink, E. R. T. *Inorg. Chem.,* **2000**, *39*, 881–892.
435. Bucher, C.; Duval, E.; Barbe, J.-M.; Verpeaux, J.-N.; Amatore, C.; Guilard, R.; Le Pape, L.; Latour, J.-M.; Dahaoui, S.; Lecomte, C. *Inorg. Chem.* **2001**, *40*, 5722–5726.
436. Hubin, T. J.; McCormick, J. M.; Collinson, S. R.; Busch, D. H.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1998**, 1675–1676.
437. Franceschi, F.; Hesschenbrouck, J.; Solari, E.; Floriani, C.; Re, N.; Rizzoli, C.; Chiesi-Villa, A. *J. Chem. Soc., Dalton Trans.* **2000**, 593–604.
438. Anderson, B. A.; Jackels, S. C. *Inorg. Chem.* **1986**, *25*, 1085–1088.
439. Chaudhary, A.; Jaroli, D. P.; Singh, R. V. *Met.-Based Drugs* **2001**, *8*, 347–353.
440. Mishra, R.; Sharma, K.; Singh, R. V. *Oriental J. Chem.* **2002**, *18*, 85–88.
441. Howlader, M. B. H.; Islam, M. S.; Karim, M. R. *Indian J. Chem.* **2000**, *39A*, 407–409.
442. Louloudi, M.; Kolokytha, C.; Hadjiliadis, N. *J. Mol. Catal. A: Chem.* **2002**, *180*, 19–24.
443. Costa, J.; Delgado, R. *Inorg. Chem.* **1993**, *32*, 5257–5265.
444. Costa, J.; Delgado, R.; Drew, M. G. B.; Felix, V. *J. Chem. Soc., Dalton Trans.* **1998**, 1063–1072.
445. Herron, N.; Busch, D. H. *Inorg. Chem.* **1983**, *22*, 3470–3475.
446. Ahmad, N.; Misra, M.; Shukla, P. R. *Synth. React. Inorg. Met-Org. Chem.* **1992**, *22*, 1455–1470.
447. Shakir, M; Varkey, S. P.; Khan, T. A. *Indian J. Chem.* **1995**, *34A*, 72–75.
448. Khan, T. A.; Hasan, S. S.; Mohamed, A. K.; Islam, K. S.; Shakir, M. *Synth. React. Inorg. Met-Org. Chem.* **2000**, *30*, 815–828.
449. Khan, T. A.; Hasan, S. S.; Jahan, N; Mohamed, A. K.; Islam, K. S. *Indian J. Chem.* **2000**, *39A*, 1090–1092.
450. Chanda, S.; Gupta, K. *Indian J. Chem.* **2001**, *40A*, 775–779.
451. Chandra, S.; Sharma, S. D. *Transition Met. Chem.* **2002**, *27*, 732–735.
452. Bu, X.-H.; Chen, W.; Mu, L.-J.; Zhang, Z.-H.; Zhang, R.-H.; Clifford, T. *Polyhedron* **2000**, *19*, 2095–2100.
453. Di Vaira, M.; Mani, F.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1127–1130.
454. Jackels, S. C.; Durham, M. M.; Newton, J. E.; Henninger, T. C. *Inorg. Chem.* **1992**, *31*, 234–239.
455. Geraldes, C. F. G. C.; Sherry, A. D.; Brown, R. D. III; Koenig, S. H. *Magn. Res. Med.* **1986**, *3*, 242–250.
456. Jackels, S. C.; Kroos, B. R.; Hinson, W. H.; Karstaedt, N.; Moran, P. R. *Radiology* **1986**, 159, 525–530.
457. Weiss, R. H.; Neumann, W. L.; Franklin, G. W.; Brown, T. M.; Henke, S. L.; Lennon, P. J.; Riley, D. P. *212th ACS Conf., Abstr.* **1996**, 25–29.
458. Riley, D. P.; Weiss, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 387–388.
459. Black, S. C.; Schasteen, C. S.; Weiss, R. H.; Riley, D. P.; Driscoll, E. M.; Lucchesi, B. R. *J. Pharm. Acol. Exp. Ther.* **1994**, *270*, 1208–1215.
460. Riley, D. P.; Henke, S. L.; Lennon, P. J.; Weiss, R. H.; Neumann, W. L.; Rivers, W. J, Jr.; Aston, K. W.; Sample, K. R.; Rahman, H. *Inorg. Chem.* **1996**, *35*, 5213–5231.
461. Weiss, R. H.; Fretland, D. J.; Baron, D. A.; Ryan, U. S.; Riley, D. P. *J. Biol. Chem.* **1996**, *271*, 26149–26156.
462. Riley, D. P.; Lennon, P. J.; Neumann, W. L.; Weiss, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 6522–6528.
463. Riley, D. P.; Henke, S. L.; Lennon, P. J.; Neumann, W. L.; Aston, K. *Inorg. Chem.* **1999**, *38*, 1908–1917.
464. Salvemini, D.; Wang, Z.-Q.; Zweier, J. L.; Samouilov, A.; MacArthur, H.; Misko, T. P.; Currie, M. G.; Cuzzocrea, S.; Sikorski, J. A.; Riley, D. P. *Science* **1999**, *286*, 304–306.
465. Udipi, K.; Ornberg, R. L.; Thurmond, K. B. II; Settle, S. L.; Forster, D.; Riley, D. *J. Biol. Mater. Res.* **2000**, *51*, 549–560.
466. Aston, K.; Rath, N.; Naik, A.; Slomczynska, U.; Schall, O. F.; Riley, D. P. *Inorg. Chem.* **2001**, *40*, 1779–1789.
467. Bienvenue, E.; Choua, S.; Lobo-Recio, M.-A.; Marzin, C.; Pacheco, P.; Seta, P.; Tarrago, G. *J. Inorg, Biochem.* **1995**, *57*, 157–168.
468. Fenton, D. E. *NATO ASI Ser., Ser. C* **1994**, *448*, 153–169.
469. Collinson, S.; Alcock, N. W.; Raghunathan, A.; Kahol, P. K.; Busch, D. H. *Inorg. Chem.* **2000**, *39*, 757–764.
470. Ansell, C. W. G.; Lewis, J.; Ramsden, J. N.; Schroeder, M. *Polyhedron* **1983**, *2*, 489–491.
471. Ansell, C. W. G.; Lewis, J.; Raithby, P. R.; O'Donoghue, T. D. *J. Chem. Soc., Dalton Trans.* **1983**, 177–179.
472. Newton, J. E.; Jackels, S. C. *J. Coord. Chem.* **1988**, *19*, 265–277.
473. Anacona, J. R.; Rivas, A.; Marquez, V. E. *Transition Met. Chem.* **1995**, *20*, 239–241.
474. Jimenez-Sandoval, O.; Ramirez-Rosales, D.; Rosales-Hoz, M. del J.; Sosa-Torres, M. E.; Zamorano-Ulloa, R. *J. Chem. Soc., Dalton Trans.* **1998**, 1551–1556.
475. Fenton, D. E. *Pure Appl. Chem.* **1986**, *58*, 1437–1444.
476. Wagnon, B. K.; Jackels, S. C. *Inorg. Chem.* **1989**, *28*, 1923–1927.
477. Wang, J.; Martell, A. E.; Motikatis, R. J. *Inorg. Chim. Acta* **2001**, *322*, 47–55.
478. Raghunathan, S.; Stevenson, C.; Nelson, J.; McKee, V. *J. Chem. Soc., Chem. Commun.* **1989**, 5–7.
479. Harding, C.; McDowell, D.; Nelson, J.; Raghunathan, S.; Stevenson, C.; Drew, M. G. B.; Yates, ppC. *J. Chem. Soc., Dalton Trans.* **1990**, 2521–2533.

480. Bencini, A.; Bianchi, A.; Micheloni, M.; Paoletti, P.; Garcia-Espana, E.; Nino, M. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1171–1174.
481. Coyle, J.; Drew, M. G. B.; Harding, C. J.; Nelson, J.; Town, R. M. *J. Chem. Soc., Dalton Trans.* **1997**, 1123–1125.
482. Nelson, J.; Murphy, B. P.; Drew, M. G. B.; Yates, P. C.; Nelson, S. M. *J. Chem. Soc., Dalton Trans.* **1988**, 1001–1010.
483. Fenton, D. E.; Murphy, B. P.; Price, R.; Tasker, P. A.; Winter, D. J. *J. Inclusion Phenom.* **1987**, *5*, 143–148.
484. Adams, H.; Bailey, N. A.; Debaecker, N.; Fenton, D. E.; Kanda, W.; Latour, J.-M.; Okawa, H.; Sakiyama, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2535–2537.
485. Brooker, S.; Kelly, R. J. *J. Chem. Soc., Dalton Trans.* **1996**, 2117–2122.
486. Arpadjan, S.; Mitewa, M.; Bontchev, P. R. *Talanta* **1987**, *34*, 953–956.
487. Blain, S.; Appriou, P.; Chaumeil, H.; Handel, H. *Anal. Chim. Acta* **1990**, *232*, 331–336.
488. Li, G. Q.; Govind, R. *Inorg. Chim. Acta* **1995**, *231*, 225–228.
489. Colton, R.; Mitchell, S.; Traeger, J. C. *Inorg. Chim. Acta* **1995**, *231*, 87–93.
490. Zagorevskii, D. V.; Holmes, J. L.; Watson, C. H.; Eyler, J. R. *Eur. Mass. Spec.* **1997**, *3*, 27–36.
491. Chadwick, R. B.; Mcdowell, W. J.; Baes, C. F. *Sep. Sci. Technol.* **1988**, *23*, 1311–1324.
492. Moyer, B. A.; Delmau, L. H.; Lumetta, G. J.; Baes, C. F. *Solv. Extr. Ion Exch.* **1993**, *11*, 889–921.
493. Burns, J. H.; Lumetta, G. J. *Acta. Crystallogr. C* **1991**, *47*, 2069–2073.
494. Fenton, D. E.; Murphy, B. P.; Leong, A. J.; Lindoy, L. F.; Bashall, A.; McPartlin, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2543–2553.
495. McKee, V.; Shepard, W. B. *J. Chem. Soc., Chem. Commun.* **1985**, 158–159.
496. Brooker, S.; McKee, V.; Shepard, W. B.; Pannell, L. K. *J. Chem. Soc., Dalton Trans.* **1987**, 2555–2562.
497. Mikuriya, M.; Nakadera, K.; Tokii, T. *Inorg. Chim. Acta* **1992**, *194*, 129–131.
498. McKee, V.; Tandon, S. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1334–1336.
499. Brychcy, K.; Draeger, K.; Jens, K.-J.; Tilset, M.; Behrens, U. *Chem. Ber.* **1994**, *127*, 1817–1826.
500. Bailey, N. A.; Fenton, D. E.; Kitchen, S. J.; Lilley, T. H.; Williams, M. G.; Tasker, P. A.; Leong, A. J.; Lindoy, L. F. *J. Chem. Soc., Dalton Trans.* **1991**, 627–637.
501. Fenton, D. E.; Matthews, R. W.; McPartlin, M.; Murphy, B. P.; Scowen, I. J.; Tasker, P. A. *J. Chem. Soc., Dalton Trans.* **1996**, 3421–3427.
502. Hay, R. W.; Hassan, M. M.; Fenton, D. E.; Murphy, B. P. *Transition Met. Chem.* **1994**, *19*, 559–560.
503. Adams, H.; Bastida, R.; Fenton, D. E.; Macias, A.; Spey, S. E.; Valencia, L. *J. Chem. Soc., Dalton Trans.* **1999**, 4131–4137.
504. Chakraborty, P.; Chandra, S. K. *Polyhedron* **1994**, *13*, 683–687.
505. Luo, Y.; Zhang, J.; Lu, L.; Qian, M.; Wang, X.; Yang, X.; Jian, F. *Transition Met. Chem.* **2002**, *27*, 469–472.
506. Korupoju, S. R.; Mangayarkarasi, N.; Ameerunisha, S.; Valente, E. J.; Zacharias, P. S. *J. Chem. Soc., Dalton Trans.* **2000**, 2845–2852.
507. Qian, M.; Zeng, Q; Gou, S. *Synth. React. Inorg. Met-Org. Chem.* **2000**, *30*, 637–647.
508. Anacona, J. R.; Bastardo, E.; Camus, J. *Transition Met. Chem.* **1999**, *24*, 478–480.
509. Watkinson, M; Whiting, A.; McAuliffe, C. A. *J. Chem. Soc., Chem. Commun.* **1994**, 2141–2142.
510. Gaye, M.; Sall, A. S. *Bull. Chem. Soc. Ethiopia* **1995**, *9*, 31–41.
511. Chaves, S.; Delgado, R.; Frausto da Silva, J. J. R. *Talanta* **1992**, *39*, 249–254.
512. Bianchi, A.; Calabi, L.; Giorgi, C.; Losi, P.; Mariani, P.; Palano, D.; Paoli, P.; Rossi, P.; Valtancoli, B. *J. Chem. Soc., Dalton Trans.* **2001**, 917–922.
513. Burai, L.; Ren, J.; Kovacs, Z.; Bruecher, E.; Sherry, A. D. *Inorg. Chem.* **1998**, *37*, 69–75.
514. Inoue, M. B.; Oram, P.; Andreu-de-Riquer, G.; Inoue, M.; Borbat, P.; Raitsimring, A.; Fernando, Q. *Inorg. Chem.* **1995**, *34*, 3528–3535.
515. Inoue, M. B.; Navarro, R. E.; Inoue, M.; Fernando, Q. *Inorg. Chem.* **1995**, *34*, 6074–6079.
516. Inoue, M. B.; Oram, P.; Inoue, M.; Fernando, Q. *Inorg. Chim. Acta* **1996**, *248*, 231–239.
517. Inoue, M. B.; Machi, L.; Munoz, I. C.; Rojas-Rivas, S.; Inoue, M.; Fernando, Q. *Inorg. Chim. Acta* **2001**, *324*, 73–80.
518. Inoue, M. B.; Villegas, C. A.; Asano, K.; Nakamura, M.; Inoue, M.; Fernando, Q. *Inorg. Chem.* **1992**, *31*, 2480–2483.
519. Miao, L.; Bell, D.; Rothremel, G. L., Jr.; Bryant, L. H., Jr.; Fitzsimmons, P. M.; Jackels, S. C. *Supramolecular Chem.* **1996**, *6*, 365–373.
520. Cabral, M. F.; Delgado, R. *Helv. Chim. Acta* **1994**, *77*, 515–524.
521. Bailey, N. A.; Fenton, D. E.; Kitchen, S. J.; Lilley, T. H.; Williams, M. G.; Tasker, P. A.; Leong, A. J.; Lindoy, L. F. *J. Chem, Soc., Dalton Trans.* **1991**, 2989–2994.
522. Chandra, R.; Jain, D. *Synth. React. Inorg. Met.-Org. Chem.* **1993**, *23*, 767–776.
523. Brooker, S.; McKee, V. *J. Chem. Soc., Chem. Commun.* **1989**, 619–620.
524. Downard, A. J.; McKee, V.; Tandon, S. S. *Inorg. Chim. Acta* **1990**, *173*, 181–190.
525. Chaves, S.; Cerva, A.; Delgado, R. *Polyhedron* **1998**, *17*, 93–104.
526. Amorim, M. T. S.; Delgado, R.; Frausto da Silva, J. J. R. *Polyhedron* **1992**, *11*, 1891–1899.
527. Chaves, S.; Delgado, R.; Duarte, M. T.; Silva, J. A. L.; Felix, V.; Carrondo, M. A. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2579–2584.
528. Chaves, S.; Cerva, A.; Delgado, R. *J. Chem. Soc., Dalton Trans.* **1997**, 4181–4190.
529. Delgado, R.; Da Silva, J. J. R. F.; Vaz, M. C. T. A. *Polyhedron* **1987**, *6*, 29–38.
530. Delgado, R.; Frausto da Silva, J. J. R.; Vaz, M. C. T. A.; Paoletti, P.; Micheloni, M. *J. Chem. Soc., Dalton Trans.* **1989**, 133–137.
531. Amorim, M. T. S.; Delgado, R.; Frausto da Silva, J. J. R.; Candida, M.; Vaz, T. A.; Vilhena, M. F. *Talanta* **1988**, *35*, 741–745.
532. Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225–2236.
533. Cabral, M. F.; Delgado, R.; Duarte, M. T.; Teixeira, M. *Helv. Chim. Acta* **2000**, *83*, 702–721.
534. Bruecher, E.; Gyori, B.; Emri, J.; Jakab, S.; Kovacs, Z.; Solymosi, P.; Toth, I. *J. Chem. Soc., Dalton Trans.* **1995**, 3353–3357.
535. Adam, B.; Bill, E.; Bothe, E.; Goerdt, B.; Haselhorst, G.; Hildenbrand, K.; Sokolowski, A.; Steenken, S.; Weyhermueller, T.; Wieghardt, K. *Chem. Eur. J.* **1997**, *3*, 308–319.

536. Flassbeck, C.; Wieghardt, K.; Bill, E.; Butzlaff, C.; Trautwein, A. X.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1992**, *31*, 21–26.
537. Cho, M. H.; Lee, S. C.; Kim, S. J. *J. Korean Chem. Soc.* **1987**, *31*, 503–508.
538. Chandra, R.; Jain, D.; Singh, R.; Singh, R. M. *Synth. React. Inorg. Met.-Org. Chem.* **1993**, *23*, 229–238.
539. Blake, A. B.; Sinn, E.; Yavari, A.; Moubaraki, B.; Murray, K. S. *Inorg. Chim. Acta* **1995**, *229*, 281–290.
540. Cabral, M. F.; Costa, J.; Delgado, R.; Frausto Da Silva, J. J. R.; Vilhena, M. F. *Polyhedron* **1990**, *9*, 2847–2857.
541. Cai, H. Z.; Kaden, T. A. *Helv. Chim. Acta* **1993**, *76*, 557–562.
542. Lazar, I.; Kiraly, R.; Takacs, Z. *J. Coord. Chem.* **2000**, *51*, 293–304.
543. Cortes, S.; Brucher, E.; Geraldes, C. F. G. C.; Sherry, A. D. *Inorg. Chem.* **1990**, *29*, 5–9.
544. Delgado, R.; Quintino, S.; Teixeira, M.; Zhang, A. *J. Chem. Soc., Dalton Trans.* **1997**, 55–63.
545. Delagrange, S.; Delgado, R.; Nepveu, F. *J. Inorg. Biochem.* **2000**, *81*, 65–71.
546. Delgado, R.; Sun, Y.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chem.* **1993**, 3320–3326.
547. Wu, J. C.; Tang, N.; Liu, W. S.; Tan, M. Y.; Chan, A. S. C. *Chin. Chem. Lett.* **2001**, *12*, 757–760.
548. Luneau, D.; Savariault, J. M.; Cassoux, P.; Tuchagues, J. P. *J. Chem. Soc., Dalton Trans.* **1988**, 1225–1235.
549. Gao, J.; Martell, A. E.; Motekaitis, R. J. *Inorg. Chim. Acta* **2001**, *325*, 164–170.
550. Das, R.; Nanda, K. K.; Paul, I.; Baitalik, S.; Nag, K. *Polyhedron* **1994**, *13*, 2639–2645.
551. Furutachi, H.; Fujinami, S.; Suzuki, M.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1999**, 2197–2204.
552. Aono, T.; Wada, H.; Yonemura, M.; Ohba, M.; Okawa, H.; Fenton, D. E. *J. Chem. Soc., Dalton Trans.* **1997**, 1527–1531.
553. Fraser, C.; Johnston, L.; Rheingold, A. L.; Haggerty, B. S.; Williams, G. K.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1992**, *31*, 1835–44.
554. Fraser, C.; Ostrander, R.; Rheingold, A. L.; White, C.; Bosnich, B. *Inorg. Chem.* **1994**, *33*, 324–37.
555. Brooker, S.; McKee, V.; Metcalfe, T. *Inorg. Chim. Acta* **1996**, *246*, 171–179.
556. McCrea, J.; McKee, V.; Metcalfe, T.; Tandon, S. S.; Wikaira, J. *Inorg. Chim. Acta* **2000**, *297*, 220–230.
557. Nagata, T.; Mizukami, J. *J. Chem. Soc., Dalton Trans.* **1995**, 2825–2830.
558. Ikawa, Y.; Nagata, T.; Maruyama, K. *Chem. Lett.* **1993**, 1049–1052.
559. Sakiyama, H.; Tokuyama, K.; Matsumura, Y.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1993**, 2329–2334.
560. Nagata, T.; Ikawa, Y.; Maruyama, K. *J. Chem. Soc., Chem. Commun.* **1994**, 471–472.
561. Qian, M.; Gou, S.; Chantrapromma, S.; Sundara Raj, S. S.; Fun, H.-K.; Zeng, Q.; Yu, Z.; You, X. *Inorg. Chim. Acta* **2000**, *305*, 83–90.
562. Asato, E.; Furutachi, H.; Tamanaha, C.; Matsudaira, H.; Ohba, M.; Okawa, H.; Mikuriya, M. *Chem. Lett.* **1999**, 647–648.
563. Okawa, H.; Nishio, J.; Ohba, M.; Tadokoro, M.; Matsumoto, N.; Koikawa, M.; Kida, S.; Fenton, D. E. *Inorg. Chem.* **1993**, *32*, 2949–2957.
564. Furutachi, H.; Fujinami, S.; Suzuki, M.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1999**, 2197–2204.
565. Wada, H.; Aono, T.; Motoda, K.-I; Ohba, M.; Matsumoto, N.; Skawa, H. *Inorg. Chim. Acta* **1996**, *246*, 13–21.
566. Mohanta, S.; Nanda, K. K.; Thompson, L. K.; Floarke, U.; Nag, K. *Inorg. Chem.* **1998**, *37*, 1465–1472.
567. He, H.; Martell, A. E.; Motekaitis, R. J.; Reibenspies, J. H. *Inorg. Chem.* **2000**, *39*, 1586–1592.
568. Gao, E. Q.; Yang, G.-M.; Jiang, Z.-H.; Yan, S.-P.; Wang, G.-L.; Liao, D.-Z. *Synth. React. Inorg. Met.-Org. Chem.* **1999**, *29*, 1053–1061.
569. Tang, J.-K.; Wang, Q.-L.; Gao, E.-Q.; Chen, J.-T.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Cheng, P. *Helv. Chim. Acta* **2002**, *85*, 175–182.
570. Chandra, S.; Gupta, K. *Transition Met. Chem.* **2002**, *27*, 196–199.
571. Abe, S.; Fujii, K.; Sone, T. *Anal. Chim. Acta* **1994**, *293*, 325–330.
572. Abe, S.; Sone, T.; Fujii, K.; Endo, M. *Anal. Chim. Acta* **1993**, *274*, 141–146.
573. Cho, M. H.; Seon-Woo, K. H.; Heo, M. Y.; Lee, I. C.; Yoon, C. J.; Kim, S. J. *Bull. Korean Chem. Soc.* **1988**, *9*, 292–295.
574. Cho, M. H.; Kim, J. H.; Kim, H. R.; Chun, H. S.; Lee, I. C. *J. Korean Chem. Soc.* **1992**, *36*, 914–918.
575. Wambeke, D. M.; Lippens, W.; Herman, G. G.; Goeminne, A. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2017–2021.
576. Hall, C. D.; Danks, I. P.; Sharpe, N. W. *J. Org. Chem.* **1990**, *390*, 227–235.
577. Pomp, C.; Drueeke, S.; Kueppers, H. J.; Wieghardt, K.; Krueger, C.; Nuber, B.; Weiss, J. *Z. Naturforsch. B* **1988**, *43*, 299–305.
578. Baker, R. J.; Edwards, P. G.; Gracia-Mora, J.; Ingold, F.; Abdul, M. K. M. *J. Chem. Soc., Dalton Trans.* **2002**, 3985–3992.
579. Elias, H.; Schmidt, G.; Kueppers, H. J.; Saher, M.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1989**, *28*, 3021–3024.
580. Patel, B.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2000**, 1303–1307.
581. Messerschmidt, A.; Huber, R.; Poulos, T.; Wieghardt, K., Eds. *Handbook of Metalloproteins*; Wiley, 2001.
582. Bertini, I.; Sigel, A.; Sigel, H., Eds. *Handbook on Metalloproteins*; Marcel Dekker: New York, 2001.
583. Sigel, A.; Sigel, H., Ed., *Manganese and its Role in Biological Processes* **2000**, *37*Marcel Dekker: New York.
584. Weatherburn, D. C. In *Perspectives in Bioinorganic Chemistry*; Hay, R. W., Dilworth, J. R., Nolan, K. B., Eds.; JAI Press: Greenwich, CT, 1996; Vol. 3, pp 1–113.
585. Dismukes, G. C. *Chem. Rev.* **1996**, *96*, 2909–2926.
586. Christianson, D. W. *Prog. Biophys. Mol. Biol.* **1997**, *67*, 217–252.
587. Wikaira, J.; Gorun, S. M. In *Bioinorganic Catalysis*, 2nd ed.; Reedijk, J., Bouwman, E., Eds.; Marcel Dekker: New York, 1999; pp 355–422.
588. Yocum, C. F.; Pecoraro, V. L. *Curr. Opin. Chem. Biol.* **1999**, *3*, 182–187.
589. Crowley, J.; Traynor, D.; Weatherburn, D. C. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 208–279.
590. Law, N. A.; Caudle, M. T.; Pecoraro, V. L. *Adv. Inorg. Chem.* **1999**, *46*, 305–440.
591. Pecoraro, V. L.; Hsieh, W. Y. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 429–504.
592. Keen, C. L.; Ensunsa, J. L.; Clegg, M. S. In *Metal Ions In Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 89–121.

593. Benoit-Vical, F.; Robert, A.; Meunier, B. *Antimicrob. Agent. Chemoth.* **2000**, *44*, 2836–2841.
594. Culotta, V. L. In *Metal Ions In Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 35–56.
595. Claverys, J.-P. *Res. Microbiol.* **2001**, *152*, 231–243.
596. Hao, Z.; Chen, S.; Wilson, D. B. *Appl. Environ. Microbiol.* **1999**, *65*, 4746–4752.
597. Lawrence, M. C.; Pilling, P. A.; Epa, V. C.; Berry, A. M.; Ogunniyi, A. D.; Paton, J. C. *Structure* **1998**, *6*, 1553–1561.
598. Winge, D. R.; Jensen, L. T.; Srinivasan, C. *Curr. Opin. Chem. Biol.* **1998**, *2*, 216–221.
599. Eide, D. J. *Adv. Microbial Physiol.* **2000**, *43*, 1–38.
600. Luk, E. E.; Culotta, V. C. *J. Biol. Chem.* **2001**, *276*, 47556–47562.
601. Mandal, D.; Woolf, T. B.; Rao, R. *J. Biol. Chem.* **2000**, *275*, 23933–23938.
602. Lin, S. J.; Culotta, V. C. *Mol. Cell. Biol.* **1996**, *16*, 6303–6312.
603. Lapinskas, P. J.; Lin, S. J.; Culotta, V. C. *Mol. Microbiol.* **1996**, *21*, 519–528.
604. Rengel, Z. In *Metal Ions In Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 57–87.
605. Guerinot, M. L. *Biochim. Biophys. Acta* **2000**, *1465*, 190–198.
606. Aschner, M. *Environ. Health Perspect.* **2000**, *108*, 429–432.
607. Aschner, M.; Vrana, K. E.; Zheng, W. *Neurotoxicology* **1999**, *20*, 173–180.
608. Tjaelve, H.; Henriksson, J. *Neurotoxicology* **1999**, *20*, 181–195.
609. Verity, M. A. *Neurotoxicology* **1999**, *20*, 489–497.
610. Que, Jr., L.; Reynolds, M. F. In *Metal Ions In Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 505–525.
611. Qu, A.; Leahy, D. J. *Structure (London)* **1996**, *4*, 931.
612. Schell, U.; Helin, S.; Kajander, T.; Schlomann, M.; Goldman, A. *Proteins* **1999**, *34*, 125–136.
613. Ceccarelli, C.; Grodsky, N. B.; Ariyaratne, N.; Colman, R. F.; Bahnson, B. J. *J. Biol. Chem.* **2002**, *277*, 43454–43462.
614. Banci, L. *J. Biotechnol.* **1997**, *53*, 253–263.
615. Gold, M. H.; Youngs, H. L.; Gelpke, M. D. In *Metal Ions In Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 559–586.
616. Leonowicz, A.; Matuszewska, A.; Luterek, J.; Ziegenhagen, D.; Wojtas-Wasilewska, M.; Cho, N. S.; Hofrichter, M.; Rogalski, J. *Fungal Gen. Biol.* **1999**, *27*, 175–185.
617. Cameron, M. D.; Timofeevski, S.; Aust, S. D. *Appl. Microbiol. Biotechnol.* **2000**, *54*, 751–758.
618. Rodakiewicz-Nowak, J. *Top. Catal.* **2000**, *11*, 419–434.
619. Sundaramoorthy, M.; Kishi, K.; Gold, M. H.; Poulos, T. L. *J. Biol. Chem.* **1997**, *272*, 17574–17580.
620. Whitwam, R. E.; Brown, K. R.; Musick, M.; Natan, M. J.; Tien, M. *Biochemistry* **1997**, *36*, 9766–9773.
621. MacMillan-Crow, L. A.; Cruthirds, D. L. *Free Radical Res.* **2001**, *34*, 325–336.
622. Sayre, L. M.; Perry, G.; Atwood, C. S.; Smith, M. A. *Cell. Mol. Biol.* **2000**, *46*, 731–741.
623. Miller, A. F.; Sorkin, D. L. *Comm. Mol. Cell. Biophys.* **1997**, *9*, 1–18.
624. Raha, S.; Robinson, B. H. *Trends Biochem. Sci.* **2000**, *25*, 502–508.
625. Whittaker, J. W. In *Metal Ions In Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 587–611.
626. Edwards, R. A.; Whittaker, M. M.; Whittaker, J. W.; Baker, E. N.; Jameson, G. B. *Biochemistry* **2001**, *40*, 4622–4632.
627. Edwards, R. A.; Whittaker, M. M.; Whittaker, J. W.; Baker, E. N.; Jameson, G. B. *Biochemistry* **2001**, *40*, 15–27.
628. Edwards, R. A.; Whittaker, M. M.; Whittaker, J. W.; Jameson, G. B.; Baker, E. N. *J. Am. Chem. Soc.* **1998**, *120*, 9684–9685.
629. Sugio, S.; Hiraoka, B. Y.; Yamakura, F. *Eur. J. Biochem.* **2000**, *267*, 3487–3495.
630. Guan, Y.; Hickey, M. J.; Borgstahl, G. E. O.; Hallewell, R. O.; Lepock, J. R.; O'Connor, D.; Hseih, Y.; Nick, H. S.; Silverman, D. N.; Tainer, J. A. *Biochemistry* **1998**, *37*, 4722–4730.
631. Whittaker, M. M.; Whittaker, J. W. *Biochemistry* **1997**, *36*, 8923–8931.
632. Hsieh, Y.; Guan, Y.; Tu, C.; Bratt, P. J.; Angerhofer, A.; Lepock, J. R.; Hickey, M. J.; Tainer, J. A.; Nick, H. S.; Silverman, D. N. *Biochemistry* **1998**, *37*, 4731–4739.
633. Leveque, V. J.; Stroupe, M. E.; Lepock, J. R.; Cabelli, D. E.; Tainer, J. A.; Nick, H. S.; Silverman, D. N. *Biochemistry* **2000**, *39*, 7131–7137.
634. Jackson, S. M. J.; Cooper, J. B. *Biometals* **1998**, *11*, 159–173.
635. Vance, C. K.; Miller, A. F. *J. Am. Chem. Soc.* **1998**, *120*, 461–467.
636. Vance, C. K.; Miller, A. F. *Biochemistry* **2001**, *40*, 13079–13087.
637. Leveque, V. J. P.; Vance, C. K.; Nick, H. S.; Silverman, D. N. *Biochemistry* **2001**, *40*, 10586–10591.
638. Vance, C. K.; Miller, A. F. *Biochemistry* **1998**, *37*, 5518–5527.
639. Schwartz, A. L.; Yikilmaz, E.; Vance, C. K.; Vathyam, S.; Koder, R. L.; Miller, A. F. *J. Inorg. Biochem.* **2000**, *80*, 247–256.
640. Whittaker, M. M.; Whittaker, J. W. *J. Biol. Chem.* **1998**, *273*, 22188–22193.
641. Ramilo, C. A.; Leveque, V.; Guan, Y.; Lepock, J. R.; Tainer, J. A.; Nick, H. S.; Silverman, D. N. *J. Biol. Chem.* **1999**, *274*, 27711–27716.
642. Wagner, T.; Shumilin, I. A.; Bauerle, R.; Kretsinger, R. H. *J. Mol. Biol.* **2000**, *301*, 389–399.
643. Jordan, P. A.; Bohle, D. S.; Ramilo, C. A.; Evans, J. N. *Biochemistry* **2001**, *40*, 8387–8396.
644. Leppänen, V. M.; Nummelin, H.; Hansen, T.; Lahti, R.; Schäfer, G.; Goldman, A. *Protein Sci.* **1999**, *8*, 1218–1231.
645. Heikinheimo, P.; Lehtonen, J.; Baykov, A.; Lahti, R.; Cooperman, B. S.; Goldman, A. *Structure* **1996**, *4*, 1491–1508.
646. Heikinheimo, P.; Pohjanjoki, P.; Helminen, A.; Tasanen, M.; Cooperman, B. S.; Goldman, A.; Baykov, A.; Lahti, R. *Eur. J. Biochem.* **1996**, *239*, 138–143.
647. Harutyunyan, E. H.; Kuranova, I. P.; Vainshtein, B. K.; Höhne, W. E.; Lamzin, V. S.; Dauter, Z.; Teplyakov, A. V.; Wilson, K. S. *Eur. J. Biochem.* **1996**, *239*, 220–228.
648. Harutyunyan, E. H.; Oganessyan, V. Y.; Oganessyan, N. N.; Avaeva, S. M.; Nazarova, T. I.; Vorobyeva, N. N.; Kurilova, S. A.; Huber, R.; Mather, T. *Biochemistry* **1997**, *36*, 7754–7760.
649. Samygina, V. R.; Popov, A. N.; Rodina, E. V.; Vorobyeva, N. N.; Lamzin, V. S.; Polyakov, K. M.; Kurilova, S. A.; Nazarova, T. I.; Avaeva, S. M. *J. Mol. Biol.* **2001**, *314*, 633–645.

650. Samygina, V. R.; Antonyuk, S. V.; Lamzin, V. S.; Popov, A. N. *Acta Crystallogr. D* **2000**, *56*, 595–603.
651. Avaeva, S. M. *Biochemistry (Moscow)* **2000**, *65*, 361–372.
652. Young, T. W.; Kuhn, N. J.; Wadeson, A.; Ward, S.; Burges, D.; Cooke, G. D. *Microbiology* **1998**, *144*, 2563–2571.
653. Shintani, T.; Uchiumi, T.; Yonezawa, T.; Salminen, A.; Baykov, A. A.; Lahti, R.; Hachimori, A. *FEBS Lett*. **1998**, *439*, 263–266.
654. Kuhn, N. J.; Wadeson, A.; Ward, S.; Young, T. W. *Arch. Biochem. Biophys*. **2000**, *379*, 292–298.
655. Kuhn, N. J.; Ward, S. *Arch. Biochem. Biophys*. **1998**, *354*, 47–56.
656. Parfenyev, A. N.; Salminen, A.; Halonen, P.; Hachimori, A.; Baykov, A. A.; Lahti, R. *J. Biol. Chem*. **2001**, *276*.
657. Merckel, M. C.; Fabrichniy, I. P.; Salminen, A.; Kalkkinen, N.; Baykov, A. A.; Lahti, R.; Goldman, A. *Structure* **2001**, *9*, 289–297.
658. Ahn, S.; Milner, A. J.; Fuetterer, K.; Konopka, M.; Ilias, M.; Young, T. W.; White, S. A. *J. Mol. Biol*. **2001**, *313*, 797–811.
659. Tanner, A.; Bowater, L.; Fairhurst, S. A.; Bornemann, S. *J. Biol. Chem*. **2001**, *276*, 43627–43634.
660. Anand, R.; Dorrestein, P. C.; Kinsland, C.; Begley, T. P.; Ealick, S. E. *Biochemistry* **2002**, *41*, 7659–7669.
661. Woo, E. J.; Dunwell, J. M.; Goodenough, P. W.; Marvier, A. C.; Pickersgill, R. W. *Nature Struct. Biol*. **2000**, *7*, 1036–1040.
662. Yamahara, T.; Shiono, T.; Suzuki, T.; Tanaka, K.; Takio, S.; Sato, K.; Yamazaki, S.; Satoh, T. *J. Biol. Chem*. **1999**, *274*, 33274–33278.
663. Ramos-Valdivia, A. C.; Van der Heijden, R.; Verpoorte, R. *Planta* **1997**, *203*, 155–161.
664. Ramos-Valdivia, A. C.; Van der Heijden, R.; Verpoorte, R.; Camara, B. *Eur. J. Biochem*. **1997**, *249*, 161–170.
665. Durbecq, V.; Sainz, G.; Oudjama, Y.; Clantin, B.; Bompard-Gilles, C.; Tricot, C.; Caillet, J.; Stalon, V.; Droogmans, L.; Villeret, V. *EMBO J*. **2001**, *20*, 1530–1537.
666. Bonanno, J. B.; Edo, C.; Eswar, N.; Pieper, U.; Romanowski, M. J.; Ilyin, V.; Gerchman, S. E.; Kycia, H.; Studier, F. W.; Sali, A.; Burley, S. K. *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 12896–12901.
667. Richard, S. B.; Ferrer, J.-L.; Bowman, M. E.; Lillo, A. M.; Tetzlaff, C. F.; Cane, D. E.; Noel, J. P. *J. Biol. Chem*. **2002**, *277*, 8667–8672.
668. Antharavally, B. S.; Poyner, R. P.; Ludden, P. W. *J. Am. Chem. Soc*. **1998**, *120*, 8897–8898.
669. Antharavally, B. S.; Poyner, R. R.; Zhang, Y.; Roberts, G. P.; Ludden, P. W. *J. Bacteriol*. **2001**, *183*, 5743–5746.
670. Kelly, B. S.; Antholine, W. E.; Griffith, O. W. *J. Biol. Chem*. **2001**, *23*, 23.
671. Haaf, A.; LeClaire, III. L.; Roberts, G.; Kent, H. M.; Roberts, T. M.; Stewart, M.; Neuhaus, D. *J. Mol. Biol*. **1998**, *284*, 1611–1624.
672. Kelly, D. P.; Shergill, J. K.; Lu, W. P.; Wood, A. P. *Antonie van Leeuwenhoek* **1997**, *71*, 95–107.
673. Bonet, M. L.; Liorca, F. I.; Cadenas, E. *Int. J. Biochem*. **1993**, *25*, 7–12.
674. Kim, G. J.; Kim, H. S. *Biochem. J*. **1998**, *330*, 295–302.
675. Baur, H.; Luethi, E.; Stalon, V.; Mercenier, A.; Haas, D. *Eur. J. Biochem*. **1989**, *179*, 53–60.
676. Carvajal, N.; V, L.; Salas, M.; Uribe, E.; Herrera, P.; Cerpa, J. *Biochem. Biophys. Res. Commun*. **1999**, *258*, 808–811.
677. Perozich, J.; Hempel, J.; Morris, S. M. *Biochim. Biophys. Acta* **1998**, *1382*, 23–37.
678. Conyers, G. B.; Wu, G.; Bessman, M. J.; Mildvan, A. S. *Biochemistry* **2000**, *39*, 2347–2354.
679. Harris, T. K.; Wu, G.; Massiah, M. A.; Mildvan, A. S. *Biochemistry* **2000**, *39*, 1655–1674.
680. Griepenburg, U.; Blasczyk, K.; Kappl, R.; Huettermann, J.; Auling, G. *Biochemistry* **1998**, *37*, 7992–7996.
681. Cunningham, D. F.; O'Connor, B. *Biochim. Biophys. Acta* **1997**, *1343*, 160–186.
682. Bazan, J. F.; Weaver, L. H.; Roderick, S. L.; Huber, R.; Matthews, B. W. *Proc. Natl. Acad. Sci. USA* **1994**, *91*, 2473–2477.
683. Baldwin, G. S.; Gormley, N. A.; Halford, S. E. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 345–364.
684. Hwang, K. Y.; Chung, J. H.; Kim, S. H.; Han, Y. S.; Cho, Y. *Nature Struct. Biol*. **1999**, *6*, 691–696.
685. Blaszczyk, J.; Tropea, J. E.; Bubunenko, M.; Routzahn, K. M.; Waugh, D. S.; Court, D. L.; Ji, X. *Structure* **2001**, *9*, 1225–1236.
686. Benning, M. M.; Shim, H.; Raushel, F. M.; Holden, H. M. *Biochemistry* **2001**, *40*, 2712–2722.
687. Kalb (Gilboa), A. J.; Habash, J.; Hunter, N. S.; Price, H. J.; Raftery, J.; Helliwell, J. R. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 279–304.
688. Kalb (Gilboa), A. J.; Helliwell, J. R. In *Handbook of Metalloproteins*; Messerschmidt, A., Huber, R., Poulos, T., Wieghardt, K., Eds.; Wiley: New York, 2001.
689. Gonzales, T.; Robertbaudouy, J. *FEMS Microbiol. Rev*. **1996**, *18*, 319–344.
690. Guss, J. M.; Freeman, H. C. In *Handbook of Metalloproteins*; Messerschmidt, A., Huber, R., Poulos, T., Wieghardt, K., Eds.; Wiley: New York, 2001.
691. Lowther, W. T.; Orville, A. M.; Madden, D. T.; Lim, S. J.; Rich, D. H.; Matthews, B. W. *Biochemistry* **1999**, *38*, 7678–7688.
692. Wilce, M. C. J.; Bond, C. S.; Dixon, N. E.; Freeman, H. C.; Guss, J. M.; Lilley, P. E.; Wilce, J. A. *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 3472–3477.
693. Cottrell, G. S.; Hooper, N. M.; Turner, A. J. *Biochemistry* **2000**, *39*, 15121–15128.
694. Zhang, L. B.; Crossley, M. J.; Dixon, N. E.; Ellis, P. J.; Fisher, M. L.; King, G. F.; Lilley, P. E.; MacLachlan, D.; Pace, R. J.; Freeman, H. C. *J. Biol. Inorg. Chem*. **1998**, *3*, 470–483.
695. Christianson, D. W.; Cox, J. D. *Annu. Rev. Biochem*. **1999**, *68*, 33–57.
696. Ash, D. E.; Cox, J. D.; Christianson, D. W. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 407–428.
697. Bewley, M. C.; Flanagan, J. M. In *Handbook of Metalloproteins*; Messerschmidt, A., Huber, R., Poulos, T., Wieghardt, K., Eds.; Wiley: New York, 2001.
698. Bewley, M. C.; Jeffrey, P. D.; Patchett, M. L.; Kanyo, Z. F.; Baker, E. N. *Structure* **1999**, *7*, 435–448.
699. Kanyo, Z. F.; Scolnick, L. R.; Ash, D. E.; Christianson, D. W. *Nature* **1996**, *383*, 554–557.
700. Scolnick, L. R.; Kanyo, Z. F.; Cavalli, R. C.; Ash, D. E.; Christianson, D. W. *Biochemistry* **1997**, *36*, 10558–10565.
701. Cox, J. D.; Cama, E.; Colleluori, D. M.; Pethe, S.; Boucher, J. L.; Mansuy, D.; Ash, D. E.; Christianson, D. W. *Biochemistry* **2001**, *40*, 2689–2701.

702. Cox, J. D.; Kim, N. N.; Traish, A. M.; Christianson, D. W. *Nature Struct. Biol.* **1999**, *6*, 1043–1047.
703. Kim, N. N.; Cox, J. D.; Baggio, R. F.; Emig, F. A.; Mistry, S. K.; Harper, S. L.; Speicher, D. W.; Morris, S. M.; Ash, D. E.; Traish, A.; Christianson, D. W. *Biochemistry* **2001**, *40*, 2678–2688.
704. Sossong, Jr., T. M.; Khangulov, S. V.; Cavalli, R. C.; Soprano, D. R.; Dismukes, G. C.; Ash, D. E. *J. Biol. Inorg. Chem.* **1997**, *2*, 433–443.
705. Elkins, J. M.; Clifton, I. J.; Hernandez, H.; Doan, L. X.; Robinson, C. V.; Schofield, C. J.; Hewitson, K. S. *Biochem. J.* **2002**, *366*, 423–434.
706. Yoder, D. W.; Hwang, J.; Penner-Hahn, J. E. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H. Eds.; Marcel Dekker: New York, 2000; Vol.37, pp 527–557.
707. Stemmler, T. L.; Sturgeon, B. E.; Randall, D. W.; Britt, R. D.; Penner-Hahn, J. E. *J. Am. Chem. Soc.* **1997**, *119*, 9215–9225.
708. Meier, A. E.; Whittaker, M. M.; Whittaker, J. W. *Biochemistry* **1996**, *35*, 348–360.
709. Barynin, V. V.; Whittaker, M. M.; Antonyuk, S. V.; Lamzin, V. S.; Harrison, P. M.; Artymiuk, P. J.; Whittaker, J. W. *Structure* **2001**, *9*, 725–738.
710. Antonyuk, S. V.; Melik-Adamyan, V. R.; Popov, A. N.; Lamzin, V. S.; Hempstead, P. D.; Harrison, P. M.; Artymyuk, P. J.; Barynin, V. V. *Cryst. Rep.* **2000**, *45*, 105–116.
711. Oddie, G. W.; Schenk, G.; Angel, N. Z.; Walsh, N.; Guddat, L. W.; De Jersey, J.; Cassady, A. I.; Hamilton, S. E.; Hume, D. A. *Bone (New York)* **2000**, *27*, 575–584.
712. Twitchett, M. B.; Sykes, A. G. *Eur. J. Inorg. Chem.* **1999**, 2105–2115.
713. Schenk, G.; Korsinczky, M. L. J.; Hume, D. A.; Hamilton, S.; DeJersey, J. *Gene* **2000**, *255*, 419–424.
714. Schenk, G.; Guddat, L. T.; Ge, Y.; Carrington, L. E.; Hume, D. A.; Hamilton, S.; de Jersey, J. *Gene* **2000**, *250*, 117–125.
715. Durmus, A.; Eicken, C.; Spener, F.; Krebs, B. *Biochim. Biophys. Acta* **1999**, *1434*, 202–209.
716. Durmus, A.; Eicken, C.; Sift, B. H.; Kratel, A.; Kappl, R.; Hüttermann, J.; Krebs, B. *Eur. J. Biochem.* **1999**, *260*, 709–716.
717. Sift, B. H.; Durmus, A.; Meyer-Klaucke, W.; Krebs, B. *J. Synchrot. Rad.* **1999**, *6*, 421–422.
718. Schenk, G.; Boutchard, C. L.; Carrington, L. E.; Noble, C. J.; Moubaraki, B.; Murray, K. S.; de Jersey, J.; Hanson, G. R.; Hamilton, S. *J. Biol. Chem.* **2001**, *276*, 19084–19088.
719. Schenk, G.; Ge, Y.; Carrington, L. E.; Wynne, C. J.; Searle, I. R.; Carroll, B. J.; Hamilton, S.; de Jersey, J. *Arch. Biochem. Biophys.* **1999**, *370*, 183–189.
720. Klabunde, T.; Sträter, N.; Frohlich, R.; Witzel, H.; Krebs, B. *J. Mol. Biol.* **1996**, *259*, 737–748.
721. Uppenberg, J.; Lindqvist, F.; Svensson, C.; Ek-Rylander, B.; Andersson, G. *J. Mol. Biol.* **1999**, *290*, 201–211.
722. Guddat, L. W.; McAlpine, A. S.; Hume, D.; Hamilton, S.; de Jersey, J.; Martin, J. L. *Structure* **1999**, *7*, 757–767.
723. Schenk, G.; Carrington, L. E.; Hamilton, S. E.; de Jersey, J.; Guddat, L. W. *Acta Crystallogr. D* **1999**, *55*, 2051–2052.
724. Barford, D.; Das, A. K.; Egloff, M. P. *Annu. Rev. Biophys. Biomol. Struct.* **1998**, *27*, 133–164.
725. Barford, D. *Biochem. Soc. Trans.* **1999**, *27*, 751–766.
726. Rusnak, F. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H. Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 305–343. .
727. Rusnak, F.; Mertz, P. *Physiol. Rev.* **2000**, *80*, 1483–1521.
728. Dobson, S.; May, T.; Berriman, M.; Del Vecchio, C.; Fairlamb, A. H.; Chakrabarti, D.; Barik, S. *Mol. Biochem. Parasitol.* **1999**, *99*, 167–181.
729. Endo, S.; Connor, J. H.; Forney, B.; Zhang, L.; Ingebritsen, T. S.; Lee, E. Y. C.; Shenolikar, S. *Biochemistry* **1997**, *36*, 6986–6992.
730. Maynes, J. T.; Bateman, K. S.; Cherney, M. M.; Das, A. K.; Luu, H. A.; Holmes, C. F. B.; James, M. N. G. *J. Biol. Chem.* **2001**, *276*, 44078–44082.
731. Nishito, Y.; Usui, H.; Shinzawa-Itoh, K.; Inoue, R.; Tanabe, O.; Nagase, T.; Murakami, T.; Takeda, M. *FEBS Lett.* **1999**, *447*, 29–33.
732. Nishito, Y.; Usui, H.; Tanabe, O.; Shimizu, M.; Takeda, M. *J. Biochem.* **1999**, *126*, 632–638.
733. Kissinger, C. R.; Parge, H. E.; Knighton, D. R.; Lewis, C. T.; Pelletier, L. A.; Tempczyk, A.; Kalish, V. J.; Tucker, K. D.; Showalter, R. E.; Moomaw, E. W.; Gastinel, L. N.; Habuka, N.; Chen, X. H.; Maldonado, F.; Barker, J. E.; Bacquet, R.; Villafranca, J. E. *Nature* **1995**, *378*, 641–644.
734. White, D. J.; Reiter, N. J.; Sikkink, R. A.; Yu, L.; Rusnak, F. *Biochemistry* **2001**, *40*, 8918–8929.
735. Voegtli, W. C.; White, D. J.; Reiter, N. J.; Rusnak, F.; Rosenzweig, A. C. *Biochemistry* **2000**, *39*, 15365–15374.
736. Das, A. K.; Helps, N. R.; Cohen, P. T. W.; Barford, D. *EMBO J.* **1996**, *15*, 6798–6809.
737. Jedrzejas, M. J.; Chander, M.; Setlow, P.; Krishnasamy, G. *EMBO J.* **2000**, *19*, 1419–1431.
738. Jedrzejas, M. J.; Chander, M.; Setlow, P.; Krishnasamy, G. *J. Biol. Chem.* **2000**, *275*, 23146–23153.
739. Chander, M.; Setlow, P.; Lamani, E.; Jedrzejas, M. J. *J. Struct. Biol.* **1999**, *126*, 156–165.
740. Garcia-Dominguez, M.; Reyes, J. C.; Florencio, F. J. *Eur. J. Biochem.* **1997**, *244*, 258–264.
741. Gill, H. S.; Eisenberg, D. *Biochemistry* **2001**, *40*, 1903–1912.
742. Gill, H. S.; Pfluegl, G. M.; Eisenberg, D. *Biochemistry* **2002**, *41*, 9863–9872.
743. Bhosale, S. H.; Rao, M. B.; Deshpande, V. V. *Microbiol. Rev.* **1996**, *60*, 280 ff .
744. Moneke, A. N.; Obi, S. K. C.; Bisswanger, H. *Appl. Microbiol. Biotechnol.* **1998**, *50*, 552–557.
745. Kristo, P.; Saarelainen, R.; Fagerstrom, R.; Aho, S.; Korhola, M. *Eur. J. Biochem.* **1996**, *237*, 240–246.
746. Bogumil, R.; Kappl, R.; Hüttermann, J. In *Metal Ions In Biological Systems*; Sigel, A., Sigel, H. Eds.; Marcel Dekker: New York, 2000; Vol.37, pp 365–405.
747. Asboth, B.; Naray-Szabo, G. *Curr. Protein Pept. Sci.* **2000**, *1*, 237–254.
748. Weatherburn, D. C. In *Handbook on Metalloproteins*; Bertini, I., Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2001; Chapter 8.
749. Giraud, M.-F.; Naismith, J. H. *Curr. Opin. Struct. Biol.* **2000**, *10*, 687–696.
750. Korndorfer, I. P.; Fessner, W. D.; Matthews, B. W. *J. Mol. Biol.* **2000**, *300*, 917–933.
751. Seemann, J. E.; Schulz, G. E. *J. Mol. Biol.* **1997**, *273*, 256–268.
752. Focia, P. J.; Craig, S. P.; Nievesalicea, R.; Fletterick, R. J.; Eakin, A. E. *Biochemistry* **1998**, *37*, 15066–15075.
753. Focia, P. J.; Craig III, S. P.; Eakin, A. E. *Biochemistry* **1998**, *37*, 17120–17127.

754. Heroux, A.; White, E. L.; Ross, L. J.; Davis, R. L.; Borhani, D. W. *Biochemistry* **1999**, *38*, 14495–14506.
755. Heroux, A.; White, E. L.; Ross, L. J.; Borhani, D. W. *Biochemistry* **1999**, *38*, 14485–14494.
756. Heroux, A.; White, E. L.; Ross, L. J.; Kuzin, A. P.; Borhani, D. W. *Structure Fold. Des.* **2000**, *8*, 1309–1318.
757. Sharma, V.; Grubmeyer, C.; Sacchettini, J. C. *Structure* **1998**, *6*, 1587–1599.
758. Boix, E.; Zhang, Y.; Swaminathan, G. J.; Brew, K.; Acharya, K. R. *J. Biol. Chem.* **2002**, *277*, 28310–28318.
759. Boix, E.; Swaminathan, G. J.; Zhang, Y. N.; Natesh, R.; Brew, K.; Acharya, K. R. *J. Biol. Chem.* **2001**, *276*, 48608–48614.
760. Gastinel, L. N.; Bignon, C.; Misra, A. K.; Hindsgaul, O.; Shaper, J. H.; Joziasse, D. H. *EMBO J.* **2001**, *20*, 638–649.
761. Persson, K.; Ly, H. D.; Dieckelmann, M.; Wakarchuk, W. W.; Withers, S. G.; Strynadka, N. C. *Nature Struct. Biol.* **2001**, *8*, 166–175.
762. Ramakrishnan, B.; Qasba, P. K. *J. Mol. Biol.* **2001**, *310*, 205–218.
763. Ramakrishnan, B.; Shah, P. S.; Qasba, P. K. *J. Biol. Chem.* **2001**, *276*, 37665–37671.
764. Moréra, S.; Larivière, L.; Kurzeck, J.; Aschke-Sonnenborn, U.; Freemont, P. S.; Janin, J.; Rüger, W. *J. Mol. Biol.* **2001**, *311*, 569–577.
765. Tarbouriech, N.; Charnock, S. J.; Davies, G. J. *J. Mol. Biol.* **2001**, *314*, 655–661.
766. Charnock, S. J.; Davies, G. J. *Biochemistry* **1999**, *38*, 6380–6385.
767. Ünligil, U. M.; Zhou, S. H.; Yuwaraj, S.; Sarkar, M.; Schachter, H.; Rini, J. M. *EMBO J.* **2000**, *19*, 5269–5280.
768. Ünligil, U. M.; Rini, J. M. *Curr. Opin. Struct. Biol.* **2000**, *10*, 510–517.
769. Pedersen, L. C.; Tsuchida, K.; Kitagawa, H.; Sugahara, K.; Darden, T. A.; Negishi, M. *J. Biol. Chem.* **2000**, *275*, 34580–34585.
770. Shan, S.; Kravchuk, A. V.; Piccirilli, J. A.; Herschlag, D. *Biochemistry* **2001**, *40*, 5161–5171.
771. Shan, S.-o.; Yoshida, A.; Sun, S.; Piccirilli, J. A.; Herschlag, D. *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 12299–12304.
772. Johnson, K. A.; Chen, L.; Yang, H.; Roberts, M. F.; Stec, B. *Biochemistry* **2001**, *40*, 618–630.
773. Horton, N. C.; Connolly, B. A.; Perona, J. J. *J. Am. Chem. Soc.* **2000**, *122*, 3314–3324.
774. Chevalier, B. S.; Monnat, R. J.; Stoddard, B. L. *Nature Struct. Biol.* **2001**, *8*, 312–316.
775. Baykov, A. A.; Hyytia, T.; Turkina, M. V.; Efimova, I. S.; Kasho, V. N.; Goldman, A.; Cooperman, B. S.; Lahti, R. *Eur. J. Biochem.* **1999**, *260*, 308–317.
776. Faller, P.; Debus, R. J.; Brettel, K.; Sugiura, M.; Rutherford, A. W.; Boussac, A. *Proc. Natl. Acad. Sci. USA* **2001**, *27*, 27.
777. Bricker, T. M.; Ghanotakis, D. F. *Adv. Photosynth.* **1996**, *4*, 113–136.
778. Barber, J.; Morris, E.; Buchel, C. *Biochim. Biophys. Acta* **2000**, *1459*, 239–247.
779. Barber, J.; Kuhlbrandt, V. *Curr. Opin. Struct. Biol.* **1999**, *9*, 469–475.
780. Renger, G. *Biochim. Biophys. Acta* **2001**, *1503*, 210–228.
781. Hankamer, B.; Barber, J.; Boekema, E. J. *Annu. Rev. Plant Physiol. Plant Mol. Biol.* **1997**, *48*, 641–671.
782. Debus, R. J. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 657–711.
783. Dau, H.; Iuzzolino, L.; Dittmer, J. *Biochim. Biophys. Acta* **2001**, *1503*, 24–39.
784. Robblee, J. H.; Cinco, R. M.; Yachandra, V. K. *Biochim. Biophys. Acta* **2001**, *1503*, 7–23.
785. Tracewell, C. A.; Vrettos, J. S.; Bautista, J. A.; Frank, H. A.; Brudvig, G. W. *Arch. Biochem. Biophys.* **2001**, *385*, 61–69.
786. Vrettos, J. S.; Limburg, J.; Brudvig, G. W. *Biochim. Biophys. Acta* **2001**, *1503*, 229–245.
787. Ono, T. *Biochim. Biophys. Acta* **2001**, *1503*, 40–51.
788. Nugent, J. H.; Rich, A. M.; Evans, M. C. *Biochim. Biophys. Acta* **2001**, *1503*, 138–146.
789. Hillier, W.; Wydrzynski, T. *Biochim. Biophys. Acta* **2001**, *1503*, 197–209.
790. Hoganson, C. W.; Babcock, G. T. In *Metal Ions in Biological Systems*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2000; Vol. 37, pp 613–656.
791. Messinger, J. *Biochim. Biophys. Acta* **2000**, *1459*, 481–488.
792. Klimov, V. V.; Baranov, S. V. *Biochim. Biophys. Acta* **2001**, *1503*, 187–196.
793. Van Rensen, J. J. S.; Xu, C.; Govindjee, *Physiol. Plant.* **1999**, *105*, 585–592.
794. Seidler, A.; Rutherford, A. W. *Biochemistry* **1996**, *35*, 12104–12110.
795. Debus, R. J. *Biochim. Biophys. Acta* **2001**, *1503*, 164–186.
796. Chroni, S.; Ghanotakis, D. F. *Biochim. Biophys. Acta* **2001**, *1504*, 432–437.
797. Rappaport, F.; Lavergne, J. *Biochim. Biophys. Acta* **2001**, *1503*, 246–259.
798. Dekker, J. P.; Van Grondelle, R. *Photosynth. Res.* **2000**, *63*, 195–208.
799. Diner, B. A. *Biochim. Biophys. Acta* **2001**, *1503*, 147–163.
800. Debus, R. J.; Campbell, K. A.; Gregor, W.; Li, Z. L.; Burnap, R. L.; Britt, R. D. *Biochemistry* **2001**, *40*, 3690–3699.
801. Debus, R. J.; Campbell, K. A.; Peloquin, J. M.; Pham, D. P.; Britt, R. D. *Biochemistry* **2000**, *39*, 470–478.
802. Kuzek, D.; Pace, R. J. *Biochim. Biophys. Acta* **2001**, *1503*, 123–137.
803. Chu, H. A.; Hillier, W.; Law, N. A.; Babcock, G. T. *Biochim. Biophys. Acta* **2001**, *1503*, 69–82.
804. Cua, A.; Stewart, D. H.; Reifler, M. J.; Brudvig, G. W.; Bocian, D. F. *J. Am. Chem. Soc.* **2000**, *122*, 2069–2077.
805. Berthomieu, C.; Hienerwadel, R.; Boussac, A.; Breton, J.; Diner, B. A. *Biochemistry* **1998**, *37*, 10547–10554.
806. Ivancich, A.; Mattioli, T. A.; Un, S. *J. Am. Chem. Soc.* **1999**, *121*, 5743–5753.
807. Noguchi, T.; Inoue, Y.; Tang, X.-S. *Biochemistry* **1997**, *36*, 14705–14711.
808. Hillier, W.; Babcock, G. T. *Biochemistry* **2001**, *40*, 1503–1509.
809. Mukerji, I.; Andrews, J. C.; DeRose, V. J.; Latimer, M. J.; Yachandra, V. K.; Sauer, K.; Klein, M. P. *Biochemistry* **1994**, *33*, 9712–9721.
810. Hasegawa, K.; Ono, T.; Inoue, Y.; Kusunoki, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1013–1023.
811. Meinke, C.; Sole, V. A.; Pospisil, P.; Dau, H. *Biochemistry* **2000**, *39*, 7033–7040.
812. Cinco, R. M.; McFarlane Holman, K. L.; Robblee, J. H.; Yano, J.; Pizarro, S. A.; Bellacchio, E.; Sauer, K.; Yachandra, V. K. *Biochemistry* **2002**, *41*, 12928–12933.
813. Cinco, R. M.; Robblee, J. H.; Rompel, A.; Fernandez, C.; Yachandra, V. K.; Sauer, K.; Klein, M. P. *J. Phys. Chem. B* **1998**, *102*, 8248–8256.
814. Roelofs, T. A.; Liang, W. C.; Latimer, M. J.; Cinco, R. M.; Rompel, A.; Andrews, J. C.; Sauer, K.; Yachandra, V. K.; Klein, M. P. *Proc. Natl. Acad. Sci. USA* **1996**, *93*, 3335–3340.

815. Roelofs, T. A.; Liang, W.; Latimer, M. J.; Cinco, R.; Rompel, A.; Andrews, J. C.; Yachandra, V. K.; Sauer, K.; Klein, M. P.*Light Biosphere*, Proceedings of the 10th International Photosynthesis Congress; 1995; Vol. 2, pp 459-462.
816. Messinger, J.; Robblee, J. H.; Bergmann, U.; Fernandez, C.; Glatzel, P.; Visser, H.; Cinco, R. M.; McFarlane, K. L.; Bellacchio, E.; Pizarro, S. A.; Cramer, S. P.; Sauer, K.; Klein, M. P.; Yachandra, V. K. *J. Am. Chem. Soc.* **2001**, *123*, 7804–7820.
817. Carrell, T. G.; Tyryshkin, A. M.; Dismukes, G. C. *J. Biol. Inorg. Chem.* **2002**, *7*, 2–22.
818. Peloquin, J. M.; Britt, R. D. *Biochim. Biophys. Acta* **2001**, *1503*, 96–111.
819. Britt, R. D.; Peloquin, J. M.; Campbell, K. A. *Annu. Rev. Biophys. Biomol. Struct.* **2000**, *29*, 463–495.
820. Boussac, A.; Rutherford, A. W. *Biochim. Biophys. Acta* **2000**, *1457*, 145–156.
821. Boussac, A.; Sugiura, M.; Inoue, Y.; Rutherford, A. W. *Biochemistry* **2000**, *39*, 13788–13799.
822. Manchanda, R.; Brudvig, G. W.; Crabtree, R. H. *Coord. Chem. Rev.* **1995**, *144*, 1–38.
823. Limburg, J.; Vrettos, J. S.; Liable-Sands, L. M.; Rheingold, A. L.; Crabtree, R. H.; Brudvig, G. W. *Science* **1999**, *283*, 1524–1527.
824. Limburg, J.; Vrettos, J. S.; Chen, H. Y.; de Paula, J. C.; Crabtree, R. H.; Brudvig, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 423–430.
825. Ruettinger, W. F.; Dismukes, G. C. *Inorg. Chem.* **2000**, *39*, 1021–1027.
826. Ruettinger, W.; Yagi, M.; Wolf, K.; Bernasek, S.; Dismukes, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 10353–10357.
827. Yagi, M.; Wolf, K. V.; Baesjou, P. J.; Bernasek, S. L.; Dismukes, G. C. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2925–2928.
828. Rhee, K. H.; Morriss, E. P.; Barber, J.; Kuhlbrandt, W. *Nature* **1998**, *396*, 283–286.
829. Zouni, A.; Jordan, R.; Schlodder, E.; Fromme, P.; Witt, H. T. *Biochim. Biophys. Acta* **2000**, *1457*, 103–105.
830. Kuhl, H.; Kruip, J.; Seidler, A.; Krieger-Liszkay, A.; Bunker, M.; Bald, D.; Scheidig, A. J.; Rogner, M. *J. Biol. Chem.* **2000**, *275*.
831. Shen, J.-R.; Kamiya, N. *Biochemistry* **2000**, *39*, 14739–14744.
832. Zouni, A.; Witt, H.-T.; Kern, J.; Fromme, P.; Krauβ, N.; Saenger, W.; Orth, P. *Nature* **2001**, *409*, 739–743.
833. Rutherford, A. W.; Faller, P. *Trends Biochem. Sci.* **2001**, *26*, 341–344.
834. Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.
835. Allen, F. H.; Hoy, V. J. *Encycl. Computat. Chem.* **1998**, *1*, 155–167.

Comprehensive Coordination Chemistry II
ISBN (set): 0-08-0437486

Volume 5, (ISBN 0-08-0443273); pp 1–125

5.2 Technetium

R. ALBERTO
University of Zürich, Switzerland

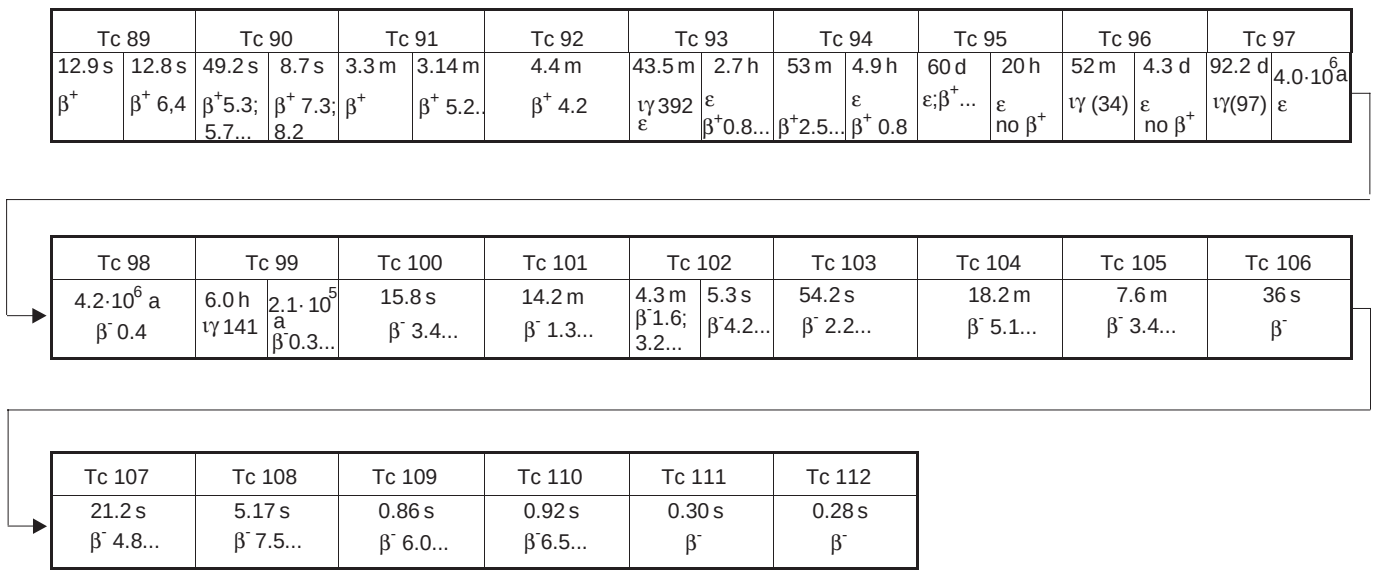
5.2.1 INTRODUCTION

Technetium chemistry was covered in part in the first edition of *Comprehensive Coordination Chemistry* (*CCC*,1987) only under the heading of nuclear medicine in the Chapter 65 (Volume 6) by C. Jones. This section therefore gives an account of technetium coordination chemistry from its discovery in 1937 to the present day. According to its place in the periodic table, technetium is a second-row transition element and as such exhibits a rich and potentially useful coordination chemistry, ranging from oxidation state +VII to −I. However, the driving force for the development of the chemistry has been the potential application of technetium complexes in nuclear medicine and this has led to a focus on the middle oxidation states, which offers a contrast to the chemistry of the neighboring element in the periodic table. The radioactivity of the most abundant isotope of technetium, ^{99}Tc, and its limited availability from fission reactors after processing burned-out nuclear fuel, restricted its application in fields other than nuclear medicine, such as catalysis. The position of technetium in the periodic table would suggest very interesting properties for such purposes. Nevertheless, many different types of coordination compound have been reported and are here categorized, primarily using the formal oxidation states of technetium. Further subdivisions are made based on the types of ligand involved. Separate sections cover more specialized areas, such as ^{99}Tc NMR and radiopharmaceutical chemistry. Space restrictions have prevented the coverage from being totally comprehensive.

Technetium was the last element of the transition-metal series to be discovered. During the late nineteenth century, different groups claimed to have discovered the element predicted by Mendelejev to be between molybdenum and ruthenium, with an atomic weight of about 100. They gave various names to this element, such as illmenium, but the existence of the element was not substantiated. Investigations by Noddack and Tacke[1] in the first quarter of the twentieth century led to the unambiguous discovery of rhenium. From their systematic studies they also claimed to have evidence for the X-ray spectroscopic detection of the element with the number 43[2], which they named masurium. Although weighable amounts of element 75 were isolated at that time,[3] this was not the case for element 43. The element 75 received the name rhenium, as proposed by Noddack and Tacke, but masurium (43) was not recognized since no evidence for its isolation was given. Obviously, the interpretation of the X-ray results was wrong, although the lines which were assigned to this element fitted quite well with the calculated numbers. Through the 1920s the existence of element 43 remained in doubt, but its postulated existence by Noddack and Tacke could not be ruled out completely. It was not until 1934 that the situation was resolved, when Mattauch formulated his rule of stability of nuclei (rule of stable isobars),[4] which predicted that there would be no stable, directly neighboring isobars in the table of isotopes. This ruled out the existence of any stable isotopes of element 43, since all the corresponding places were already occupied by stable isotopes of the neighboring elements molybdenum and ruthenium. Nowadays the series 4 elements which seemed to be in contradiction of this rule are known to be radioactive, although sometimes with an exceptionally long half-life.

In 1937 Perrier and Segré discovered that molybdenum irradiated with deuterons exhibited a strong, unknown radioactivity.[5] After ruling out that it originated from unstable isotopes of other neighboring elements or impurities, it was concluded that the radioactivity must be related to element 43.[6] In 1947, at the suggestion of Paneth,[7] the element was given the name technetium, and this was then universally accepted. With the discovery of fission in 1939,[8] it became clear that element 43 would be a fission product.[9] With the availability of fission reactors in the late 1940s, the production of macroscopic amounts of technetium started. Within a short time the chemical and physico-chemical properties, as determined by Perrier and Segré with microscopic amounts of the element, were confirmed on the macroscopic level. Nowadays, about 21 isotopes of technetium are known, produced by different nuclear reactions, and there is a range of half-life times from 0.3 s (^{111}Tc) to 5.2×10^6 yr (^{98}Tc). The properties of a number of the most important isotopes can be seen in Scheme 1.

The three isotopes with the longest half-life times, ^{97}Tc, ^{98}Tc, and ^{99}Tc, were produced in small quantities as early as 1955 by the bombardment of molybdenum with 22 MeV protons.[10] Although ^{97}Tc is the isotope with the longest half-life time, it is not the major isotope available from nuclear


Tc 89
12.9 s
β+
12.8 s
β+ 6,4
Tc 90
49.2 s
β+5.3; 5.7...
8.7 s
β+ 7.3; 8.2
Tc 91
3.3 m
β+
3.14 m
β+ 5.2..
Tc 92
4.4 m
β+ 4.2
Tc 93
43.5 m
ιγ 392
ε
2.7 h
ε
β+0.8...
Tc 94
53 m
β+2.5...
4.9 h
ε
β+ 0.8
Tc 95
60 d
ε;β+...
20 h
ε
no β+
Tc 96
52 m
ιγ (34)
4.3 d
ε
no β+
Tc 97
92.2 d
ιγ(97)
4.0·10^6 a
ε
Tc 98
4.2·10^6 a
β- 0.4
Tc 99
6.0 h
ιγ 141
2.1· 10^5 a
β-0.3...
Tc 100
15.8 s
β- 3.4...
Tc 101
14.2 m
β- 1.3...
Tc 102
4.3 m
β-1.6; 3.2...
5.3 s
β-4.2...
Tc 103
54.2 s
β- 2.2...
Tc 104
18.2 m
β- 5.1...
Tc 105
7.6 m
β- 3.4...
Tc 106
36 s
β-
Tc 107
21.2 s
β- 4.8...
Tc 108
5.17 s
β- 7.5...
Tc 109
0.86 s
β- 6.0...
Tc 110
0.92 s
β-6.5...
Tc 111
0.30 s
β-
Tc 112
0.28 s
β-

Scheme 1

fission. After fission, neutron-rich isotopes decay along an isobar line to the most stable isotopes. All these lines are blocked by stable molybdenum isotopes with the exception of ^{99}Mo, which is unstable and decays to ^{99}Tc with a half-life time of 2.12×10^5 yr. This is the important isotope of technetium and virtually all the chemistry described in the following sections has been performed using it. In nuclear fission reactors, the fission yield for ^{99}Tc is about 6.1%.[11] Therefore, a 100 MW reactor produces about 2.5 g of ^{99}Tc per day.[12] Integration of the energy produced over the years in such reactors suggests that the total amount of ^{99}Tc currently on earth should be in the range of 2,000 kg.

The relatively short half-life times of all the technetium isotopes clearly reveal that no primordial technetium can be left on earth. However, technetium does occur in nature. Spontaneous fission of ^{235}U leads to ^{99}Tc, albeit in very tiny amounts. According to different determinations of ^{99}Tc in pitchblende,[13,14] 5.3 kg of pitchblende contains about 10^{-3} μg of ^{99}Tc, a result which is in good agreement with the theoretical value for the spontaneous fission yield for ^{99}Tc. About 2×10^9 yr ago a remarkable geological event occurred in Oklo, Africa.[15] It was found in certain uranium mines in the republic of Gabon that the ratio of ^{235}U/^{238}U was much lower than in other native ores. A much higher content of ^{99}Ru was also detected, clearly indicating that a spontaneous and permanent fission reaction must have taken place at this location.[16] Although large amounts of ^{99}Tc must have been produced, they decayed completely over time.

Technetium has played an important role in the confirmation of modern cosmological theories, and in particular the concept of the nucleosynthesis of heavy elements by a slow-neutron capture process (the so called *s*-process).[17] Since the longest-lived isotope has a half life of 5.2×10^6 yr, the presence of technetium has been widely accepted as palpable evidence for ongoing nucleosynthesis.[18,19] It was originally believed that the heavy elements were created in primordial events, according to the ideas of Gamow and his colleagues. But in 1952 Merrill detected technetium Tc$^{\text{I}}$ absorption lines at 4,031, 4,238, 4,268, and 4,297 Å in S-type stars, which have a relatively cold surface temperature of about 3,000 K.[20,21] Later on technetium was also found in other stars. Stellar spectra reveal that technetium has about the same abundance as other heavy elements, clearly demonstrating its continuous synthesis by the *s*-process. In recent times, the thorough study of the stellar spectra of a series of S-stars reveals that not all display the Tc$^{\text{I}}$ lines. Those exhibiting the lines belong to a so-called intrinsic system, whereas those without the lines belong to an extrinsic system, i.e., a binary star system. From the data it was concluded that in the binary systems mass transfer must have taken place from the S-star to its companion, resulting in significant technetium depletion and hence a lack of observable spectral lines due to technetium (Figure 1).[22]

As mentioned earlier, ^{99}Tc is the most important technetium isotope since it is produced in large amounts by nuclear fission. The recycling of nuclear fuel waste by the Purex process produces a waste solution with a ^{99}Tc concentration of about 5–100mg L^{-1}. ^{99}Tc pertechnetate (about 18 g) was first isolated in 1952 by precipitation of $[^{99}TcO_4]^-$ with $[As_4P]^+$ as the counterion.[23] In a very convenient process, $[^{99}TcO_4]^-$ is extracted with pyridine from an aqueous solution, and after several further steps crystallized and recrystallized as $[NH_4][^{99}TcO_4]$ in a purity of better than 99.99%.[24] It is available in this form from several suppliers (Amersham or Oak Ridge National Laboratory). Reduction with H_2 at 400–500 °C gives the element in the amorphous metallic form, with a melting point of 2,172 °C.[25] Although effectively an artificial element, technetium is relatively cheap and the actual price is determined by the cost of transportation rather than by the cost of production. Technetium-99 is only generally available as a $[TcO_4]^-$ salt, either as the solid or in aqueous solution, which largely determines the methodology of technetium coordination chemistry. Any other starting material has ultimately to be prepared from $[NH_4][^{99}TcO_4]$ in water, and it is a significant challenge to prepare coordination compounds directly and solely from this source. The technetium chemist does not have the luxury of access to a wide range of halides or low-valent carbonyls as precursors. The metastable ^{99m}Tc isotope

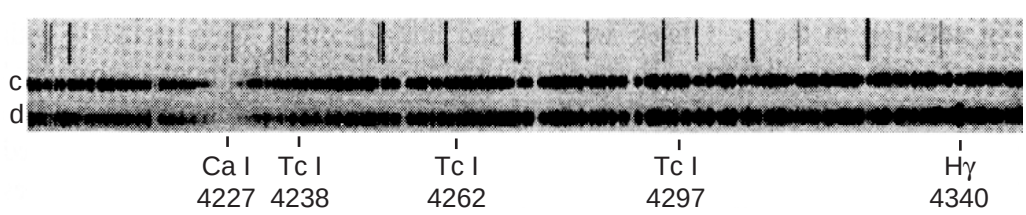
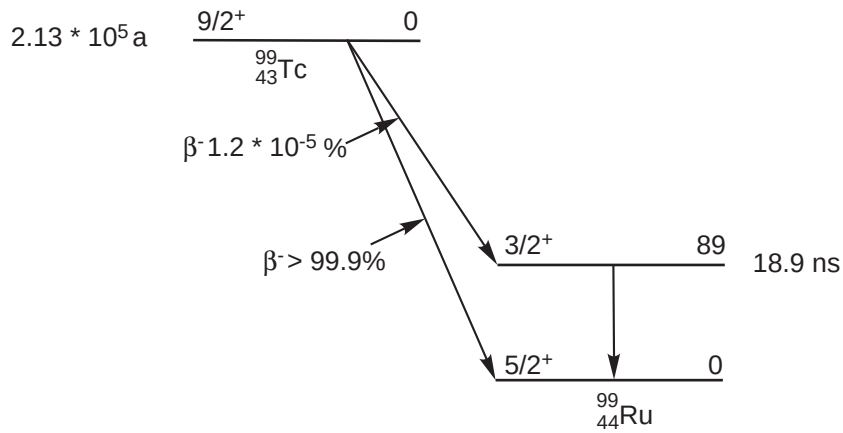


Figure 1 Spectrum of Tc I in the evolved giant Band.

used for medical imaging also is exclusively available as solutions of $[^{99m}TcO_4]^-$ in water, but at significantly higher dilution (10^{-8} M).

The ^{99}Tc isotope is a weak β^--emitter, with no γ-radiation and with a half-life of 2.12×10^5 yr. The β^- energy is 292 keV and 203 keV, the latter having a very low probability of 1.2×10^{-5}%.[26,27] A 89 keV γ-line results from an internal transition of ^{99m}Ru to stable ^{99}Ru, which is also the end product of direct ^{99}Tc decay. The nuclear spin of ^{99}Tc is 9/2, with a nuclear magnetic moment of +5.6847 nuclear magnetons.[28] The specific activity of $[NH_4][^{99}TcO_4]$ is 629 MBq g^{-1} (or 17mCi g^{-1}). The decay properties permit the handling of ^{99}Tc for normal chemical studies in quantities from 20 mg up to 1 g. Special shielding precautions are generally not required, since the low-energy β^- radiation is usually completely absorbed by glass. With large amounts of ^{99}Tc compounds, bremsstrahlung radiation is produced from glass and precautions must be taken. Gloves and safety glasses are essential at all times, since β-reduction can cause damage to living tissue. For the same reason ingestion or inhalation of technetium should be avoided; although only a weak β-emitter, ^{99}Tc can cause serious biological damage in the body. Appropriate dosimetry data are compiled in official regulations.[29–31] Glove boxes are normally not required: a well-ventilated hood or conventional Schlenk glassware is sufficient, provided that no volatile products are formed. It is the experience of the authors, however, that it is preferable to work in plexiglass glove boxes fitted with a cover, using fixed gloves that can be opened and closed. This allows working with a minimum of contamination for the worker and the laboratory.

For work with solutions, and in particular with solid materials, precautions against electrostatic charging and the effects of air currents have to be taken, and standard radiochemical techniques should be used. The handling techniques required for other technetium isotopes such as ^{99m}Tc are described below (Scheme 2).



Scheme 2

The major interest in technetium chemistry is linked to its practical application in radiopharmacy or nuclear medicine. The ^{99}Tc isotope is of the utmost importance for coordination chemistry, whereas its isomeric precursor ^{99m}Tc is the workhorse in nuclear-medicine applications. The unstable parent of ^{99m}Tc is ^{99}Mo, which is a β^--emitter and decays to ^{99m}Tc, which then decays to the nuclear ground state ^{99}Tc by γ-emission, with a half-life time of about 6 h. The transition between ^{99m}Tc and ^{99}Tc is nuclear-spin forbidden and therefore relatively slow. The energy of the γ-photon is about 140 keV, which is sufficiently low to prevent a high dose burden to a patient but sufficiently energetic to penetrate tissue and emerge from internal organs. The distribution of ^{99m}Tc can be monitored externally using a scintillation counter. During the late 1950s it was discovered by chance that ^{99m}Tc can be continuously separated from the parent ^{99}Mo "generator system."[32–34] A generator consists of a column, in general aluminum oxide, loaded with some immobile parent nuclide, in this case ^{99}Mo. The affinity of the daughter product is much less than that of the parent, usually as a result of a reduced charge. Therefore, the daughter can be eluted whereas the parent remains adsorbed on the stationary phase, which supplies a continuous supply of the daughter radionuclide for a time period depending on the half-life time of the parent nuclide. The ^{99m}Tc generator uses this principle, and is crucial to the success and widespread application of ^{99m}Tc in nuclear medicine. The physician can "milk" a sufficient amount of activity for the preparation of the compounds required for the patient in imaging.

After the discovery the generator system was quickly developed to a stage where its application on a routine basis was feasible. The first medical experiments were performed in the early 1960s with a study of thyroid physiology using $[^{99m}TcO_4]^-$, among other isotopes.[35] The requirement for various diagnostic procedures then initiated a rapid expansion of the coordination chemistry of technetium.[36] Many coordination compounds were tested for *in vivo* applications and some are still in clinical use. The chemistry of these compounds is treated in detail in Section 5.2.3 below. Simple coordination compounds for radiopharmaceutical applications are often referred to as first-generation radiopharmaceuticals. For a number of these first-generation compounds the exact structure is not known, although they are in regular clinical use. For full characterization of a radiopharmaceutical it is necessary to prepare and completely characterize the same compound on the macroscopic ^{99}Tc level and then to confirm the structure of the ^{99m}Tc compound by comparative HPLC or thin-layer chromatography methods. However, in some cases this approach is not possible, since at the high dilutions needed for ^{99m}Tc the thermodynamics of complexation are different and other products form at the macroscopic level. Frequently, then, chemistry performed with ^{99}Tc cannot be extrapolated to the no-carrier-added (n.c.a.) level with ^{99m}Tc.

Since about 1990, a second generation of radiopharmaceuticals has emerged. The market for first-generation agents is now more or less saturated, but the interest in second-generation radiopharmaceuticals has increased exponentially. While in the first generation the Tc center was an essential part of the "bioactive" molecule, it plays only the role of a radioactive label in the second generation. This is a result of the demand for more specific radiopharmaceuticals that must rely on the targeting capability of the biomolecule, rather than on the random behavior of a pure coordination compound. A few examples are also described in the last section for which the recognition of a receptor is an intrinsic feature of the technetium coordination compound. In these compounds the technetium is essential in the way that it is part of a compound mimicking a bioactive entity like a steroid hormone. Examples from all three kinds of radiopharmaceuticals will be discussed in Section 5.2.3.

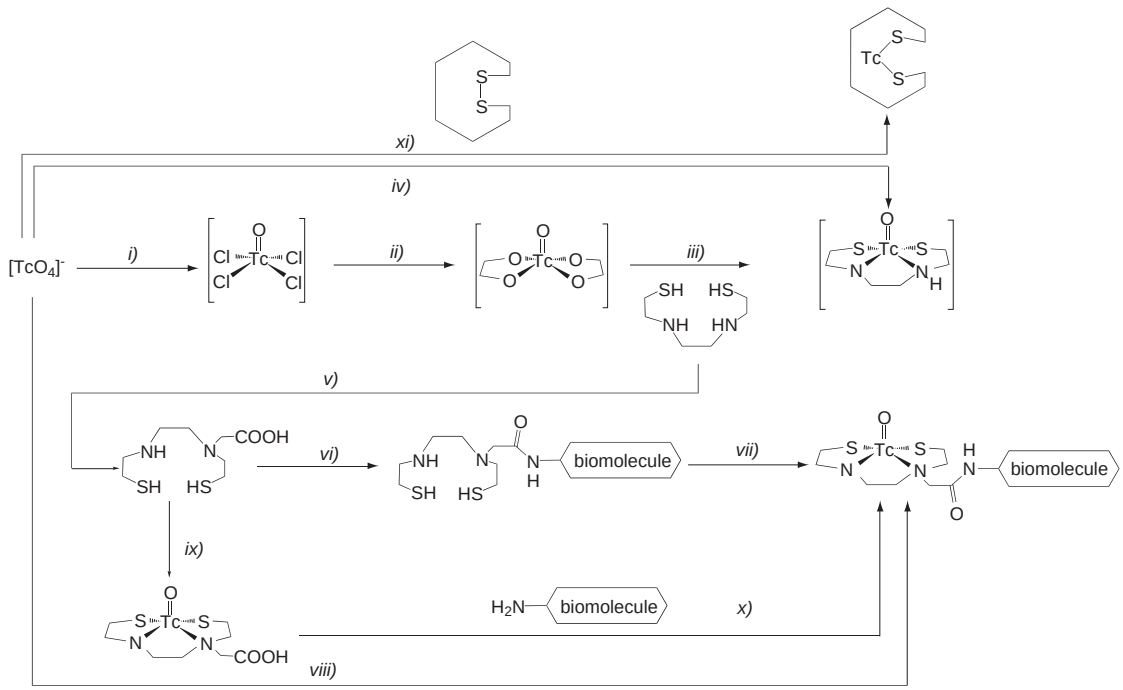
The interest in the coordination chemistry is based on the features described in this last paragraph. It is a challenge to prepare a Tc complex that is stable towards metabolical or chemical degradation in physiological media. Additionally such a coordination compound must be prepared, in one single step and in quantitative yield, directly from aqueous $[^{99m}TcO_4]^-$ solution as received from the generator. Furthermore, in combination with a targeting biomolecule the ligand must be bifunctional: one function for covalent attachment to the biomolecule and the second function for chelating to the Tc center. It is a real challenge to synthesize suitable complexes under such circumstances, and the range of complexes produced is a tribute to coordination chemistry. The requirements for the application are clearly not a restriction, but rather they force the coordination chemist to find and develop pathways to new and undiscovered chemical reactions. The major part of technetium chemistry has been developed within this scenario. (Scheme 3)

The major sequence towards new complexes and radiopharmaceuticals is:

(i) synthesis of reactive precursor complexes, any condition;
(ii) coordination chemistry, new compounds, any condition;
(iii) synthesis, characterization of stabilized complexes, with water/air stability, serum stability, *in vivo* behavior, if promising;
(iv) one-pot kit based preparation in saline;
(v) bifunctionalization, if favorable *in vivo* behavior, and covalent coupling to targeting biomolecule, and labeling under any condition, purification, assessment of *in vivo* behavior, affinity, stability, etc.;
(vi) if good biological properties, labeling in one step in saline → new targeting radiopharmaceutical with pendant metal complex (pendant, postlabeling approach);
(vii) if (vi) not possible, synthesis of complex and coupling to biomolecule, not preferred but possible, two-step prelabeling approach;
(viii) functionalities in the biomolecule are used for labeling, i.e., disulfide bridges are reduced and coordinate to Tc → integrated approach, structure often not very well known.

Steps (i) through (v) are crucial prerequisites from coordination or organometallic chemistry for the development of novel radiopharmaceuticals. There are a number of excellent reviews on the coordination chemistry of technetium which have appeared over the past 30 to 50 years. Some

covered all aspects of both classical and nonclassical technetium chemistry,[37–57] others structural aspects[58–60] and special topics such as cluster compounds or organometallic chemistry.[61–63] In addition, the radiopharmaceutical applications of technetium compounds have also been reviewed on a regular basis, both from the medicinal aspects and those of the coordination chemistry.[64–78] Notably, a monograph on technetium chemistry appeared which covers many aspects of the chemistry of the element, including environmental aspects, organometallic chemistry, solid-state chemistry, intermetallic compounds, properties of alloys, and technical aspects of the applications of technetium.[79] A further valuable source of information on the chemistry of technetium and its applications in radiopharmacy is the series of books comprising abstracts of a biannual conference largely devoted to the chemistry of technetium and rhenium.[80]



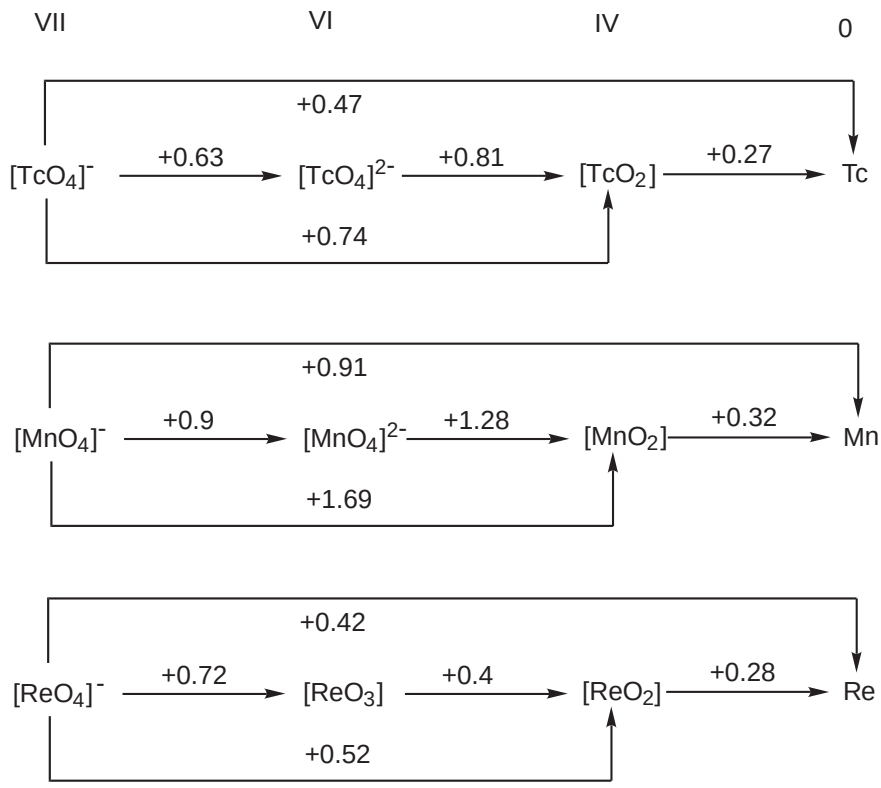
Scheme 3

5.2.2 SYSTEMATIC CHEMISTRY

5.2.2.1 Oxidation state (VII)

Throughout this review Tc always relates to the isotope ^{99}Tc unless otherwise stated. The only form in which technetium is commercially available is $[NH_4][TcO_4]$, either in aqueous solutions or as a solid. The salt is of medium solubility in water and recrystallization is used for purification. For the alkali-metal series, only the Li^+ and Na^+ salts show a reasonable solubility in water, the latter being about 68 g per 100 mL.[12,81,82] Addition of large organic cations like $[NBu_4]^+$ or $[AsPh_4]^+$ is used to precipitate $[TcO_4]^-$ almost quantitatively from aqueous solution or to extract it into an organic phase. $[NBu_4][TcO_4]$ is, for instance, soluble in most polar organic solvents such as CH_2Cl_2 or THF and can be used in a reaction in nonaqueous media, as described later. In contrast to permanganate, pertechnetate salts are essentially colorless and wave numbers are shifted by about 200 nm to higher energy. The UV/Vis spectrum in aqueous solutions shows major charge-transfer bands at 290 nm and 246 nm, with extinction coefficients of 2,150 L mol^{-1}cm^{-1} and 5,700 L mol^{-1}cm^{-1}, respectively.[83] Pronounced vibrational fine structures, as in the case of $[MnO_4]^-$, are present.

The redox behavior of the $[TcO_4]^-$ ion is important in terms of understanding its chemistry. The Latimer diagram of important oxidation states and standard redox potentials is given in Scheme 4. The electrochemistry of technetium has been reviewed on several occasions.[84–86]



Scheme 4

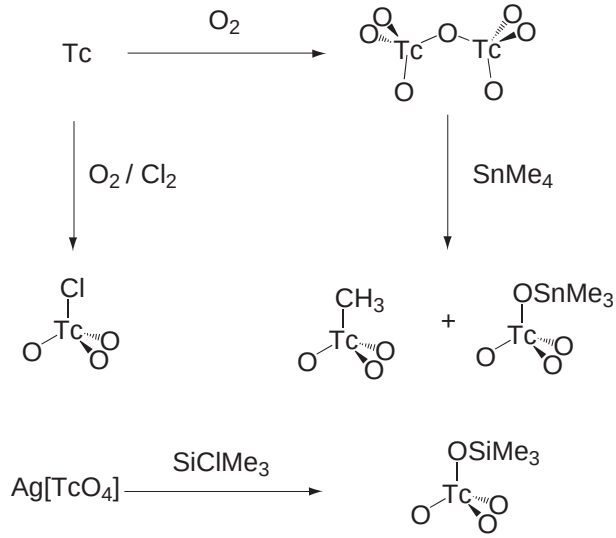
In accordance with the general features of the chemistry of first-, second-, and third-row transition elements, the reduction potentials for the tetraoxometallates follow the sequences $[MnO_4]^- \gg [TcO_4]^- > [ReO_4]^-$. The comparatively facile reduction of Tc^{VII}, as evident from the Latimer diagram, limits the range of chemistry accessible for this oxidation state.

5.2.2.1.1 Complexes with oxo-ligands

The anhydride of pertechnetic acid, $[Tc_2O_7]$ (**1**), represents an important starting material for high-valent technetium chemistry. With TcO_2 it is the only binary oxide of technetium unambiguously characterized so far. The structure is best described as comprising TcO_4 tetrahedra sharing one vertex. The angle at the bridging oxygen atom is 180°. Tc_2O_7 is best prepared by burning Tc metal in a stream of oxygen between 400 °C and 600 °C.[87,88] Lower oxides are formed as well, but they too can be completely oxidized by repeated transport through the hot zone of the oven. It has a melting point of 119.5 °C and boils at 311 °C[89] and is extremely hygroscopic, readily forming pertechnetic acid $[HTcO_4]$ when placed in contact with water. $[Tc_2O_7]$ behaves chemically as though it is $[TcO_4]^-[TcO_3]^+$, as shown by characteristic reactions of $[TcO_4]^-$ upon addition of ligands and by the isolation and identification of $[TcO_3][AsF_6]$ by the addition of $[AsF_6]^-$.[90] Due to its difficult preparation and very hygroscopic behavior, $[Tc_2O_7]$ is not the precursor of choice for high-valent technetium coordination chemistry, and the only chemistry that has been performed with it was in the field of high-valent organometallic chemistry.

A more useful compound has been prepared by the action of 18M H_2SO_4 on $K[TcO_4]$ in the presence of concentrated HCl, which gave the strongly oxidizing and volatile $[TcO_3Cl]$ (**2**).[91] The same compound was also prepared by controlled oxidation of Tc metal in the presence of Cl_2 and O_2.[92] The analogous compounds containing bromide and iodide have been characterized by mass spectrometry, but have not been isolated as solids.[93] A recent theoretical study of the electronic structure and properties of group 7 oxychlorides provides additional data which fit well with the experimental information.[94] The effective charge on the metal for $[MO_3Cl]$ is highest for Tc and lowest for Re, reflecting the increased covalency of M=O going down group 7, which correlates with the generally lower reactivity of Re=O relative to Tc=O.

Two further Tc^{VII} compounds have been described which are of potential use as sources of the "$[TcO_3]^+$" unit in coordination chemistry. $Ag[TcO_4]$ is converted into the silanolester $[O_3TcOSiMe_3]$ (**3**) by reaction with $SiClMe_3$.[95,96] The reaction of Tc_2O_7 with $SnMe_4$ produced some high-valent organometallic species, together with the corresponding Sn analogue $[O_3TcOSnMe_3]$ (**4**).[97,98] (Scheme 5.) The rhenium homologue is a very versatile starting point for the synthesis of rhenium compounds containing the $[ReO_3]^+$ core.

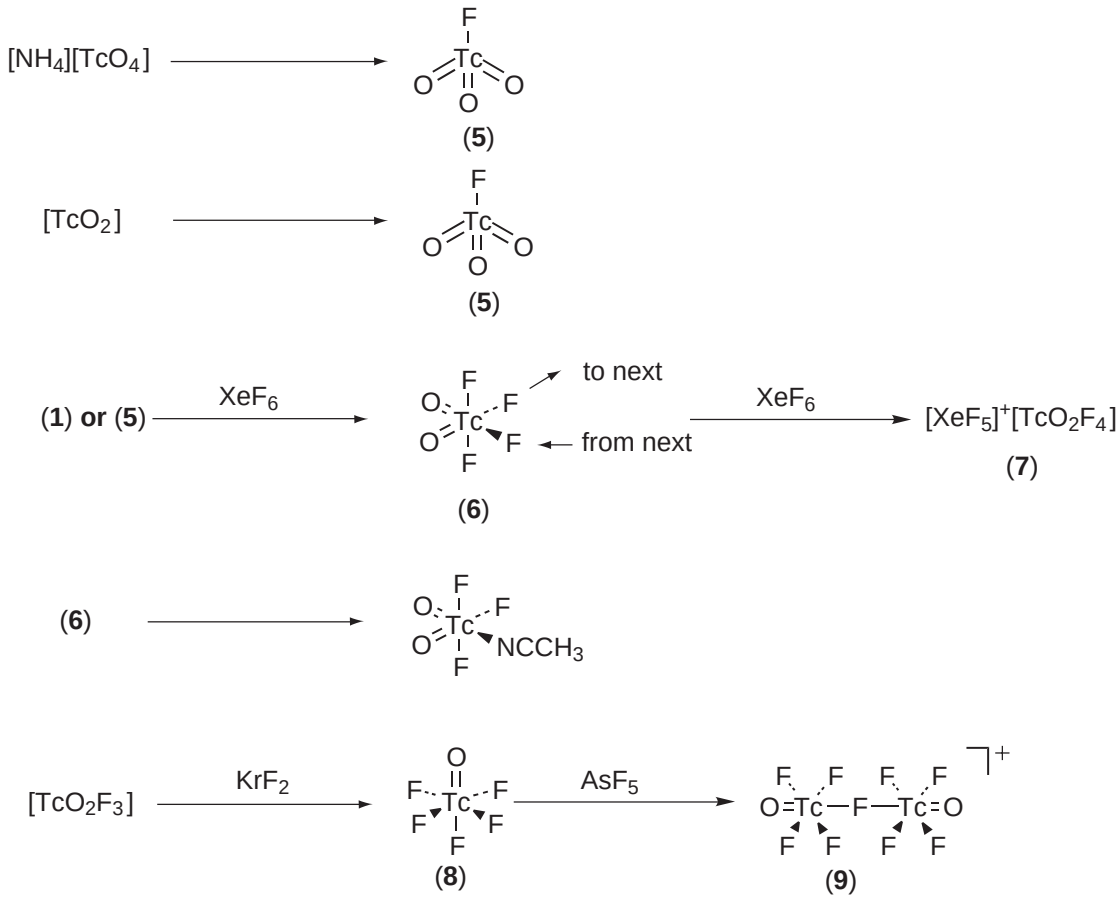


Scheme 5

The chemistry of Tc^{VII} mixed oxo–fluoride complexes is well established. Yellow crystals of $[TcO_3F]$ (**5**) are produced by the reaction of F_2 on TcO_2 at 150 °C or by the dissolution of $[NH_4][TcO_4]$ in liquid HF.[99,100] From vibrational spectroscopic studies, $[TcO_3F]$ is assigned C_{3v} symmetry. Complex (**5**) has been studied thoroughly with respect to its behavior as a Lewis acid, but there are few reports of its chemistry due to its high reactivity and difficult synthesis. The reaction of $[Tc_2O_7]$ or $[TcO_3F]$ with XeF_6 in anhydrous HF results in oxide/fluoride metathesis and the formation of $[TcO_2F_3]$ (**6**).[101] Further fluorination does not occur. The X-ray structure has been elucidated and shows fluoride-bridged octahedra in a zigzag chain. It has the same *cis* arrangement of the two oxo-ligands as other known six-coordinate oxo-fluoride complexes.

$[TcO_2F_3]$ is lemon yellow with a melting point of 200 °C, and reacts further with excess XeF_6 to form the octahedral $[TcO_2F_4]^-$ ion (**7**).[101] In order to get more information about the Lewis acidity of (**6**), ^{19}F, ^{17}O, ^{99}Tc NMR, and Raman spectroscopy studies have been performed in combination with theoretical calculations.[102] Although (**6**) is essentially insoluble in anhydrous HF, it readily dissolves in the presence of MF forming $M[TcO_2F_4]$.[102] The Li^+ salt of (**7**) can be isolated and the X-ray crystal structure has been determined. Coordinating solvents such as CH_3CN also dissolve $[TcO_2F_3]$ and, based on spectroscopic measurements, the corresponding mononuclear adduct $[TcO_2F_3(NCCH_3)]$ is formed. Line broading in NMR spectroscopic studies indicate a rapid exchange of coordinated CH_3CN with the bulk solvent. Solution structural studies of (**6**) in SO_2ClF by NMR spectroscopy give evidence for cyclic, tri- and tetranuclear, fluoride-bridged structures in equilibrium. The infinite fluoride-bridged chain structure is replaced by oligomeric cyclic structures.[103] ^{99}Tc NMR data for these compounds are compiled in Section 5.2.2.8.1.

Although further fluorination of $[TcO_2F_3]$ with XeF_6 under moderate conditions is not possible, fluorination with the stronger fluorinating agent KrF_2 results in the formation of volatile $[TcOF_5]$ (**8**). This compound exhibits a reversible melting point of about 57 °C. The structure of the compound was established by ^{19}F NMR experiments and vibrational spectroscopic studies, and it was shown to have the expected pseudo-octahedral geometry.[104] A subsequent X-ray crystal structure study confirmed these spectroscopic studies.[105] The fluoride-donating properties of (**8**) were studied in a reaction with the strong Lewis acids AsF_5 and SbF_5. In the presence of an excess of these acids yellow precipitates are formed, which were shown by X-ray structural studies to contain the fluoride-bridged cation $[Tc_2O_2F_9]^+$ (**9**). As anticipated, the Tc—O bonds are shorter and less polarized than in $[TcOF_5]$ (average 1.632 Å vs. 1.670(1) Å).[105] A summary of the structures and syntheses of the mixed oxo/fluoride complexes of Tc^{VII} is given in Scheme 6.



Scheme 6

The reaction of $[TcO_4]^-$ in water with strong acid leads to dehydration, coordination by the anion of the conjugate base, and by any bidentate ligand present. A number of Tc^{VII} compounds have been prepared in this way, all with retention of the structural *fac*-$[TcO_3]^+$ group. It is assumed that the anhydride $[Tc_2O_7]$ is formed as intermediate and is then substituted by the bidentate ligand. A representative compound of major importance is $[TcO_3Cl(phen)]$ (**10**), which readily precipitates from a solution of concentrated HCl and in the presence of phen.[106] Isolation and redissolution in water regenerates $[TcO_4]^-$. Clearly the compound is not stable towards hydrolysis and its isolation is due to its insolubility. Comparable compounds with bipy, 5-NO_2-phen, and tetramethylphenanthroline can be prepared in an analogous manner. Although the structures of these compounds are not known, the composition and stereochemistry can be deduced from spectroscopic studies. Interestingly, rhenium behaves similarly in the presence of aromatic amines, but differently in their absence. In concentrated hydrochloric acid, $[ReO_4]^-$ forms a coordination compound of composition $[ReO_3Cl_3]^{2-}$. Spectroscopic evidence for the unstable Tc^{VII} analogue has been presented. The compound exists for a short period of time in solution, but could not be isolated.[54,107] Although the differences in oxidation potentials are not large, the slightly higher oxidation potential of Tc^{VII} under these conditions is sufficient to induce a rapid reduction to $[TcOCl_4]^-$, which is the final product of the reaction if $[TcOCl_4]^-$ with concentrated HCl is precipitated with a large cation.[108]

The reaction of $[TcO_4]^-$ with 3,6-bis(2′-pyridyl)-1,2,4,5-tetrazine (**11**) and 4-phenyl-3,6-bis (2′-pyridyl)pyridazine (**12**) yielded two unique complexes of heptavalent technetium. The binuclear, dark-indigo complex $[\{TcO_3(OC_2H_5\}_2(\mu\text{-}\mathbf{11})]$ (**13**) and mononuclear, yellow $[TcO_3Cl(\mathbf{12})]$ (**14**) were prepared and characterized starting from $[TcO_4]^-$. Some mono- and dinuclear complexes from Tc^V were prepared by the same route, but starting from $[TcOCl_4]^-$.[109] Characterization was performed by spectroscopic methods only.

A further difference in the reactivity between rhenium and technetium is demonstrated by the behavior of the two homologues $[MO_3Cl(bipy)]$ or $[MO_3Cl(phen)]$. The technetium complex cleanly reacts under reduction with various aliphatic alkenes such as ethylene to form the corresponding Tc^{V}—diolato complex $[TcOCl(bipy)(OCH_2CH_2O)]$ and $[TcOCl(phen)(OCH_2CH_2O)]$ (**15**), respectively.[110] The analogous rhenium compounds are unreactive towards alkenes under the same conditions. However, the Re^{V} analogue $[ReOCl(phen)(OCH_2CH_2O)]$, prepared from $[ReOCl_4]^-$, releases alkenes when heated to 220 °C with concomitant formation of $[ReOCl_3(phen)]$, a reaction which does not occur with technetium.

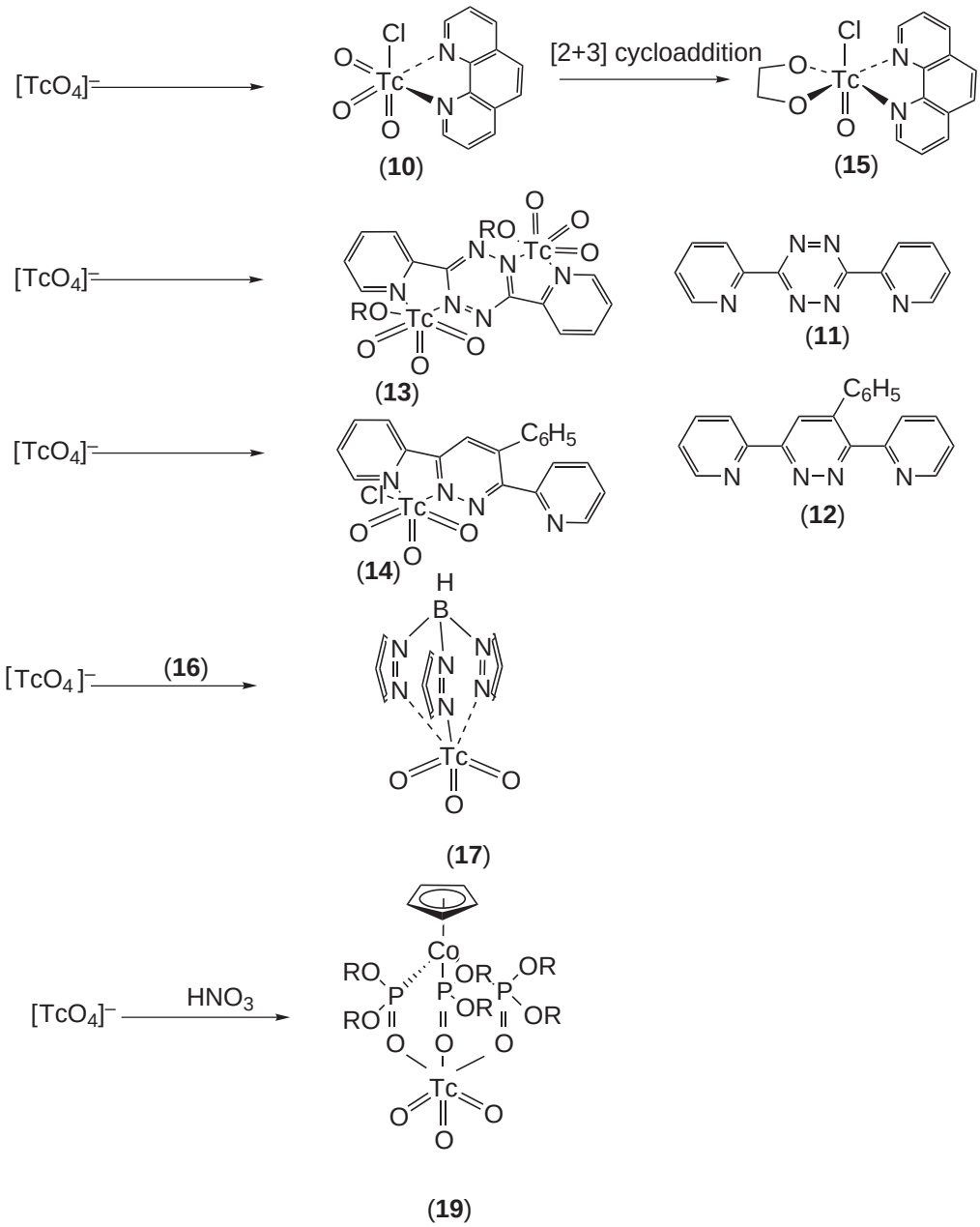
A theoretical study of the [2+3] cycloaddition of ethylene to $[MO_3]^+$ has been carried out by application of density functional methods and the Marcus theory.[111] In agreement with the experimental data, it was found that the activation barrier for the cycloaddition reaction increases down both group 7 and group 8. For $[MO_4]^-$ the activation barriers are 8.2, 27.3, and 38.4 kcal mol^{-1} for Mn, Tc, and Re, respectively. The calculations also show a linear correlation between the reaction energy and the bond dissociation energy for M—O. As mentioned earlier, the Tc—O bond is weaker (105 kcal mol^{-1}) than the Re—O (122 kcal mol^{-1}) in the M^{VII} compounds and consequently the reaction energies for rhenium are lower (−75 kcal mol^{-1} vs. −45 kcal mol^{-1}). The corresponding Tc^{VI} and Tc^{V} fragments show similar trends. A number of other DF studies of the electronic and structural properties of Mn, Tc, and Re have been reported.[112–114]

Two complexes of heptavalent technetium with the *fac*-$[TcO_3]^+$ core and tripodal ligands have been prepared. The tris(1-pyrazolyl)-borate $[HB(pz)_3]^-$ anion (**16**) reacts with an ethanolic solution of $[TcO_4]^-$ in the presence of H_2SO_4 to give $[TcO_3\{HB(pz)_3\}]$ (**17**).[115] The same compound can also be obtained by oxidation of the Tc^{V} complex $[TcOCl_2\{HB(pz)_3\}]$ with nitric acid, or by the reaction of $K[HB(pz)_3]$ with (**1**) in THF.[116] This complex behaves analogously to $[TcO_3Cl(phen)]$ and ethylene and undergoes reductive [2 + 3] cycloaddition with C_2H_4 to form $[TcO(eg)\{HB(pz)_3\}]$.[117] The Kläui ligands $[(\eta^5\text{-Cp})Co\{PO(OR)_2\}_3]^-$ (**18**) are another type of tripodal ligand which are able to stabilize a broad variety of oxidation states. The reaction of $[(\eta^5\text{-Cp})Co\{PO(OR)_2\}_3]^-$ with $[TcO_4]^-$ in the presence of concentrated HNO_3 results in formation of the neutral complex $[TcO_3\{(\eta^5\text{-Cp})Co\{PO(OR)_2\}_3\}]$ (**19**). The structure of this complex has been fully elucidated.[118,119] The reactive intermediate in this last synthesis is probably a mixed pertechnetic–nitric acid anhydride of $[Tc_2O_7]$. Scheme 7 summarizes the synthesis of six-coordinate complexes containing the *fac*-$[TcO_3]^+$ core.

5.2.2.1.2 *Nitrido- and imido-ligands*

The nitrido-ligand N^{3-} is a stronger π-donor than O^{2-} and is also able to stabilize metal centers in high oxidation states. One would therefore expect the preparation of mixed nitrido–oxo species of heptavalent technetium from the reaction of, e.g., $[Tc_2O_7]$ with NH_3 or other potential nitrido sources. However, all attempts to do so have failed so far and no evidence for the existence of oxide–nitride complexes is available. Oxidations of the Tc^{VI} species $Cs_2[TcNCl_5]$ (see Section 5.2.2.2.2) with H_2O_2 gives the unique, heptavalent, peroxo complex $Cs[TcN(O_2)_2Cl]$ (**20**),[120] which has been isolated and structurally characterized. The compound is yellow-orange and explosive, but the corresponding $[AsPh_4]^+$ salt is thermally more stable. The geometry structure about the Tc complex is distorted pentagonal pyramidal, with the nitrido ligand in the apical position. The Tc—N bond length is 1.63(2) Å, and comparable to other Tc^{VI} nitrido species. Formally this compound has 14 valence electrons, and it could be expected that two additional two-electron donor ligands could be accommodated. Reactions with bipy, phen, or oxalic acid (H_2ox) with $[TcNCl_4]^-$ in 10% H_2O_2 gave the corresponding heptacoordinated Tc^{VII} complexes $[TcN(O_2)_2(L)]$ (**21**) for L = phen or bipy[121], but the unique, dinuclear, oxalato-bridged Tc^{VII} complex $[\{TcN(O_2)_2\}_2(ox)]$ (**22**) in the case of H_2ox. The coordination geometry around the Tc center in the last complex is a distorted pentagonal bipyramid.[122] These compounds belong to a comparatively rare class of M^{VII} η^2-peroxo complexes. It is also of interest in this context that the $[TcN(O_2)_2]$ core is isoelectronic with the very well-established "$[MoO(O_2)_2]$" core. Some selected chemistry of Tc^{VII} nitrido complexes is summarized in Scheme 8.

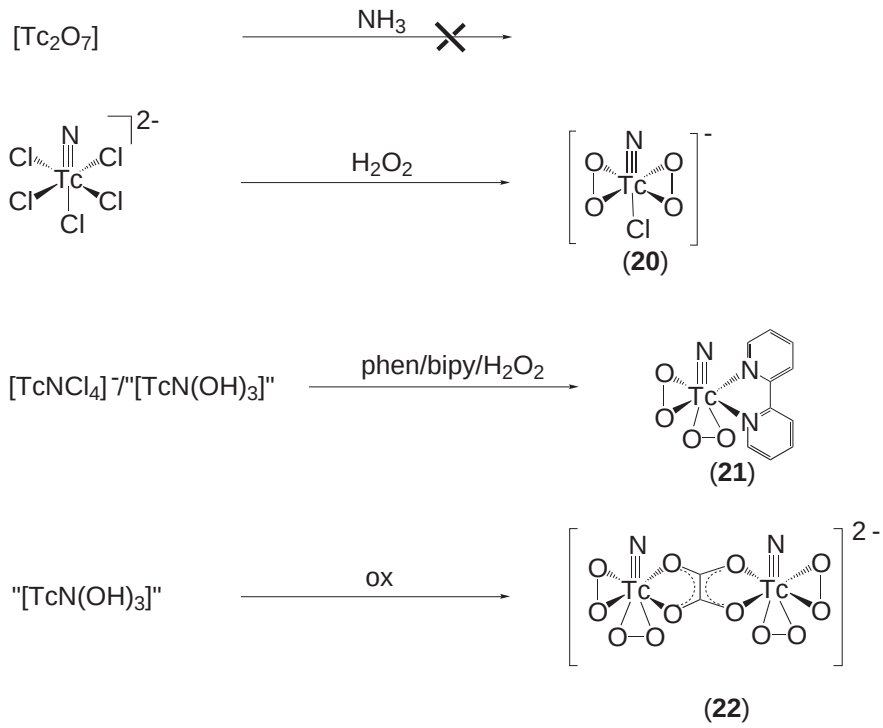
Another example of a Tc^{VII} nitrido-complex is obtained from the reaction of $[TcOCl_4]^-$ with 1,1-diphenylhydrazine (H_2NNPh_2) (**23**) in the presence of thiophenol. Unexpectedly, the dinuclear, formally Tc^{VII} complex $[\{TcN(NNPh_2)(SAr)(\mu\text{-SAr})\}_2]$ (**24**) is formed in good yields.[123] The nitrido-group results from the cleavage of the organohydrazine. This unusual reaction is shown in Scheme 9.



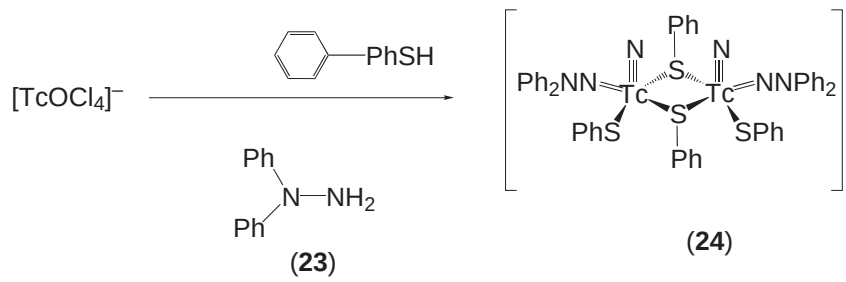
Scheme 7

The ability of multiple π-donors to stabilize high oxidation states has been used in the preparation of the first poly(imido) compounds of Tc^{VII}. While this type of compound has been known for a long time for other neighboring elements, it was introduced relatively recently for technetium. The reaction of $[TcO_3(OSiMe_3)]$[95] with 2,6-diisopropyl-phenylisocyanate (**25**) at elevated temperature leads to elimination of CO_2 and formation of the corresponding tris-imido complex $[Tc(NAr')_3(OSiMe_3)]$ (**26**) ($Ar' = 2,6\text{-}^{i}Pr_2\text{-}C_6H_3$).[96] The reaction is also possible with other arene substituents, but the temperature must be lowered, otherwise metal-mediated dimerization to the corresponding urylene intermediate and subsequent decomposition takes place. The X-ray structures of the compounds have been elucidated for the urylene intermediate with rhenium, but only spectroscopic data suggested the same structure for the technetium analogue. The ligands around the technetium center in $[Tc(NAr')_3(OSiMe_3)]$ adopt a distorted tetrahedral coordination geometry, with average O—Tc—N angles of 110°. Furthermore, the $[OSiMe_3]^-$ group in $[Tc(NAr')_3(OSiMe_3)]$ can be substituted by alkyl groups such as $—CH_3$ or $—C_2H_5$ by reaction

with the corresponding Grignard reagents. This produced the deep blue-green compounds of the type $[Tc(NAr')_3R]$ (**27**) ($R = CH_3$). Treatment of $[Tc(NAr)_3(OSiMe_3)]$ with $SiIMe_3$ leads to the substitution of $[OSiMe_3]^-$ by I^-, formation of $[Tc(NAr)_3I]$ (**28**), and release of hexamethyldisiloxane. The complex (**28**) was further reacted with K[Cp] to yield the water- and air-stable complex $[(Tc(NAr)_3(\eta^1\text{-Cp})]$ (**29**), in which $[Cp]^-$ is monodentately bound.[96,124,125] The structure shows only minor deviations from an ideal tetrahedral coordination geometry. It was anticipated that η^1-Cp would favour η^5-coordination, with formation of the imido analogue of, e.g., $CpReO_3$. It was suggested that the stronger donating properties of imido- compared to oxo-ligands are responsible for this difference. Treatment of (**26**) with [PPN][F] cleaves the O—$SiMe_3$ bond, and the unique mixed oxo/imido complex anion $[TcO(NAr)_3]^-$ (**30**) is formed. Reaction with an excess of K[Cp] results in the formation of $K[(Cp)_2Tc(NAr)_3]$, which was characterized by NMR spectroscopy.[124] (Scheme 10).



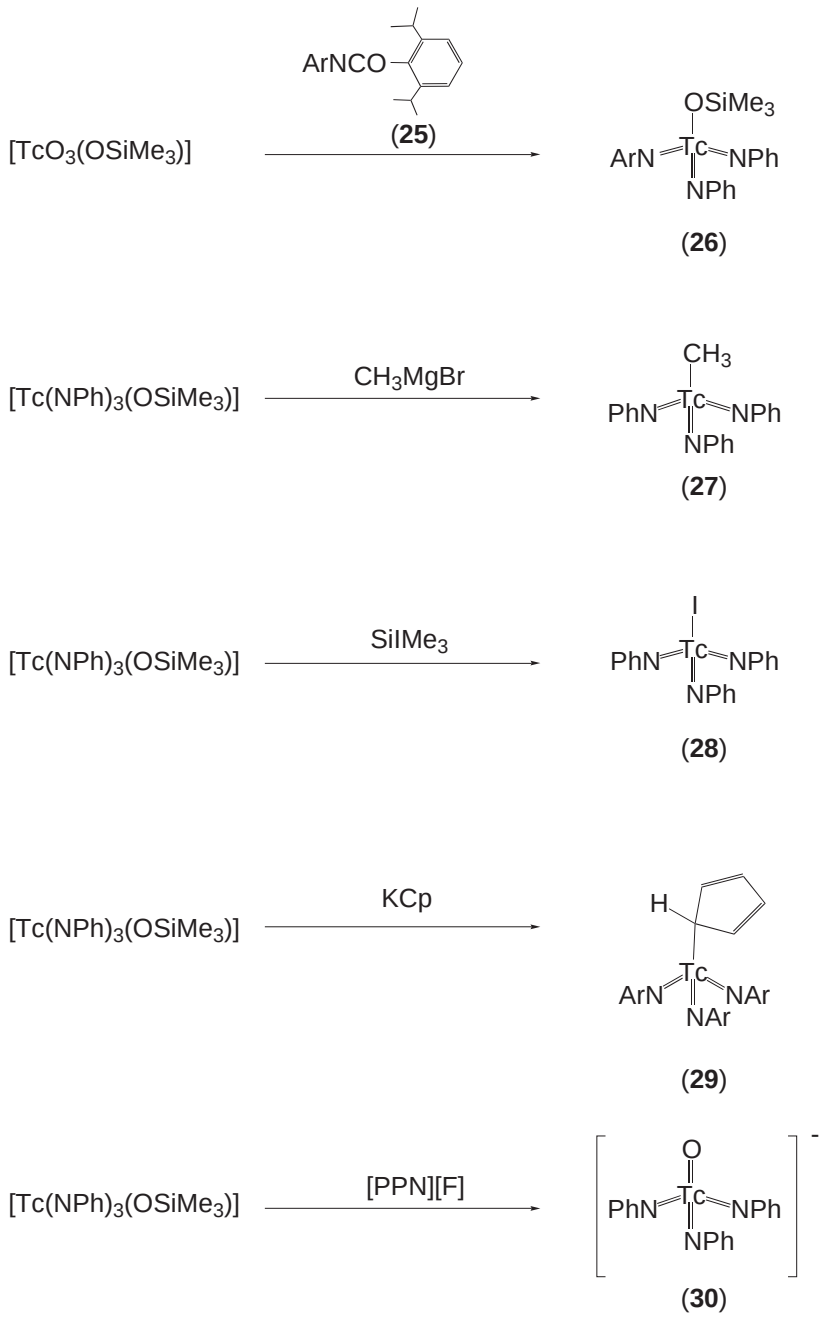
Scheme 8



Scheme 9

The number of Tc^{VII} complexes containing no metal–main-group element multiple bond is very small. The reaction of $[TcO_4]^-$ with 1,2-diaminobenzene (**31**) (H_2dab) in refluxing methanol gives the green, cationic, trigonal-prismatic complex $[Tc(HNC_6H_4NH)_3]^+$ (**32**) in high yield. In the presence of a reducing agent, the Tc^V complex $[TcO(HNC_6H_4NH)_2]^-$ (**33**) is formed.[126] Both amino groups of the dab ligand are mono-deprotonated. This compound belongs to the rare class of technetium complexes in which the Tc center is coordinated to three bidentate ligands. As anticipated, trigonal-prismatic geometry is preferred for low numbers of *d* electrons; the complexes are

in this case formally d^0. The other two structurally characterized complexes with this type of geometry are $[Tc(HNC_6H_4S)_3]$ (d^1) [127] and $[Tc(SC_6H_4S)_3]^-$ (d^2).[128] The two triangular faces are almost parallel and the distance of the metal center to these faces is 1.24 Å. The complex is surprisingly stable, but despite this no subsequent adaption of this chemistry has so far been described.



Scheme 10

A compound which appears in many textbooks is the highly reactive enneahydridotechnetate $[TcH_9]^{2-}$ dianion. This complex is synthesized by the unusual reaction of a potassium reduction of $[NH_4][TcO_4]$ in ethylenediamine/ethanol.[129] The structure is isomorphous with the rhenium analogue, trigonal prismatic, with each of the three tetragonal faces capped by an additional hydride ligand.[130] Thus the coordination number is nine, which is the highest known for technetium to date. From the tetragonal-capped, trigonal-prismatic structure, two different types of hydride could be expected. ^{1}H NMR studies in alkaline D_2O showed a single resonance, indicating highly fluxional behavior.

5.2.2.2 Oxidation State (VI)

Compounds in the oxidation state +VI have a d^1 electronic configuration. As is evident from electrochemical data, Tc^{VI} has a pronounced tendency to disproportionate into the more stable Tc^{V} and Tc^{VII} states. However, some stable compounds have been prepared and characterized. This is possible if nitrido or imido ligands are present, which stabilize by strong π-donation. In a few cases, as with other elements of the same electronic configuration, the formation of dinuclear complexes with a metal–metal single bond is observed. The hexavalent state can also be stabilized by bidentate aromatic thiolato or alkoxide ligands. Due to paramagnetism, NMR is not useful for structure assignment, but EPR spectroscopy has proven to be a versatile tool.

The compound $[TcO_4]^{2-}$ can be produced electrochemically from $[TcO_4]^-$ at a Pt electrode with a reduction potential of −0.63 V. Once formed, the compound readily disproportionates into $[TcO_4]^-$ and $[TcO_4]^{3-}$.[131,132] $[TcO_4]^{2-}$ can be produced in significant amounts as the $[N(CH_3)_4]^+$ salt by electrochemical reductions of $[TcO_4]^-$ in acetonitrile. Despite its air sensitivity, the structure of $[TcO_4]^{2-}$ has been elucidated.[133,134] The existence of the corresponding anhydride of $[TcO_4]^{2-}$, ditechnetium pentoxide $[Tc_2O_5]$, has been suggested on the basis of mass spectrometry, but its existence is still not unambiguously proven.[88,93,135]

In general, Tc^{VI} complexes are prepared by concomitant substitution/reduction or oxidation processes, rather than from direct substitution of weak labile ligands such as halides. The only exceptions are reactions with $[TcNCl_4]^-$. This is due to the lack of reactive but reasonably stable direct precursors for this oxidation state and, as a consequence, all other Tc^{VI} chemistry necessarily arises from redox processes.

5.2.2.2.1 Binary halogen and halogen/oxo-containing complexes

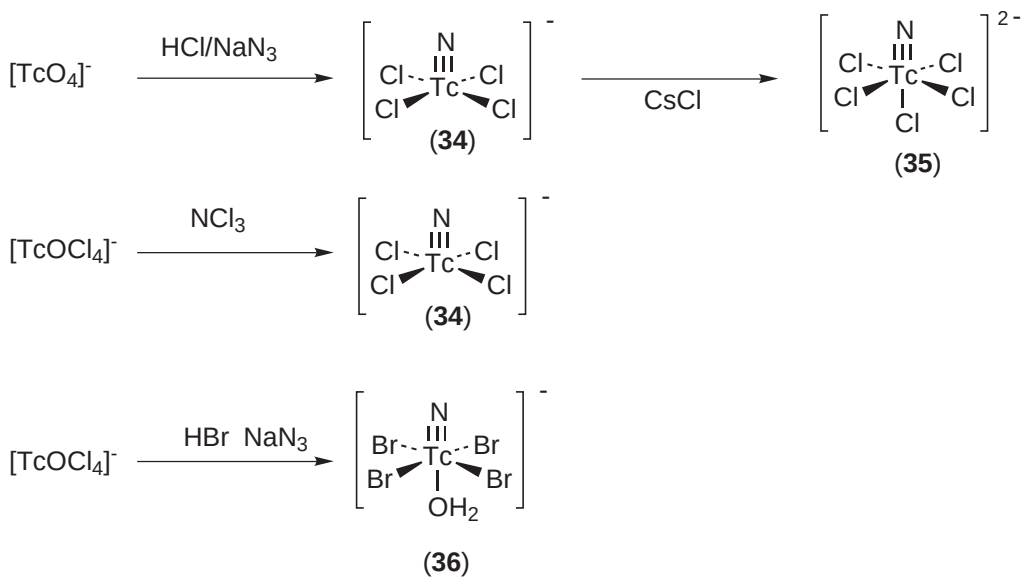
Technetium hexafluoride $[TcF_6]$ is available from the reaction of technetium metal with excess F_2 at 400 °C.[136] It is golden yellow, melts at 37.4 °C and is extremely water sensitive, reacting to give mainly TcO_2 with $[TcOF_4]$ as a by-product.[137–139] An X-ray crystal structure reveals a trinuclear structure with monofluoride bridges. Several phases have been identified and these interconvert readily. $[TcF_6]$ reacts with nitrosyl fluoride NOF and nitryl fluoride $[NO_2F]$ to yield the octa- and heptacoordinated complexes $[NO]_2[TcF_8]$ and $[NO_2][TcF_7]$, respectively.[140] The complexes have magnetic moments of 1.72 B.M and 1.62 B.M., respectively, close to the spin-only value. The pentachlorooxotechnetate(VI) anion $[TcOCl_5]^-$ was prepared by the reaction of $K[TcO_4]$ in concentrated sulfuric acid, with HCl as the reducing agent. The formation of this Tc^{VI} complex was tentatively proposed on the basis of a deep blue color which bleached over a one-hour period. The compound $[NH_4]_2[TcO_2Cl_4]$, the probable precursor of $[NH_4][TcOCl_5]$, is isolated as the sulfuryl-chloride adduct by reaction of thionylchloride SO_2Cl_2 with $[NH_4][TcO_4]$.[141]

5.2.2.2.2 Nitrido and imido ligands

The only neutral compound containing nitrido and chloride ligands known to date is $[TcNCl_3]$. This is prepared by the reaction of IN_3 with $TcCl_4$, or by the reaction of $[TcNCl_4]^-$ (see below) with the strong Lewis acid $GaCl_3$.[142] According to IR spectroscopy, the polymeric structure is linked by Tc—N—Tc and Tc—Cl—Tc bridges. Upon addition of Lewis bases to this insoluble substance in various solvents, the polymeric structure is cleaved, with reformation of $[TcNCl_4]^-$ (**34**). This complex anion is one of the most suitable for studies of the coordination chemistry of technetium in the oxidation state (VI) containing the $[Tc{\equiv}N]^{3+}$ core. It was originally prepared by heating $[TcO_4]^-$ under reflux in HX in the presence of NaN_3, and it was precipitated with bulky organic cations such as $[As(Ph)_4]^+$.[143] The salts are air stable and the nitrido-group shows a very high resistance to acidic hydrolysis, as shown by the method of preparation. Since the nitrido ligand shows a strong *trans* influence, it is not surprising that only five-coordinated Tc^{VI} complexes are available by this route. If the reaction mixture is taken to dryness, the residue can be extracted by acetonitrile to give an orange solution, possibly containing the acid $H[TcNCl_4]$. On addition of CsCl to this solution, the six-coordinate compound $Cs_2[TcNCl_5]$ (**35**) can be isolated.[144] If an alkylammonium salt is added instead, the sixth position is occupied by water and the interesting complex $[NEt_4][TcNCl_4(OH_2)]$ is formed. The bromide analogue $[NEt_4][TcNBr_4(OH_2)]$ (**36**) of this complex can be prepared directly in high yields by reduction of $[TcO_4]^-$ with conc. HBr in the presence of NaN_3.[145]

The Tc^{VI}–nitrido complexes show some interesting structural features when compared to their Tc^{V} oxo-analogues. The stronger *trans* influence of the nitrido ligand in comparison with the oxo group produces, as expected, a longer bond to the *trans* ligand. Such a comparison is directly possible with aquated complexes $[TcNBr_4(OH_2)]^-$ and $[TcO(OH_2)Br_4]^-$, respectively. For $[TcOBr_4(OH_2)]^-$ the Tc—OH_2 bond length *trans* to the oxo group is 2.317(9) Å, whereas for $[TcNBr_4(OH_2)]^-$ the corresponding Tc—OH_2 distance is 2.443(7) Å.[145,146] The Tc≡N bond length is 1.559 Å, compared with 1.618(8) Å for Tc=O. The $\nu_{Tc\equiv N}$ stretching vibration occurs at 1,076 cm^{-1}, whereas the $\nu_{Tc=O}$ vibration is found at 1,025cm^{-1}.[143,147] This difference implies a slightly stronger Tc≡N bond in comparison with Tc=O, but calculations assuming a simple harmonic oscillator show that the difference is less than that calculated. Therefore the bond strengths are comparable and are consistent with the convention of a Tc≡O multiple bond having triple-bond character, with a partial positive charge on oxygen. The coordination of one water ligand to the *trans* position results in a shift of the Tc≡N frequency by only about 5 cm^{-1}, indicative of a very weakly bound aquo-ligand. $[NEt_4][TcNCl_4(OH_2)]$ can therefore easily be dehydrated. The corresponding bromo complex must be more stable, since dehydration does not take place under comparable conditions for the bromo analogue.

Alternatively, the complex (**34**) can also be obtained from the reaction of $[TcOCl_4]^-$ in CH_2Cl_2 when mixed with a solution of NCl_3 in the same solvent. This elegant reaction involves oxidative nitrogen transfer to technetium(V). NOCl and Cl_2 were detected as by-products.[142] Complexes containing the $[Tc\equiv N]^{3+}$ core are also available through controlled oxidation of Tc^{V} nitrido complexes.[148–150] Therefore complex (**35**), which is obtained from the $[TcO_4]^-/HCl/N_3^-$ system only in minor amounts, can also be prepared in good yields by oxidation of "$[Tc^{V}N]^{2-}$" species with Cl_2 or substitution/oxidation of $[TcOCl_4]^-$ with azide.[148] (Scheme 11)



Scheme 11

When (**34**) is dissolved in dilute aqueous HCl, a rather poorly defined brown precipitate forms ("nitridotechnetic acid"), which probably contains bridging oxo groups (see below).[151,152] According to EPR investigations, this precipitate can be redissolved in concentrated HF with formation of $[TcNF_4]^-$.[151] This complex has not been isolated, but the EPR data strongly support this formulation. Furthermore, the fluoride ligands can be exchanged with a number of other halide or pseudohalide ligands, such as CN^-, SCN^-, N_3^-, and with complex anions such as $[H_2PO_4]^-$ or $[HSO_4]^-$. Most of the mixed-ligand species have been identified through their EPR spectra, demonstrating the power of this analytical tool in Tc^{VI} chemistry.[153–155]

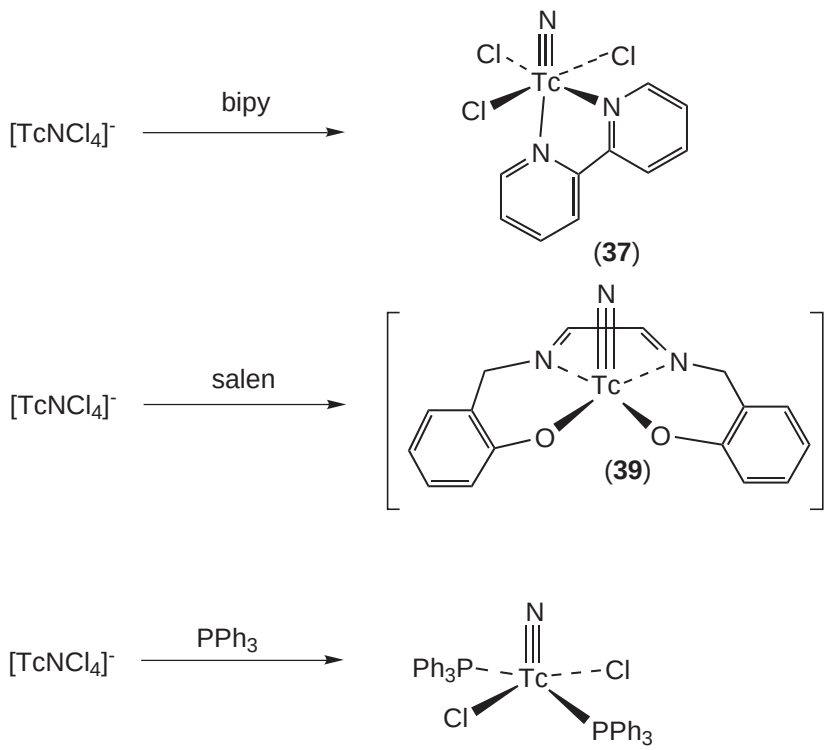
Systematic spectroelectrochemical and computational studies of tetrahalide complexes of the $[Tc\equiv N]^{3+}$ cores in the +V and +VI oxidation states have been published and comparisons made with the corresponding $[Tc=O]^{3+}$ systems. Significant differences in the redox potentials between $[Tc=O]^{3+}$ and $[Tc\equiv N]^{3+}$ complexes are observed. The 6+/5+ couple for $[TcNBr_4]^-$ is reversible at +0.32 V vs. SCE, whereas the corresponding couple for $[TcOBr_4]^-$ is irreversible at +1.73 V.

The values for the corresponding chloro complexes are +0.21 V and +1.84 V, respectively. It was concluded that these dramatic differences are a result of greater interaction of the nitrido ligand with the technetium center in comparison to the oxo ligand. This leads to stronger destabilization of the axial ligands for the nitrido species and hence to an increased susceptibility for an oxidation process. Thus, the d^2/d^1 oxidation is easier for $[TcNCl_4]^-$ than for $[TcOCl_4]^-$, and even a subsequent oxidation of d^1 to d^0 is possible for $[TcNCl_4]^-$ but unobservable for $[TcOCl_4]^-$. This experimental observation is in agreement with the theoretical calculations.[156]

$[TcNCl_4]^-$ reacts in aqueous or organic solution with a variety of multidentate chelators. Although the nitrido ligand stabilizes the formally high oxidation state, substitution of halide by other ligands often occurs with concomitant reduction to the +V state (see Section 5.2.2.3.3). Therefore, reaction with ligands such as PPh_3, KNCS, and $Na(S_2CNEt_2)$ produces the corresponding Tc^V complexes $[TcNCl_2(PPh_3)_2]$, $[NEt_4]_2[TcN(NCS)_4(CH_3CN)]$, and $[TcN(S_2CNEt_2)_2]$.[144] The same reductive substitution process even occurs with nonreducing ligands such as phen or bipy[157,158], but the reaction depends in the latter case on the solvent. It is found that reaction of $[TcNCl_4]^-$ with 2,2′-bipyridine (bipy) in acetonitrile gives the Tc^{VI} complex $[TcNCl_3(bipy)]$ (**37**), whereas the same reaction in methanol leads to concerted substitution/reduction to the bis-substituted Tc^V complex $[TcNCl(bipy)_2]^+$. EPR investigation and an X-ray structure analysis of $[TcNCl_3(bipy)]$ have been reported. The Tc—N distance for the bipy in the *trans* position to the nitrido ligand is 2.371(4) Å, significantly longer than the Tc—N bond *cis* to the nitrido ligand, (2.136(5) Å).[159]

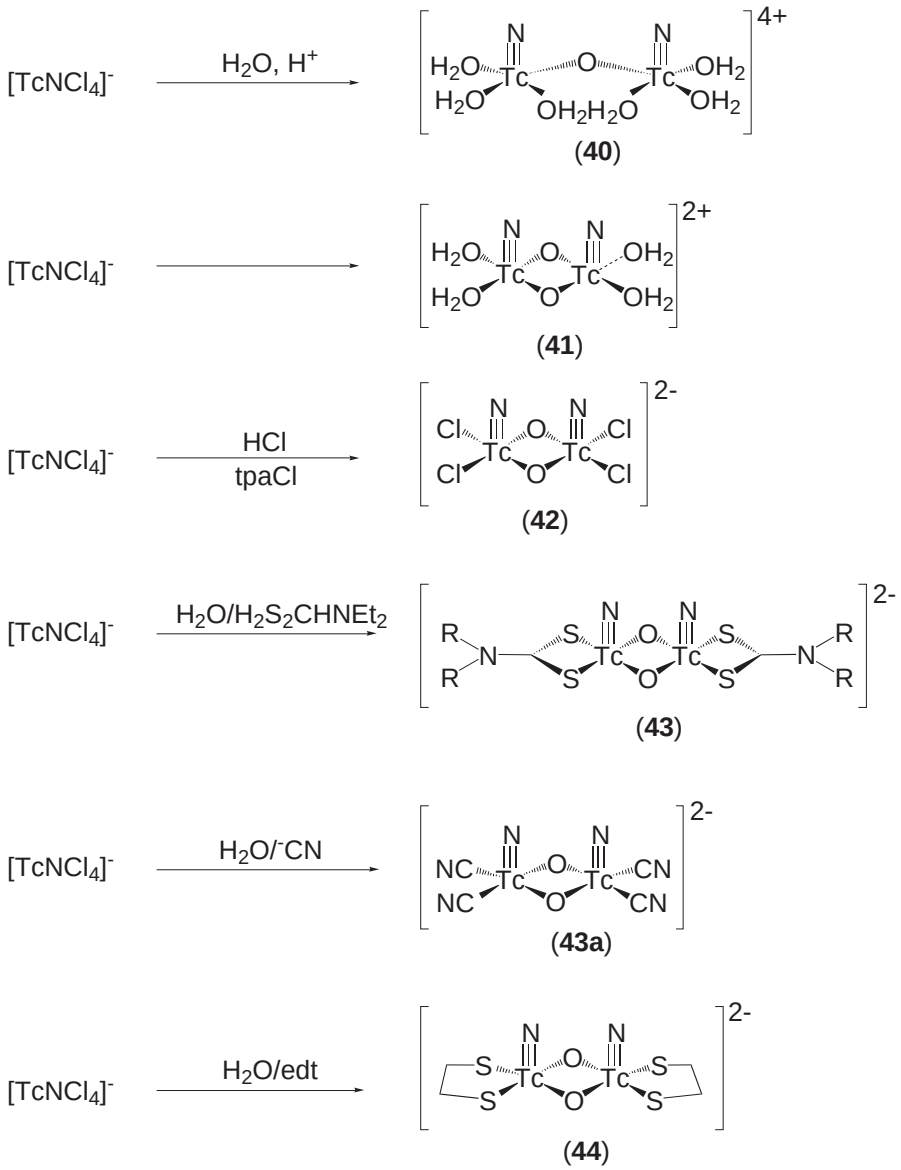
Chloro and bromo ligands in (**34**) can be substituted by multidentate N,O ligands without reduction. Thus reaction with the Schiff base *N*,*N*′-ethylene-bis(salicylideneimine) (H_2salen) (**38**) in acetone gives the Tc^{VI} cation $[TcN(salen)]^+$ (**39**)[160], and the reaction with Na_2H_2edta produces a violet precipitate which was first formulated as [TcN(Hedta)]. Later, based on a strong absorption at 504 nm and a comparison of the spectra with Tc^{IV}EDTA compounds comprising the "$[Tc_2(\mu\text{-}O)_2]$" core, the compound was reformulated as $Na_4[Tc_2N_2(\mu\text{-}O_2)(edta)_2]$. This band is diagnostic for systems which contains the $Tc_2(\mu\text{-}O)_2$ group.[161–163] (Scheme 12)

In aqueous solution, the reactivity of (**34**) is unique and does not have parallels among other transition-element nitrido complexes. For instance, a characteristic feature is the formation of "$[NTc(\mu\text{-}O)TcN]^{4+}$" or "$[NTc(\mu\text{-}O)_2TcN]^{2+}$" structural units by hydrolysis (see Scheme 13). As observed with many high-valent M=O species, substitution of halides by water leads to highly



Scheme 12

cationic and hence strongly acidic aqua complexes, which tend to reduce the charge by deprotonation and concomitant formation of (μ-OH) or (μ-O) bridges. This is a common feature for oxo complexes, but is rarely observed for nitrido complexes. As mentioned earlier, reaction of $[TcNCl_4]^-$ with excess of water gives $[TcN(OH)_3]$, the so called nitridotechnetic acid. From EPR spectra the compound must be at least dinuclear, and the presence of a ν(TcOTc) vibration band in the IR leads to tentative formulation of the complex as $[\{TcN(OH)(OH_2)_2\}_2(\mu\text{-}OH)_2]$.[145,152]



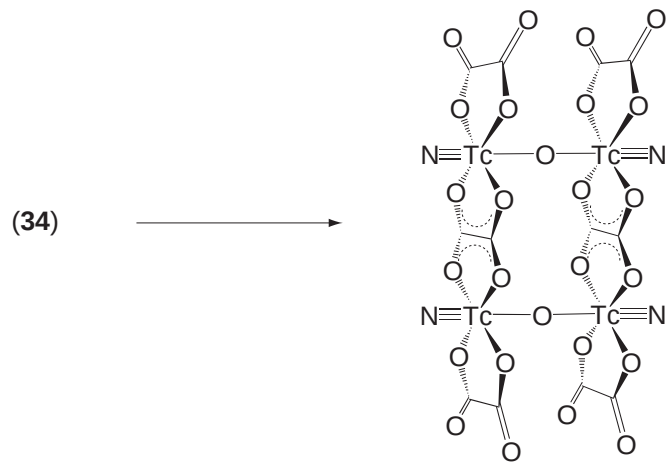
Scheme 13

The $[OH]^-$ ligands in nitridotechnetic acid can be protonated in strongly acidic media, a process leading to the μ-oxo aqua cation $[\{TcN(OH_2)_4\}_2(\mu\text{-}O)]^{4+}$ (**40**) which, upon dilution, gives the bis(μ-oxo) aqua nitrido species $[\{TcN(OH_2)_3\}_2(\mu\text{-}O)_2]^{2+}$ (**41**).[145,164] Although not structurally characterized, the formulation results from a comparison of the electronic spectra with the well-characterized isoelectronic species $[\{MoO(OH_2)_3\}_2(\mu\text{-}O)_2]^{2-}$, the absence of EPR signals, and the isolation and structural characterization of subsequent coordination compounds. The addition of $[As(Ph)_4]Cl$ and then HCl to a strongly acidic solution of the precipitate obtained after dissolution of $Cs_2[TcNCl_5]$ in water gave in high yields the complex $[\{TcNCl_2\}_2(\mu\text{-}O)_2]^{2-}$ (**42**).[165] The X-ray structure of (**42**) was determined and exhibited the predicted structural feature of a

bent, four-membered [Tc(μ-O)$_2$Tc] ring. The structure is best described as two square pyramids sharing one edge. The Tc—Tc distance is ca. 2.55 Å, clearly indicating a single bond and rationalizing the absence of EPR spectra. Similarly, complexes containing this central [Tc_2O_2] group could also be prepared with cyanide, dithiocarbamate, and ethanedithiolate ligands to yield the corresponding complexes [{TcN(CN)$_2$}$_2$(μ-O)$_2$]$^{2-}$(**43a**), [{TcN(S_2CNEt_2)}$_2$(μ-O)$_2$] (**43**), and [{TcN(SCH_2CH_2S)}$_2$(μ-O)$_2$]$^{2-}$ (**44**).[165,166] As mentioned earlier, the [Tc≡N]$^{3+}$ core is very susceptible to reduction and with the dithiocarbamato ligand immediate reduction to the Tc^{V} complex occurs in acid. Obviously under neutral reaction conditions, the [Tc(μ-O)$_2$Tc] unit is readily formed and decreases the tendency for reduction. Upon acidification of a solution of [{TcN(S_2CNEt_2)}$_2$(μ-O)$_2$] with HCl, the monomeric species [$TcNCl_2(S_2CNEt_2)$] is isolated in good yields, a compound which is not accessible by partial substitution of the chloro ligands in [$TcNCl_4$]$^-$. (Scheme 13)

The formation of complexes with the "[NTc(μ-O)$_2$TcN]$^{2+}$" central structural unit has parallels in molybdenum chemistry, where isostructural complexes such as [{MoO(S_2CNEt_2)}$_2$(μ-O)$_2$] are well established.[167] In the MoO system, the differences for the oxo ligand compared to the nitrido ligand are again obvious, since the Mo sites about 0.73 Å above the basal plane of the square pyramid, compared to 0.65 Å in the technetium case.[166]

In all of the above-mentioned complexes a bis-(μ-O)-bridged Tc^{VI} unit is present. There is, however, one unique complex in which a mono-(μ-O) bridge is the central structural feature. The reaction of [As(Ph)$_4$][$TcNCl_4$] with oxalic acid in water/acetone results in the cyclic tetranuclear Tc^{VI} complex [Tc_4N_4(μ-O)$_2$(μ_2,η^2-ox)$_6$]$^{4-}$ (**45**), in which oxalato and oxo alternate in bridging the four technetium centers. The remaining halides have been replaced by terminal, bidentate, coordinating oxalate ligands to achieve six-coordinate technetium.[168] The coordination of the bridging oxalate ligands is thus [(μ^2,η^2-C_2O_4)]$^{2-}$. The *trans* influence of the nitrido ligand is manifested by significant differences in bond lengths, the Tc—O distance *trans* to nitrido is about 2.400(11) Å, whereas the distance *cis* to the nitrido ligand is only 2.070(11) Å. The Tc—O—Tc angle is bent (150.4(8)°); consequently there is no spin exchange at room temperature and the compound has a magnetic moment of 1.64 B.M. This contrasts with the almost linear Tc^{V} units "[OTc^{V}—O—Tc^{V}O]$^-$ ", in which the oxo ligands are *trans* to the oxo bridge.[169] It is an unexpected feature of this complex that Tc^{VI} is not further reduced to Tc^{V} or Tc^{IV}, since stable and well-characterized complexes with oxalate ligands are also known for these oxidation states. (Scheme 14)

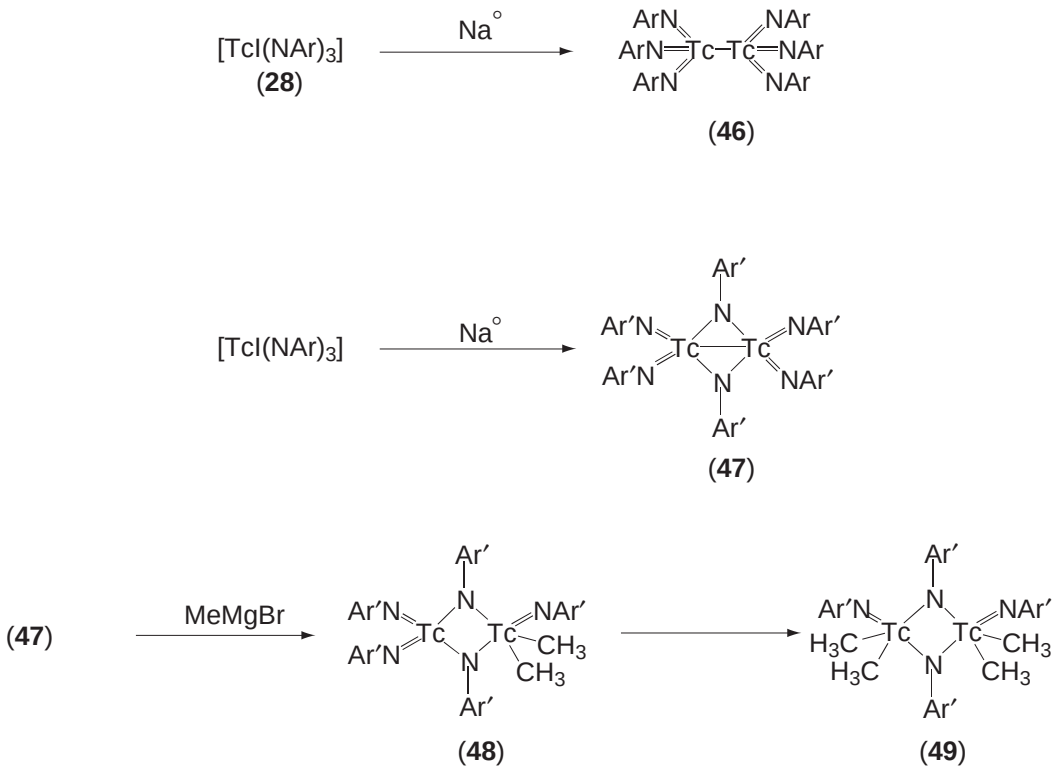


Scheme 14

The Tc^{VII} complex [TcI(N—Ar)$_3$] (**28**) (see Section 5.2.2.1.2) can be reduced with Na° in THF to yield the green, nonbridged, dinuclear compound [Tc_2(NAr)$_6$] (**46**), in which three imido-ligands are bound to the Tc^{VI} center and connected by a single bond to the second technetium. The molecule has a staggered, ethane-like structure and is diamagnetic.[170,171] Reduction of (**28**) yields another homoleptic imido-complex of Tc^{VI}, the imido-bridged, tetrahedral, dinuclear compound [Tc_2(μ-NAr′)$_2$(NAr′)$_4$] (**47**) (Ar′ = 2,6-diisopropylphenyl). The conformation could be confirmed by X-ray structure analysis; the assumption of a Tc—Tc bond is confirmed by the

diamagnetism of the complex. Supported by the bridging ligands, the Tc—Tc bond length is 2.68 Å and significantly shorter than in the nonbridged Tc^{VI}imido-compound with 2.7744(1) Å. The bonding and structure in some of this heavily π-loaded imido compound has been studied by theoretical molecular orbital calculations as well, and the results compared to those received from X-ray structure analysis.[125]

Treatment of (**47**) with Grignard reagents leads to the unprecedented successive substitution of imido-ligands by methyl groups. The reaction with two equivalents of MeMgCl substitutes one imido ligand and results in the formation of $[Tc_2(\mu\text{-}NAr')_2(CH_3)_2(NAr')_3]$ (**48**). The X-ray structure shows the two methyl ligands on the same Tc center. Addition of a further two equivalents of MeMgCl yields the symmetrically substituted tetramethyl complex $[Tc_2(\mu\text{-}NAr')_2(CH_3)_4(NAr')_2]$ (**49**). In the solid state, only the *Z*-isomer was observed.[172] The structures of the compounds are depicted in Scheme 15.



Scheme 15

5.2.2.2.3 Oxo-sulfur and nitrogen ligands

Complexes of hexavalent technetium without multiple bonds to main-group elements are rare. As is obvious from the previous section, most of the complexes contain multiple bonds to either nitrogen or oxygen, in order to compensate the highly positive charge of the technetium center. The first complex to be found without multiple bonds to N or O was the homoleptic complex with 2-aminobenzenethiol (H_2abt, (**50**)) $[Tc(abt)_3]$ (**51**).[173] Treatment of $[NH_4][TcO_4]$ in 0.1M HCl in the presence of (**50**) gave (**51**) in about 40% yield as dark green crystals. The EPR spectrum of $[Tc(abt)_3]$ shows almost isotropic g values, slightly greater than the free electron value, and very small hyperfine coupling constants, indicating that the free electron is in an orbital with mainly ligand character. A direct consequence is the observation of intermolecular exchange interactions in solution. Possible exchange pathways have been discussed under the assumption that the molecular arrangements in solution and in the solid state are similar.[127,174,175] Face-to-face or face-to-edge contacts between the benzene rings of two different molecules are considered to contribute significantly to the observed interactions. From thermodynamic considerations, it is expected that face-to-face contacts result in the strongest intermolecular interactions. The X-ray

crystal structure confirms these interactions and shows the expected trigonal-prismatic geometry, isostructural with the corresponding molybdenum complex. The distance to the trigonal N3 face is 1.265(1) Å and to the S3 face 1.482(1) Å.[127]

A similar reaction occurs between $[NH_4][TcO_4]$ and 3,5-di-*t*-butylcatechol (H_2dbcat) (**52**) in methanol yielding the tris(3,5-di-*t*-butylcatecholato)technetium(VI) complex $[Tc(dbcat)_3]$ (**53**). The catechol acts as both ligand and reducing agent. The coordination geometry around Tc^{VI} is approximately octahedral, with some distortion towards trigonal-prismatic coordination geometry. $[Tc(dbcat)_3]$ shows interesting electrochemical behavior. Two reversible reduction potentials are observed at −0.42 V and −1.09 V (vs. Fc/Fc^+), corresponding to formation of Tc^V and Tc^{IV} species, respectively, as well as one oxidation at +0.45 V to the corresponding Tc^{VII} cation $[Tc(dbcat)_3]^+$.[176] The octahedral geometry contrasts with the assumed structure of a similar complex with toluene-1,2-dithiol (H_2tdt) $[Tc(tdt)_3]$ (**54**). It was concluded from spectroscopic investigations that the geometry in this latter compound is trigonal prismatic, but no X-ray structure analysis has been performed so far. $[Tc(tdt)_3]$ can be reduced to Tc^V and to the Tc^{IV} dianion $[Tc(tdt)_3]^{2-}$, and oxidation to the Tc^{VII} cation is also possible.[173,177]

An unusual compound is produced from the reaction between the Tc^V complex $[TcO(O_2C_6Cl_4)_2]^-$ (**55**) (see Section 5.2.2.3.2.1) and *N*,*N*-diphenylhydrazine (**23**) in CH_2Cl_2. The binuclear, mixed-valence, paramagnetic, but EPR-silent Tc^V/Tc^{VI} complex $[Tc_2(NNPh_2)_2(O_2C_6H_4)_4]^-$ (**56**) is formed in about 20% yield. The hydrazido ligand in this complex adopts an unusual η^1 bridging mode. The structure of the molecular anion consists of two distorted octahedral Tc centers bridged by two hydrazido(2-) groups, and each Tc center is additionally coordinated to two catecholato ligands. The bond length of 2.612(2) Å is consistent with a Tc—Tc single bond.[178] This reaction suggests that the coordination chemistry of the $[Tc{=}O]^{3+}$ core with hydrazine derivatives does not parallel that of rhenium or molybdenum, where direct substitution of the terminal oxo group by a doubly deprotonated hydrazido ligand is the rule. Technetium hydrazido chemistry seems to be more complicated, although the substitution of terminal oxo group by substituted hydrazine has been observed as well (see Section 5.2.2.3.5). Still, the tendency toward N—N bond cleavage and the formation of nitrido and imido species of unusual bonding modes is distinct. (Scheme 16).

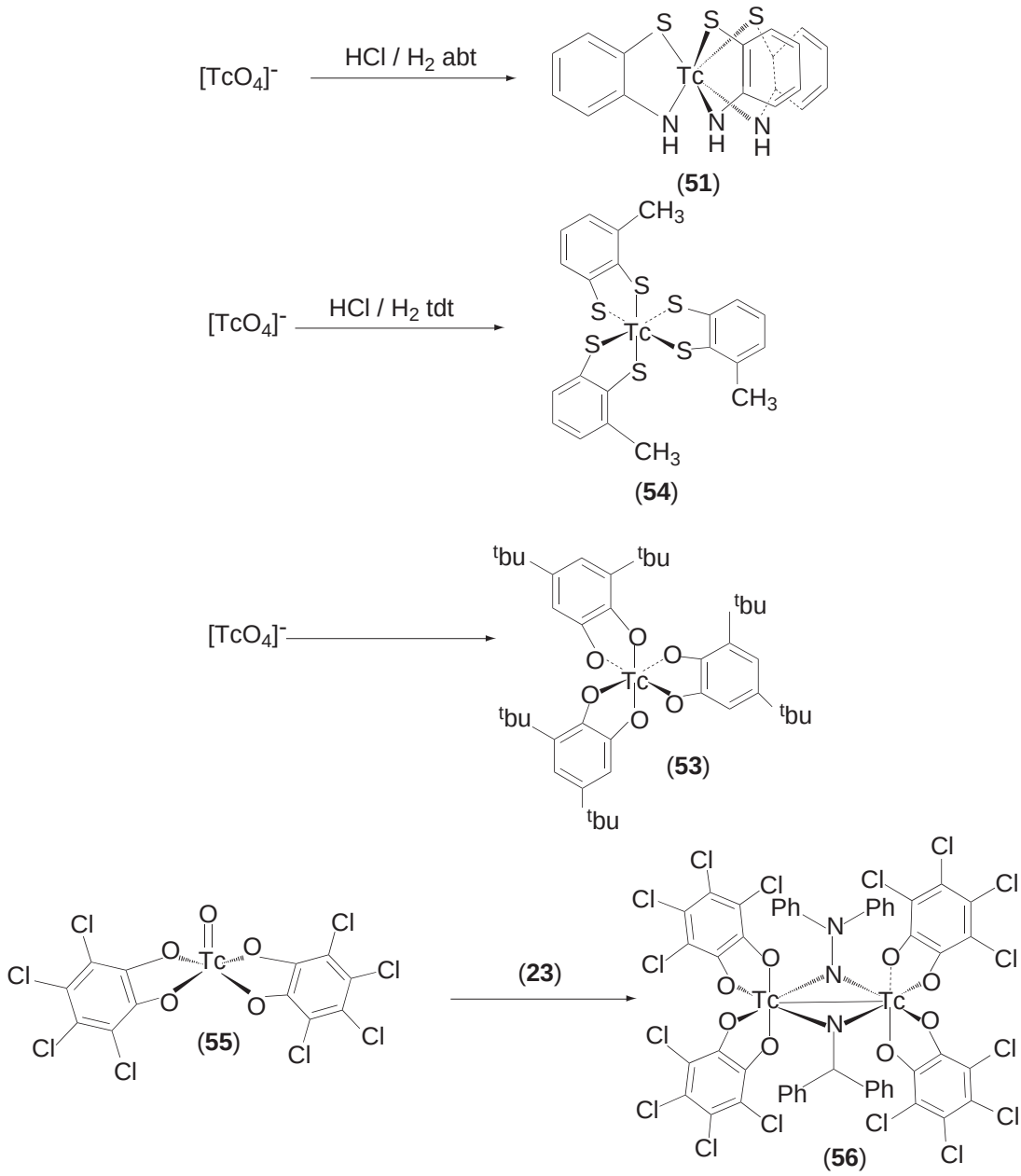
5.2.2.3 Oxidation State (V)

Of all the oxidation states of technetium, the +V state is the most thoroughly investigated. A vast number of compounds have been prepared and analyzed by crystallography, spectroscopy, electrochemistry, and other methods. This dominance is clearly related to the importance of ^{99m}Tc complexes in this oxidation state for application in nuclear medicine (see Section 5.2.3). Another important consideration is the convenient availability of reasonably stable, but also labile, complex precursors such as $[TcOCl_4]^-$ or $[TcNCl_4]^{2-}$ produced *in situ*. Hence, most of the known compounds contain the "$[Tc{=}O]^{3+}$" or "$[Tc{\equiv}N]^{2+}$" cores. These cores can be stabilized by a wide variety of mono- or multidentate ligands, yielding cationic, neutral, or anionic complexes. For applications in radiopharmacy it is essential that these cores can be prepared in one single step from $[^{99m}TcO_4]^-$ in water. Fortunately this is generally the case.

Since O^{2-} as well as N^{3-} are excellent π-donors, stabilizing high oxidation states of transition metals as emphasized in the sections before, they display a strong *trans* influence. Consequently, most of the complexes have square-pyramidal geometry with a strong tetragonal distortion. According to theoretical calculations, the *d*-orbital energy levels in compounds of C_{4v} geometry are b_2 (d_{xy}) < e (d_{xz},d_{yz}) < b_1 ($d_{x^2-y^2}$) < a_1 (d_{z^2}).[179] The two electrons are nonbonding and paired in the b_2 orbital. This results in diamagnetic complexes, or complexes showing slightly temperature-dependent paramagnetism. The $[Tc{=}O]^{3+}$ and the $[Tc{\equiv}N]^{2+}$ cores can thus be regarded as having closed-shell electronic configurations, and substitution-inert complexes are expected. However, kinetic stability is strongly influenced by the type of coligand present. As an important consequence, most of the Tc^V complexes can be characterized by means of ^{1}H NMR spectroscopy, which is a powerful tool, especially when different conformers are formed with one single, multidentate ligand. Both the $[Tc{=}O]^{3+}$ and the $[Tc{\equiv}N]^{2+}$ bonds are formally triple bonds, but unfavorable charge distribution for $[Tc{=}O]^{3+}$ results in a bond which is typically in between triple and double.

In broad terms the coordination chemistries of technetium and rhenium are similar, and isomorphous compounds are frequently found. One important exception is the behavior with phosphanes. Since Tc^V is a stronger oxidant than Re^V, the reaction with phosphanes very often leads to reduction to Tc^{III} and lower oxidation states. This is particularly the case with compounds derived from the "$[Tc{=}O]^{3+}$" core. The complex $[ReOCl_3(PPh_3)_2]$[180] is a very important starting material in Re^V

coordination chemistry, but the technetium congener does not exist. Tc^{V} in the presence of phosphanes is stable only where strongly electron-donating substituents stabilize the formal Tc^{V} core.

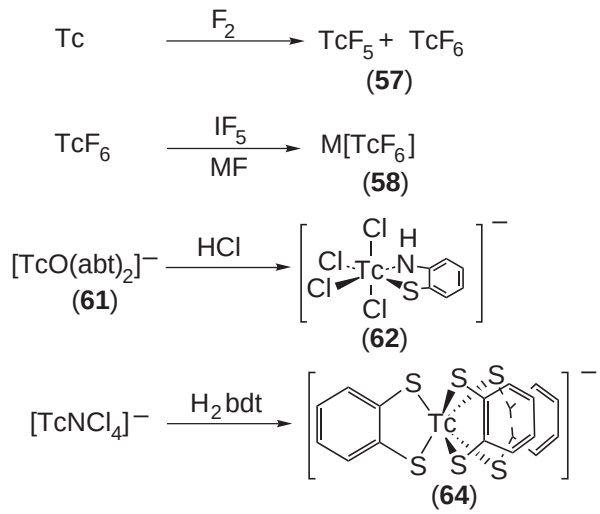


Scheme 16

5.2.2.3.1 Compounds containing no multiply bonded ligands

The number of Tc^{V} complexes containing no multiply bonded ligands is very limited. The only binary halide of this type is $[TcF_5]$ (**57**), which is formed as a by-product in the fluorination of technetium metal.[137] Cleavage of the polymeric solid-state structure to yield hexacoordinated complexes has not been reported, probably due to the difficulty of preparing and handling $[TcF_5]$. However, reduction of the more readily available $[TcF_6]$ in IF_5 and in the presence of MCl leads to reduction and to the formation of $M[TcF_6]$ (**58**).[181] With [NOF] and $[N_2H_6]^{2+}$ in H_2F_2 the corresponding salts $[NO][TcF_6]$ and $[N_2H_6][TcF_6]_2$ can be isolated.[140,182] The alkali hexafluorotechnetate salts have a magnetic moment of 2.25 B.M. at 25 °C and are isostructural with the corresponding ruthenium complexes.

Other complexes containing no multiply bonded ligands can be prepared by oxidation of a Tc^{III} precursor, or by the elimination of the multiply bound group. An example of the first pathway is provided by the oxidative addition of Cl_2 to the well-established Tc^{III} complex $[Tc(diars)_2Cl_2]^+$ (**59**) with diars = 1,2-(dimethylarsine)benzene.[183] Addition of Cl_2 to an alcoholic solution of (**59**) results in the formation of eight-coordinate Tc^V complex $[Tc(diars)_2Cl_4]^+$. The complex $[Tc(diars)_2Cl_4]^+$ (**60**) has a dodecahedral D_{2d} coordination geometry and is formally an 18-electron species.[184] The analogous phosphorus compound does not exist, probably due to the susceptibility of the phosphorus to oxidation. An example of the second route is provided by the reaction of $[TcO(abt)_2]^-$ (**61**) with concentrated HCl/MeOH.[185] Although the terminal oxo ligand is generally not very easily protonated, the unusually long Tc=O distance of 1.73(2) Å[186] in the starting material accounts for its higher basicity. Consequently, in a nonredox process, one abt ligand and the terminal oxo group are cleanly replaced by four chloride ligands, and the anionic Tc^V complex $[TcCl_4(abt)]^-$ (**62**) is formed. The X-ray crystal structure and the magnetic moment of 2.86 B.M. confirm the pentavalent oxidation state for Tc and the presence of a doubly deprotonated abt ligand. The removal of a nitrido ligand is represented by the reaction of (**34**) with H_2bdt (**63**) in acetone. This reaction gave low yields (21%) of the brown Tc^V complex $[Tc(bdt)_3]^-$ (**64**).[128] The geometry of the complex anion is close to ideal trigonal prismatic and the angle between the TcS_2 planes is 119.4°. The distance between the sulfur atoms within one ligand averages 3.06 Å, which is significantly shorter than the sum of the van der Waals radii (3.7 Å). It is suggested that the strong intersulfur interactions help in stabilizing the trigonal-prismatic geometry over the sterically more favoured octahedral geometry. As mentioned earlier, the similar Tc^{VI} complex with toluene-1,2-dithiol, $[Tc(tdt)_3]$ (**54**), is reduced at −0.58 V vs. SCE to the corresponding Tc^V complex, but has not been isolated.[177] (Scheme 17)



Scheme 17

A unique eight-coordinate Tc^V complex has been reported. The reaction of $[TcOCl_4]^-$ with cyclopentamethylenethiuram disulfide (**65**) results in the unusual, deep red, eight-coordinated Tc^V complex $[Tc(S_2C\{NC_5H_{10}\})_4]^+$ (**66**). In this complex the terminal oxygen ligand has been removed from technetium, but the oxidation state did not change. A number of dithiocarbamate compounds of Tc in lower oxidation states were already known, but this is the first example of an eight-coordinate Tc^V species. The shape of the complex cation is best described as a distorted square antiprism with Tc—S distances ranging from 2.463(2) Å to 2.494(2) Å, consistent with other dithiocarbamate complexes.[187] A mechanism for the formation of this unusual complex is proposed. The driving force is believed to be the formation of a strong Tc—S bond and the cleavage of the relatively weak S—S bond by the nucleophilic chloride ion.

5.2.2.3.2 Oxo-complexes, the "$[Tc{=}O]^{3+}$" core

Complexes of Tc^V containing the $[Tc{=}O]^{3+}$ core are in general available from two different synthetic routes. The anions $[TcOCl_4]^-$ (**67**) or $[TcOCl_5]^{2-}$ (**68**) are often used as convenient

starting materials, as in organic solvents the chloride ligands are easily substituted by a wide variety of mono- and multidentate ligands, especially with N- or S-donors. The presence of a base is often not required, since the thermodynamic stability constants are high enough and complex formation equilibria usually greatly favor complex formation.

The second approach is simultaneous reduction and substitution starting directly from $[TcO_4]^-$. This method reflects the requirements of the radiopharmacy; any useful preparation must start from $[TcO_4]^-$ in water and isolation of any intermediate or precursor is not favorable. This method is suitable for the preparation of coordination compounds on the macroscopic scale, but products formed are sometimes not as pure as from $[TcOCl_4]^-$. In the presence of water polymeric Tc^{IV} species may reduce the yield, or reduction to lower oxidation states can occur. The most widely applied starting material is (**67**), usually available as its salt with bulky counterions like $[N(Bu)_4]^+$ or $[As(Ph)_4]^+$. The original synthesis of (**67**) involved reduction of $[TcO_4]^-$ in aqueous HCl, in the presence of hypophosphorous acid as a reducing agent. From the dark green solution, the addition of large cations leads to the precipitation and isolation of salts such as $[N(Bu)_4][TcOCl_4]$.[188] The anion $[TcOCl_4]^-$ is an intermediate *en route* to the Tc^{IV} complex $[TcCl_6]^{2-}$ (**69**), which is the thermodynamic end product in the reaction of concentrated HCl with $[TcO_4]^-$.[189–191] An alternative route involves reaction of $[NH_4][TcO_4]$ with concentrated HCl without reductant and in the presence of bulky counterions like $[N(Bu)_4]^+$·$[N(Bu)_4][TcOCl_4]$ precipitates in almost quantitative yield.[192–194] This versatile availability significantly promoted the development of Tc^V complexes containing the $[Tc{=}O]^{3+}$ core. The gold-red bromide analogue $[N(Bu)_4][TcOBr_4]$ (**70**) is obtained by the same route, but in the presence of 48% HBr.[192,193] Both compounds are isostructural, with a slightly longer Tc=O bond in the case of the bromide complex (1.613(9) Å vs. 1.593(2) Å).[195] However, in the case of HBr the reaction forms the Tc^{IV} complex $[TcBr_6]^{2-}$ (**71**) more rapidly, probably due to the better reducing power of Br^- compared to Cl^-. In the presence of $[N(Et)_4]^+$ it is possible to crystallize the monoaquated species *trans*-$[TcOBr_4(OH_2)]$, in which the water ligand is *trans* to the oxo ligand, to give an overall distorted octahedral structure as confirmed by X-ray structure analysis.[196] Although both complexes are square pyramidal in the solid state, in acidic aqueous solution one loosely bound water is coordinated. $[NBu_4][TcOI_4]$ (**72**) is best synthesized by ligand exchange from the corresponding chloride complex with NaI in acetone. The direct reaction with HI leads to contamination of the product with Tc^{IV} species and with polyiodides.[108]

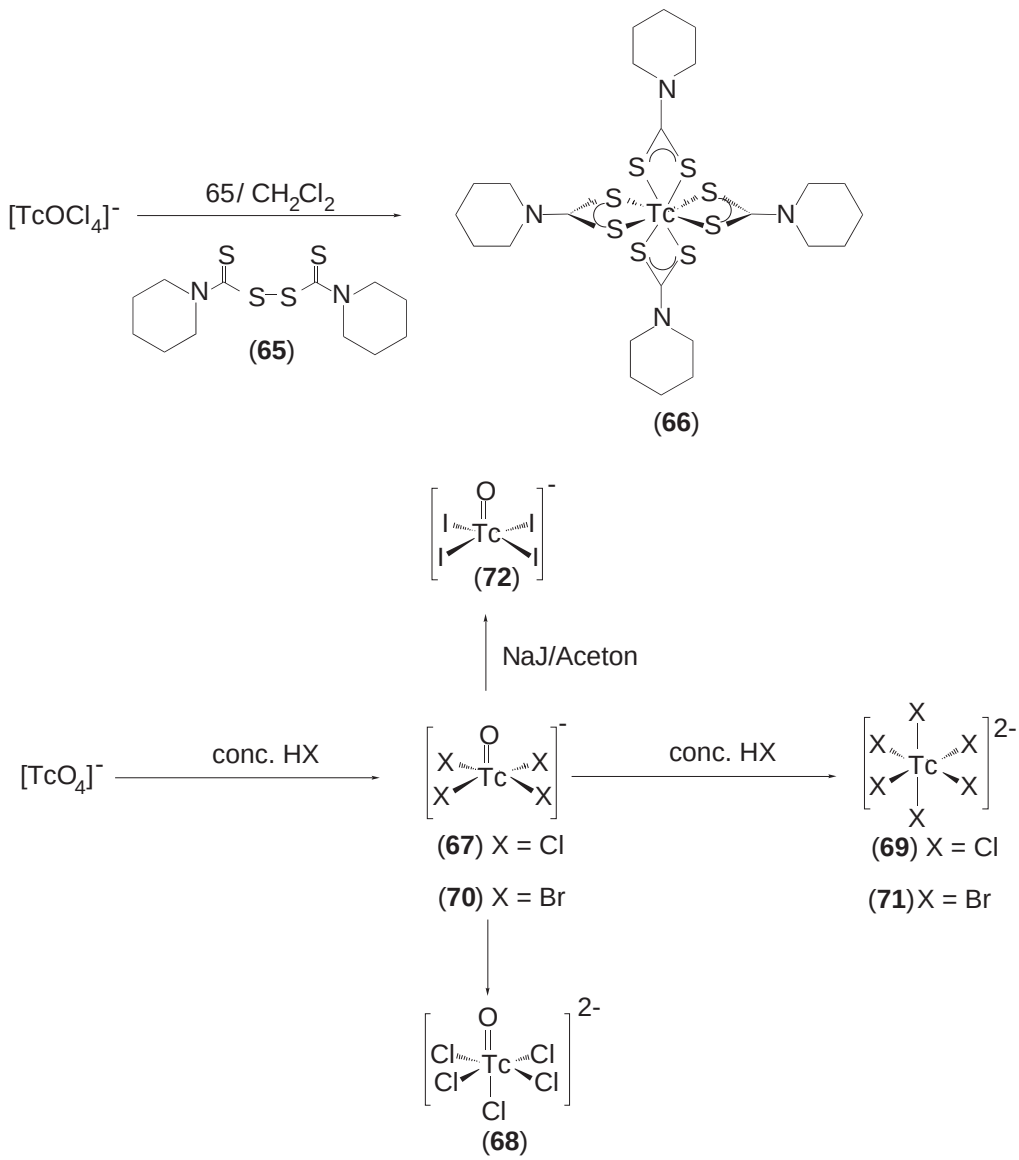
In the presence of a large concentration of chloride, complex (**68**) is formed and salts $M_2[TcOCl_5]$ ($M{=}NH_4^+$, Na^+, K^+, Cs^+) can be obtained as olive-green precipitates by addition of the appropriate chloride.[191,197] The equilibrium between $[TcOCl_4]^-$ and $[TcOCl_5]^{2-}$ has been studied by of EPR[198] and Raman spectroscopy.[197] In 12M HCl the equilibrium constant was found to be in the range of $1.5+/-1\times10^{-3}$. In water $[TcOCl_4]^-$ undergoes a fast disproportionation to polymeric $2TcO_2$ and $[TcO_4]^-$, which significantly limits its usefulness in this solvent. Slow disproportionation is found in slightly acidic solution only. In acidic aqueous solution at concentrations >2M in HCl, the disproportionation occurs very slowly.[54,199] (Scheme 18).

(i) Oxygen ligands including macrocycles

Well-defined complexes containing exclusively oxygen donors are relatively rare. Where known, the structure is usually square pyramidal, with the oxo-substituent in the apical position and significantly displaced out of the basal plane. For a summary, see Scheme 19. Among the first complexes of this kind was the bis-1,2-ethylene-glycolato (H_2eg, (**73**)) complex $[TcO(OCH_2CH_2O)_2]^-$ (**74**), prepared from the direct reaction of $[TcOCl_4]^-$ with (**73**) in the presence of a base.[200,201] Red-violet (**74**) is soluble in polar organic solvents, but unstable in the absence of excess ethylene glycol. In water at pH < 10 the complex hydrolyzes readily to TcO_2 and $[TcO_4]^-$. Since the glycolato ligand is easily replaced by other ligands and functions as a base, (**74**) represents a convenient starting material for the preparation of other Tc^V complexes. Aromatic diolato ligands such as catechol give more stable complexes. The treatment of $[TcOCl_4]^-$ in methanol with catechol (H_2cat (**75**)) in the presence of base produces $[TcO(O_2C_6H_4)_2]^-$ (**76**) as golden crystals.[200] This compound has been structurally characterized. The analogous 4-nitro catecholato- and tetrachloro-catecholato-complexes $[TcO(O_2C_6H_3NO_2)_2]^-$ (**77**) and $[TcO(O_2C_6Cl_4)_2]^-$ (**55**) have also been prepared and their structures elucidated.[178,202] Compounds of this type with C_{4v} symmetry are diamagnetic.[54] (Scheme 19).

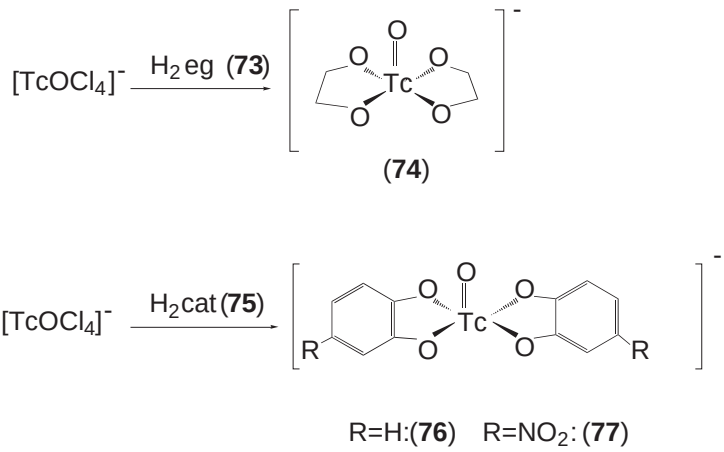
A series of Tc^V complexes with the monobasic ligands 2-methyl-3-oxy-4-pyronate (maltolate, Hma (**78**)) or 1,2-dimethyl-3-oxy-pyridinonate, (Hdpp, (**79**)) were prepared in nonaqueous solution by chloride substitution in $[TcOCl_4]^-$. Stepwise substitution is observed. The substitution of one

chloride leads to the structurally characterized complex $[TcOCl_3(ma)]^-$ (**80**), which is six-coordinate with one of the ligand oxygen donors *trans* to the oxo ligand. This Tc—O bond is weak, as indicated by the bond length of 2.152(2) Å. In the presence of a second equivalent of ligand, two further chlorides are substituted to yield the greenish-yellow neutral complex $[TcOCl(ma)_2]$ (**81**), the structure of which was determined for rhenium and with bromide instead of chloride. For (**79**) only the corresponding bis-substituted complexes were produced. An interesting difference was observed upon prolonged standing of the pure monosubstituted complex in organic solvents. Whereas the rhenium complex $[ReOBr_3(ma)]^-$ undergoes disproportionation to $[ReOBr(ma)_2]$ and $[ReOBr_4]^-$, the corresponding technetium complex is perfectly stable.[203] Both complexes are unstable towards hydrolytic decomposition and convert slowly into TcO_2 and $[TcO_4]^-$.



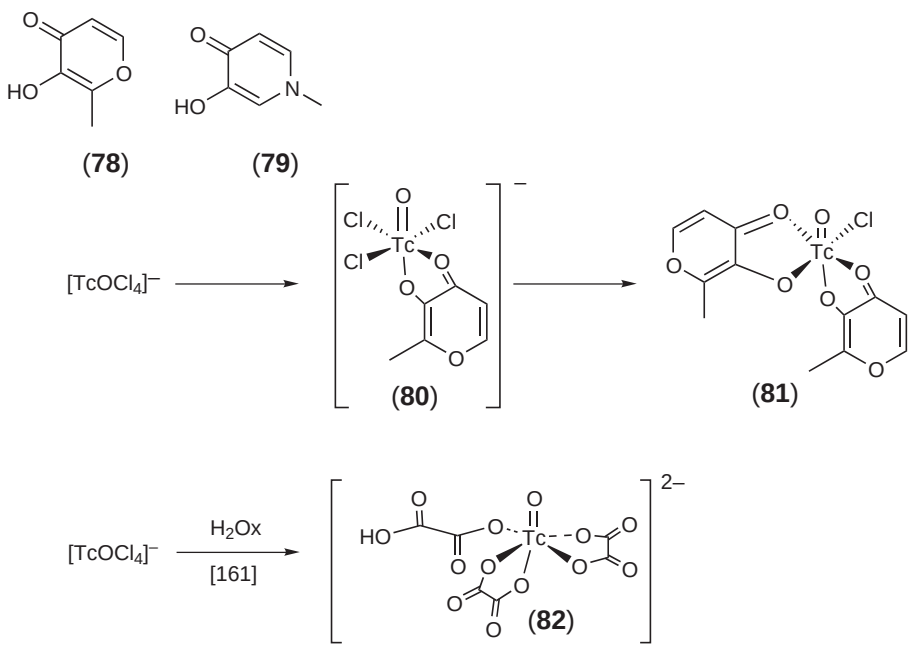
Scheme 18

Reaction of $[NBu_4][TcOCl_4]$ in aqueous acetone with oxalic acid H_2ox gives the unusual, six-coordinated Tc^V complex $[TcO(ox)_2(Hox)]^{2-}$ (**82**) as the $[As(Ph)_4]^+$ salt. One of the oxalato-ligands is coordinated through one oxygen of one carboxylic acid group only, whereas the other two are bidentate. The absence of a significant *trans* influence of the oxo ligand is also unusual. The Tc—O distance for the oxygen *trans* to the oxo group is 2.069(6) Å, similar to the Tc—O distance for the *cis* oxygens, which averages 2.016 Å.[168] The reasons for the low tendency of the oxalato ligand to show a *trans* influence are unclear.[204]



Scheme 19

Gluconate or heptagluconate complexes are among the most important starting materials for radiopharmaceutical preparation of Tc^{V} derivatives and they are used in many labeling procedures. Labeling procedures are based on the stabilizing effect of these two ligands for Tc^{V} in aqueous solution. These auxiliary ligands are subsequently exchanged for the radiopharmaceutically useful ligands which can, be attached to a biomolecule. As is frequently the case for radiopharmaceutical preparations at the tracer level, the exact structures of these precursor complexes are not known. They are generally believed to be of the type $[TcO(L_2)]^{-}$ from various spectroscopic and chromatographic analyses.[205] However, due to significant differences in reaction pathways at high dilution (^{99m}Tc) and at normal concentration (^{99}Tc), their structures are not unambiguously proven.



Scheme 20

The synthesis of a variety of β-diketonato complexes of Tc^{V} has been described.[206] None of these compounds has been structurally described, but they are formulated as $[TcO(\beta\text{-diketonate})_2Cl]$. A further variant of purely oxygen-coordinated Tc^{V} results from use of the "Kläui-ligand" (**18**).[119] Yellow-green complexes of composition $[(L_{OR})TcOCl_2]$ were prepared by reaction of $[TcO_4]^{-}$ in the presence of conc. HCl with the ligand (**18**).

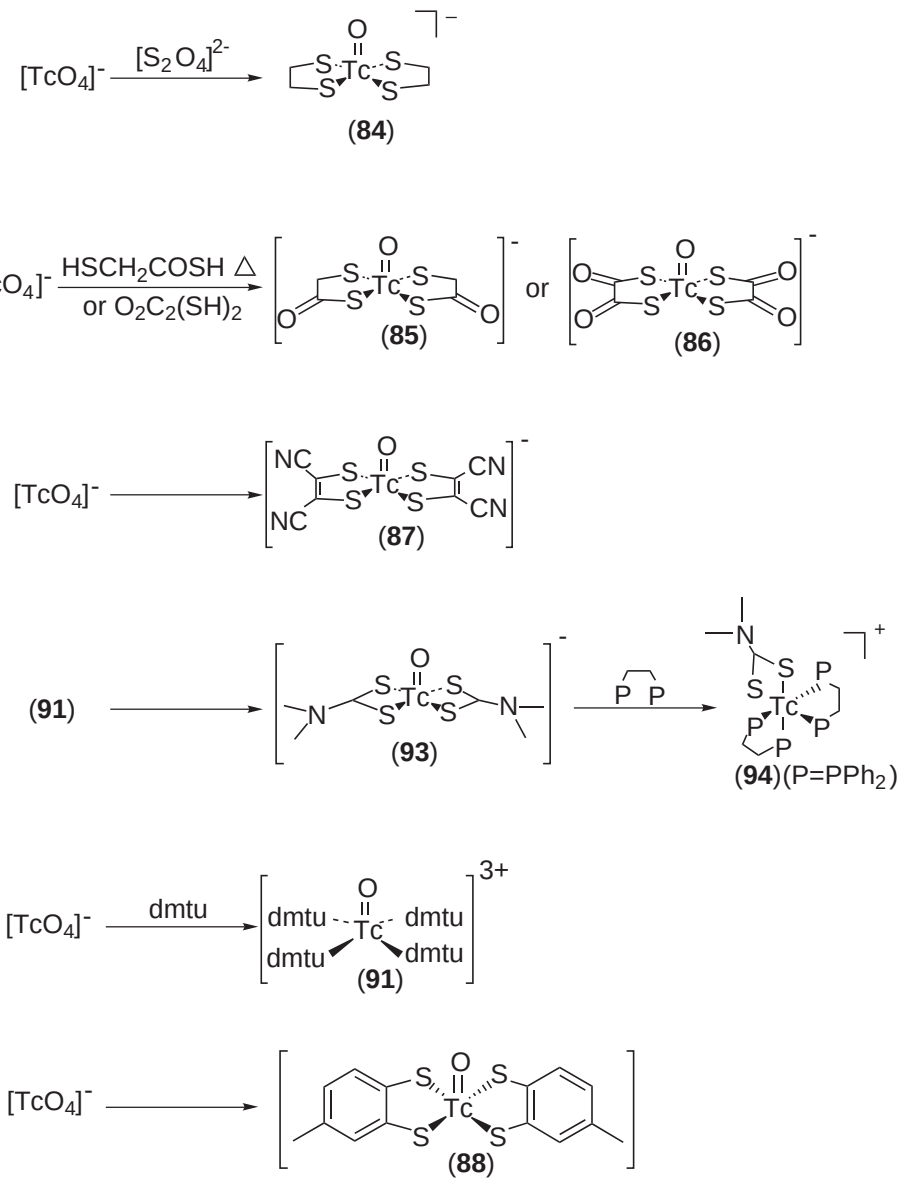
(ii) Sulphur ligands

Complexes of Tc^{V} comprising the $[Tc{=}O]^{3+}$ core with sulfur donor only as coligand are also relatively rare. Some examples are given in Scheme 21. One of the first complexes of this type was prepared directly from reaction of $[NH_4][TcO_4]$ in ethanol with 1,2-ethanedithiol (H_2edt, (**83**)) and other dithiols, with $[BH_4]^-$ present as a reducing agent. The anionic, orange compounds $[TcO\{S(CH_2)_nS\}]^-$ (**84**) can be precipitated with bulky cations such as $[N(Bu)_4]^+$ directly from solution. As expected, the complexes are square pyramidal, with the Tc located about 0.761(2) Å above the basal plane. The complexes were characterized by X-ray structure determinations and spectroscopic methods, such as IR/Raman, UV/Vis, and NMR.[207,208] An alternative method uses dithionite as a reducing agent. $[NH_4][TcO_4]$ in alkaline water was reduced with $Na_2[S_2O_4]$ and reacted with (**83**) to give (**84**) in 99% yield. The substitution reaction starting from $[TcOCl_4]^-$ gave a reduced yield of 77%.[209] According to periodicity considerations, Re is harder to reduce than Tc and this is illustrated by the ready reduction of Tc^{VII} with $[S_2O_4]^{2-}$ at room temperature, whereas the corresponding Re^{VII} requires $[BH_4]^-$ and heating under reflux. A number of other complexes with two bidentate chelating sulfur donors have been prepared similarly. The reaction of $[NH_4][TcO_4]$ with thioglycolic acid in alkaline water and in the absence of any reducing agent gives complexes of the type $[TcO(SCH_2COS)_2]^-$ (**85**), isolated in 22% yield after precipitation with a bulky cation. The complexes $[TcO(S_2C_2O_2)_2]^-$ (**86**), $[TcO(S_2C_2\{CN\}_2)_2]^-$ (**87**), and $[TcO(tdt)_2]^-$ (**88**) were prepared analogously, but could also be produced directly from $[TcOCl_4]^-$ in better yields.[209,210] All the complexes range in color from orange to red-brown. A bathochromic shift is observed for the Tc complexes compared to their rhenium analogues, as expected from periodicity considerations. The complexes are generally weakly paramagnetic, with an effective field-strength-dependent magnetic moment of 0.1–1.5 μ_B.[209] The complexes described above are stable in aqueous solution for days, which makes this type of complex very attractive for applications in nuclear medicine. Various dithiols like, e.g., (**83**) can be used as ligands and reducing agents at the same time to yield the corresponding $[TcO\{S\}_4]$ compounds. The compounds can generally be prepared in better yield, however, by the direct substitution of chloride in $[TcOCl_4]^-$. In their structure they show the expected square-pyramidal or distorted square-pyramidal geometry, with the Tc located an average of 0.74 Å above the basal plane.[211–213] The high stability of the complexes is shown by their electrochemical behavior, which shows no tendency to be oxidized to Tc^{VI} or reduced to Tc^{IV}. Any attempts to use electrochemical methods in that direction failed. The dithiolato ligands are inert to chemical exchange. The oxo group is resistant to reductive removal by triphenylphosphane, usually a versatile method to produce Tc^{III} complexes.

The radiopharmaceutical syntheses of complexes with the $[^{99m}TcO\{S\}_4]$ core is generally achieved by addition of an excess of the appropriate dithiol to *in situ*-generated Tc^{V} gluconate. The same strategy can also be applied to the synthesis of complexes with ^{99}Tc, and many $[^{99m}TcO\{S\}_4]$ derivatives have been prepared.[210,214–217]

The reaction of $[TcOCl_4]^-$ with various monodentate aromatic thiols in methanol produces complexes of the general formula $[TcO(SAr)_4]^-$ (**89**), which can be precipitated with bulky cations. The X-ray crystal structure of the complex with Ar = mesityl has been elucidated and has square-pyramidal geometry, with the Tc atom displaced from the basal plane by about 0.846 Å.[218,219] Direct reaction of $[TcO_4]^-$ in 2M HCl with thiourea (tu, (**90**)) derivatives such as tetra- or dimethylthiourea (tmtu, dmtu) gives, e.g., a five-coordinate complex $[TcO(tmtu)_4]^{3+}$ (**91**), which can be precipitated with large anions such as $[PF_6]^-$.[220] Under more forcing conditions further reduction to Tc^{III} complexes occurs with less bulky thioureas, such as tu or dmtu (see Section 5.2.2.5.4). An unexpected reaction is observed when (**91**) reacts with the bidentate phosphane ligand bis(diphenylphosphino) ethane (dppe, (**92**)) in DMF at room temperature overnight. Two of the tmtu ligands form a coordinated dithiocarbamate ligand, and the complex $[TcO(tmtu)_2(SSCN(CH_3)_2)]^{2+}$ (**93**) is formed in 30% yield. It is assumed that the metal mediates a sulfur transfer from one tmtu to another, with the release of one equivalent of tetramethylurea and diethylamine. The X-ray crystal structure confirmed that (**93**) has square-pyramidal geometry, as proposed on the basis of spectroscopy.[221] Use of the same reaction conditions but a higher dppe concentration caused reduction, with formation of the Tc^{II} complex $[Tc(S_2CNMe_2)(dppe)_2]^+$ (**94**). (Scheme 21).

Another compound of considerable radiopharmaceutical relevance and based on dithiolato donors is the Tc^{V} complex of dimercaptosuccinic acid (H_2dmsa, (**95**)). The ligand (**95**) has both a meso and optically active forms, leading to complexes of different stereochemical configuration, which have very different *in vivo* behavior. Whereas the complex from racemic (**95**) leads to a product that is renally excreted without accumulation in any other organ, the complex prepared from



Scheme 21

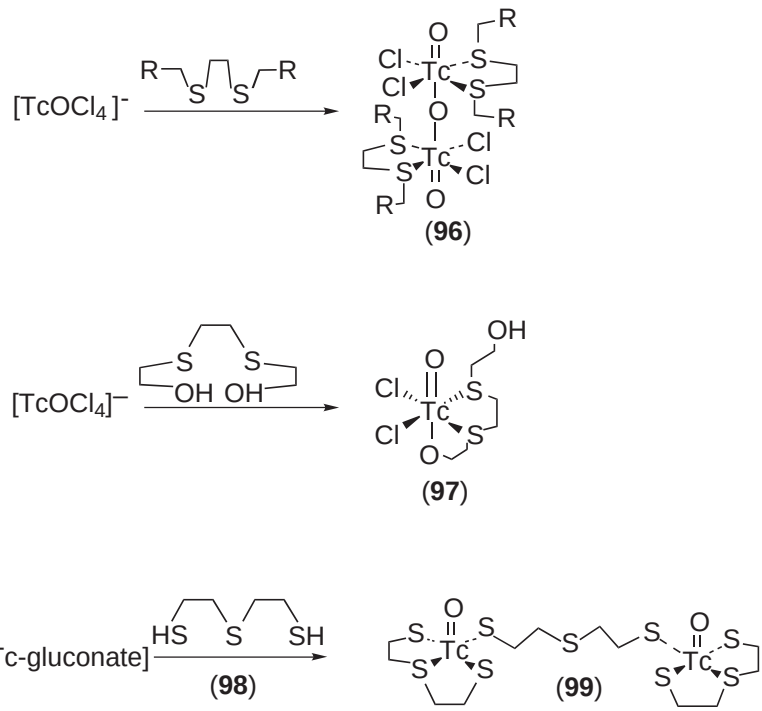
meso-dmsa is osteotropic. The corresponding dimethylester complexes $[TcO(dmsa)_2]^-$ have been prepared and structurally characterized.[222] Since the meso form of the ligand is achiral, anti, endo, and exo, configuration complexes were expected and all possible forms were present. ^1H NMR data was consistent with the syn isomer but no differentiation between the endo and exo forms was possible. The X-ray crystal structure indicated that the syn-endo isomer crystallizes preferentially.

Since the ^{99m}Tc complex of (**95**) proved to be a powerful radiopharmaceutical for the detection of bone cancer metastasis, considerable efforts have been made to provide the reasons for the specificity. In the preparation of the corresponding radiopharmaceuticals, all three stereoisomers are present from the reaction with meso-dmsa. The reason for the osteotropic behavior may arise from deprotonation of the noncoordinated carboxylic acid groups, and the active complex in solution therefore bears a 5− charge.[223,224]

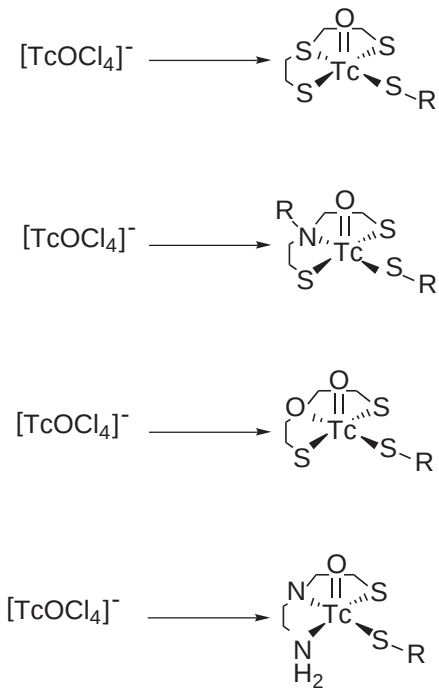
A special case of complexes containing the $[Tc{=}O]^{3+}$ moiety and exclusive coordination to sulfur donors is that of thioether coordination. Although the $[Tc{=}O]^{3+}$ core is thiophilic, thioether coligands are not sufficient to stabilize the +V state and the 3+ charge. Several attempts in that direction have failed and complexes with additional anionic donors were formed. Reaction of $[TcOCl_4]^-$ with bidentate thioethers (S_2) leads to a class of complexes containing the

$[O{=}Tc{-}O{-}Tc{=}O]^{4+}$ core. The reaction with a variety of dithia-alkanes gave complexes of the composition $\{[TcO(S_2)(Cl)_2]_2\}(\mu\text{-}O)$ (**96**) as yellow-green crystals. The X-ray crystal structure consists of two independent "$[TcO(S_2)Cl_2]$" units bridged by an almost-linear oxygen atom. The conformation is anti with respect to the bridging oxygen, and it can be concluded from the linearity of the complex that significant π-bonding between metal and oxygen is involved.[225,226] The reaction with a bidentate thioether with an additional terminal hydroxy function yields the neutral, six-coordinate, mononuclear complex $[TcO(O(CH_2)_2S(CH_2)_2S(CH_2)_2OH)Cl_2]$ (**97**), in which one of the hydroxy groups is deprotonated and coordinates *trans* to the oxo ligand.[226] The bond distances to the bridging oxygen in the dinuclear species (**96**) or to the nonbridging oxygen ligand in (**97**) are 1.98(3) Å and 1.895(4) Å, respectively: thus for both cases intermediate between clear single and double bond. Another type of dinuclear complex is derived from certain tridentate thioether/dithiol ligands. The ligand 3-thiapentane-1,5-dithiol HS-S-SH (**98**) reacts with Tc-gluconate in acetonitrile to yield the dinuclear, ligand-bridged complex $[\{TcO(S{-}S{-}S)\}_2(\mu\text{-}(S{-}S{-}S))]$ (**99**).[227] The structure of the direct precursor [TcO(S—S—S)Cl] has also been determined.[228] Other dinuclear complexes with a bridging oxygen will be treated in the sections with the respective ligand atom combinations. (Scheme 22)

Complexes of oxo-technetium(V), one tridentate ligand, and an additional monodentate thiolato ligand, the so called "[3 + 1]" mixed-ligand system, have been extensively studied for the labeling of biomolecules. In general, [3 + 1] mixed-ligand complexes of the type [TcO(SXY)(SR)] (X = O,N,S and Y = N or S) are prepared by the reaction of a potentially dianionic tridentate ligand H_2L and a monodentate, monoanionic, thiolate coligand with a suitable oxo-technetium precursor.[229–232] If R above is, for instance, a CNS-binding ligand, the complexes can be used for the imaging receptors in the central nervous system (see Section 5.2.3). Addition of a tridentate ligand to $[TcOCl_4]^-$ gives [TcO(SXY)Cl], and subsequent addition of a monodentate ligand HS—R gives the mixed-ligand complex [TcO(SXY)(SR)]. Alternatively, complexes of the same composition are prepared by ligand exchange on the Tc-gluconate precursor.[227,233] A wide variety of complexes with technetium and rhenium have been structurally characterized, in particular for the donors SNS[234–243] but also for the SNN donor set.[242] It is not only sequential addition of the tri- and the monodentate ligands to the Tc-precursor that gives the appropriate complexes, but also concerted addition of both ligands at the same time to carrier-added $[TcOCl_4]^-$ or Tc-gluconate. The "[3 + 1]" complex synthesis at n.c.a. level (^{99m}Tc) yields a mixture of products, besides the required complex.



Scheme 22



Scheme 23

Since complexes of this mixed-ligand type play an important role in the development of receptor-binding radiopharmaceuticals,[243–245] attention was paid to the preparation of pure mixed-ligand complexes with ^{99m}Tc. The preparation of [^{99m}TcO(SSS)(SR)] at the n.c.a. level in good yield and purity is possible only by subsequent HPLC separation of the mixture.[246]

Investigations with one bidentate and two monodentate ligands have also been performed and a number of complexes of the type $[TcO(NS)(SR)_2]$ have been structurally characterized (Scheme 23).[247]

One of the rare examples in which selenium is involved as a donor atom results from the reaction of Tc-gluconate with 2 equivalents of 1,1-dicyanoethene-2,2-diselenolate (dcds), which gives the selenium analogue of (**87**), $[TcO(dcds)_2]^-$, in 50% yield. The complex was structurally characterized and shown to be square pyramidal, with Tc—Se averaging 2.474 Å and the Tc 0.88 Å above the basal plane.[248]

A comparison of the IR bands due to $\nu_{Tc=O}$ for stepwise substitution of Se by S showed that $\nu_{Tc=O}$ for four Se donors is 965 cm^{-1}, whereas for two Se and two S it is 970 cm^{-1}, and for sulfur only 980 cm^{-1}.[249]

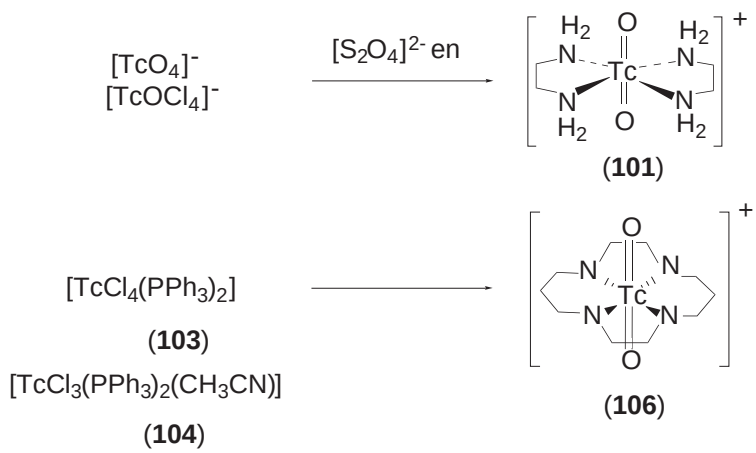
(iii) Nitrogen ligands including macrocycles

Substitution reactions on $[TcOCl_4]^-$ with aliphatic or aromatic amines yield in general complexes with the *trans* dioxo technetium core $[O{=}Tc{=}O]^+$. The neutral nitrogen donors in these ligands do not contribute much to charge compensation and are poor π-donors, which makes the formal $[Tc{=}O]^{3+}$ very susceptible to substitution by water and subsequent deprotonation. However, if other donor atoms in the multidentate, amine-containing ligand are negatively charged and serve as good π-donors, five-coordinate monoxo complexes are formed. The additional oxo probably comes from water, which is omnipresent in amines, and which explains the formation of complexes of the general type $[TcO_2(N_4)]^+$. Exceptions are complexes with deprotonated diamino-benzene ligands or with triply deprotonated, oxime-type ligands which will be described later in this section.

The reaction with aliphatic diamines is exemplified by that of 1,2-diaminoethane (en, (**100**)). Substitution of the chlorides in $[TcOCl_4]^-$ with en gave in THF the cationic complex $[TcO_2(en)_2]^+$ (**101**) as orange needles. The compound is diamagnetic and the four nitrogen atoms are essentially coplanar. The Tc=O bond lengths in this and most of the other complexes comprising the

$[O{=}Tc{=}O]^{+}$ core are significantly longer, at 1.75 Å, in comparison to the mono-oxo complexes, due to the strong *trans* influence of terminal oxo groups.[250] The complex $[TcO_2(pn)_2]^{+}$ (**102**) with 1,3-diaminopropane (pn) can be made by the same route, or directly from $[TcO_4]^{-}$ in aqueous solution with $[S_2O_4]^{2-}$ as a reducing agent. The structural properties of (**102**) are comparable to those of (**101**).[251] Another unexpected route to *trans* dioxotechnetium(V) complexes starts from the Tc^{IV} precursor $[TcCl_4(PPh_3)_2]$ (**103**) or the Tc^{III} complex $[TcCl_3(NCCH_3)(PPh_3)_2]$ (**104**) in acetonitrile. At room temperature and in the presence of (**100**), the corresponding complex (**101**) is formed in 70–80 % yield. In a similar procedure, a number of *trans* dioxo complexes with tetraaza macrocycles are formed. Reaction with 1,4,8,11-tetraaza-cylotetradecandecane (cyclam, (**105**)) gave $[TcO_2(cyclam)]^{+}$ (**106**) in good yield.[252] The additional oxygen comes from adventitious water, and the oxidizing agent is atmospheric oxygen. Other macrocycles with additional ketone groups in the backbone (mon-oxocyclam, dioxo-cyclam) were prepared similarly. Although it is claimed that the structure is similar, it is not clear whether the amide nitrogens coordinate without protonation. No structural evidence for the formulation with mono- and dioxo-cyclams is given. It is noteworthy that the reaction of $[TcCl_4(PMe_2Ph)_2]$ instead of $[TcCl_4(PPh_3)_2]$ did not yield the corresponding *trans*-$[O{=}Tc{=}O]^{+}$ complexes, or a reasonable product at all. This indicates that the strong π-acceptor PPh_3 is of importance in determining the course of the reaction. Interestingly, using $[TcOCl_4]^{-}$ as a starting material no stabilization of $[O{=}Tc{=}O]^{+}$ is obtained, and the yields of the corresponding $[TcO_2(N_4)]^{+}$ complexes are very low and comparable to an earlier preparation of $[TcO_2(tad)]^{+}$ starting directly from $[TcOCl_4]^{-}$.[250] The original procedure with 1,4,8,11-tetraazacyclotetradecane (cyclam) yielded (**106**), but started from an aqueous $[TcO_4]^{-}$ solution and $[S_2O_4]^{2-}$ as a reducing agent.[253] This reaction gave a poor yield of 7% only. Complexes with different stereoisomers of 1,2-diaminocyclohexane (DACH) have been prepared, either by ligand exchange from $[TcOCl_4]^{-}$ or by reduction of $[TcO_4]^{-}$ in conc. HCl and subsequent ligand reaction.[254]

A number of X-ray crystal structures of these complexes with aliphatic diamines and the *trans* $[O{=}Tc{=}O]^{+}$ core have been elucidated. They all have in common that the Tc=O distances are elongated in comparison to the Tc=O monooxo counterparts. Typical Tc—O bond lengths are around 1.75 Å, whereas the average Tc—N distances range from 2.15 Å to 2.2 Å.[251,255] A comparable observation concerns the IR $\nu_{Tc=O}$ stretching frequencies, which for these complexes are in the range of 800 cm^{-1}. The general reactivity of these complexes for substitution by other ligands is weak and descriptions of controlled substitution reactions of aliphatic amines by other ligands are rare. (Scheme 24)



Scheme 24

Another important class of complexes with the $[Tc^{V}O_2]^{+}$ core contain monodentate heterocyclic amines such as imidazole (im, (**107**)) or pyridines (py, (**108**)). The reaction of $[TcOCl_4]^{-}$ with excess (**107**) and derivatives in ethanol gave pink complexes of the type $[TcO_2(L)_4]^{+}$ (**109**) (L= (**107**) or 1-methyl-(**107**)), which were structurally characterized. Both structures are essentially identical. The average Tc=O and Tc—N bond lengths are 1.71(2) Å and 2.15(2) Å, respectively,[254] and the coordination geometry is distorted octahedral. The imidazole rings are twisted away from the O=Tc=O axis. The IR bands for the TcO_2 group fall within the expected range

of 790–835 cm^{-1} for the asymmetric O═Tc═O stretch. The complexes are diamagnetic and the proton signals from the imidazole rings are shifted slightly downfield. The diamagnetism in all complexes containing the $[O{=}Tc{=}O]^{3+}$ group is a consequence of the strong tetragonal distortion of the ligand field, as imposed by the two oxo-ligands. This causes the d_{xy} orbital to lie substantially below the set of degenerate d_{xz} and d_{yz} orbitals and results in a diamagnetic $^1A_1$ ground state. This interpretation agrees with the observed electronic spectrum of (**101**) and the corresponding pyridine complexes, which shows the expected three electronic transitions. For $[TcO_2(en)_2]^+$ the ligand field splitting parameter is 18,700 cm^{-1}. Comparable electronic features also occur for imidazole and pyridine complexes.[254]

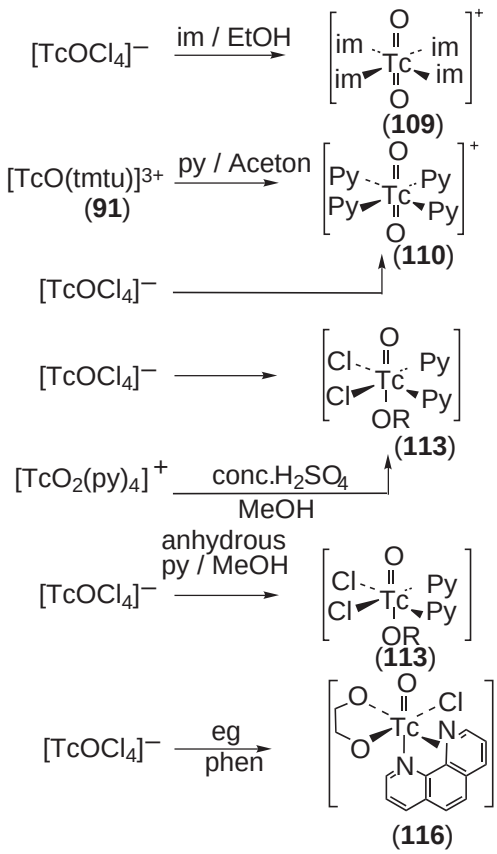
The imidazole complexes are unstable in aqueous solution and decompose rapidly to TcO_2. At lower pH the complexes undergo acid-catalyzed decomposition. None of the complexes exhibited oxidation or reduction processes by cyclic voltammetry. However, it was chemically possible to reduce the imidazole complex with Zn in 1M HCl. A defined complex formed that did not contain the Tc═O group; probably reduction to Tc^{III} complexes occurred.[254]

The first description of a Tc^V complex with pyridine (**108**) dates back to 1972. Its formulation as $[TcO_2(py)_4]^+$ (**110**) was made on the basis of IR studies and correct assignment of the vibration at 825 cm^{-1}.[256] The same complex was also obtained in later work. The reaction of $[TcO(tmtu)_4]^{3+}$ (**91**) with (**108**) in acetone also produces (**110**), but the reaction mechanism is unclear.[220] The reaction of $[TcOCl_4]^-$ with neat (**108**) gave $[TcO_2(py)_4]^+$, and the reaction with 4-*t*-butylpyridine (tbp) in methanol after 5–10 min at room temperature gave the complex $[TcO_2(tbp)_4]^+$ in yields of 80–90 % as yellow crystals.[257] The analogues with dimethylpyridine and aminopyridine can be prepared similarly. An alternative and earlier route started from (**69**) to yield the same material.[258] Infrared absorptions due to the O═Tc═O unit are observed, as expected, in the range assigned to the asymmetric $[O{=}Tc{=}O]^+$ stretch, and are between 818 cm^{-1} and 828 cm^{-1}. The high yields of complexes containing the $[O{=}Tc{=}O]^+$ core by direct combination of the pyridine ligands with $[TcOCl_4]^-$ make this synthetic approach a general method. The presence of electron-withdrawing substituents on the pyridine, such as 4-cyanopyridine (**111**) or 4-nitropyridine (**112**), gives rise to complexes of general type $[TcO(OR)Cl_2L_2]$ (**113**).[259] Recrystallization of the pyridine complexes is possible only in the presence of excess (**108**), indicating that the pyridine ligands are weakly bound. Consequently, $[TcO_2(py)_4]^+$ is an excellent starting material for complexes with the $[TcO_2]^+$ core. The lability is also demonstrated by the ready disproportionation in water to Tc^{IV} and Tc^{VII}. As in the case of complexes with imidazoles above, no observable oxidation or reduction processes are obtained with electrochemical methods. This is somewhat surprising for the high oxidation state of technetium, but is a general feature of most compounds of this type. Upon prolonged standing in neat pyridine, a mixture is produced which contains at least one reduced species. From these solutions, asymmetric μ-oxo-bridged compounds can be isolated and characterized.[260]

Further investigations on the reactivity of (**110**) as a starting material have been carried out. The assumption that mixed-ligand complexes of the type $[TcO(OR)Cl_2(L)_2]$ (L = pyridine derivative) are accessible only if L contains a strongly electron-withdrawing substituent (see above) has been disproved. Due to the high lability of the pyridine ligands, it was possible to prepare mixed-ligand complexes of the type $[TcO(OR)Cl_2(L)_2]$ with L = py or substituted pyridines as well. Two different methods are feasible. Rigorous exclusion of water in the reaction of $[TcOCl_4]^-$ with pyridine in THF produces, after addition of MeOH, $[TcO(OCH_3)Cl_2(py)_2]$ in very good yields as a green precipitate.[261] Furthermore, (**110**) in acidic alcoholic solution with chloride, also gives $[TcO(OCH_3)Cl_2(py)_2]$. This reaction requires the presence of concentrated sulfuric acid, probably to doubly protonate the oxo ligand, thereby labilizing it in the form of coordinated water. The ability of the alcohol to deprotonate and coordinate under such strongly acidic conditions is quite remarkable. As an extension to this study, analogous complexes with thiazol (tz (**114**)) $[TcO_2(tz)_2]^+$ (**115**) and $[TcO(OCH_3)Cl_2(tz)_2]$ have been prepared.[261] Similarly, the reaction between $[TcOCl_4]^-$ ethane-1,2-diol (H_2eg) and phenanthroline gives the green complex [TcOCl(eg)(phen)] (**116**) in 73% yield. The X-ray crystal structure of the complex shows that the Tc has distorted octahedral geometry. The chloride ligand is located *cis* to the terminal oxo ligand and the bond distance is longer (2.4118(2) Å) than a normal Tc—Cl bond, showing the strong *trans* influence of the deprotonated glycolato oxygen donor. The strong *trans* influence of the oxo ligand weakens the *trans* Tc—N bond to the extent that it is at the upper limit of what can still be considered to be a Tc—N bond (2.268(4) Å).[261]

The substitution of $[TcO_2(py)_4]^+$ in DMF or DMF/MeOH mixtures with monodentate ligands such as cyanide, imidazole, or multidentate chelators such as cyclam and en has been studied. For all the ligands, complete replacement of the pyridines occurs. A dependence on the added alcohol is observed, whereas there is little or no dependence on the nature of the incoming ligand. The

exchange is clearly solvent mediated and independent of the incoming or the leaving group. The rate-determining step is probably replacement of pyridine by alcohol. In DMF the reaction mechanism is likely to be dissociative.[262] (Scheme 25)



Scheme 25

Multidentate nitrogen donor ligands of the oxime type have been investigated intensively. It was observed early that complexes with the tetradentate ligand 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime (H_3pnao2, (**117**)) or 3,3,8,8-tetramethyl-4,7-diaza-decane-2,9-dione dioxime (H_3enao2, (**118**)) form neutral complexes with ^{99m}Tc which can traverse the blood brain barrier (BBB).[263–266] The ligands are shown in Scheme 26. The H_3hmpac dioxime complex [TcO(hmpac)] (**119**) was prepared directly from H_3hmpac and $[TcO_4]^-$ in acidic saline, with stannous tartrate as reducing agent, in 70% yield as rust-colored crystals. The complex could be extracted into Et_2O. The X-ray crystal structure was elucidated and showed the expected five-coordinate Tc center with square-pyramidal geometry. Upon coordination, the H_3hmpac ligand loses three protons, two from the amine nitrogens and one from one of the oxime hydroxo groups. The remaining oxime proton forms a hydrogen bridge between the two oxygens of the oximes, resulting in pseudo-macrocyclic stabilization. This produces a formal 3− charge on the ligand and a neutral complex.[267] A range of complexes with varying patterns of methyl groups can be prepared analogously and are essentially isostructural. The X-ray structures of several of these complexes show also the square-pyramidal structure, with the Tc^V core sited about 0.68 Å above the basal plane.[268] The two deprotonated Tc—N bonds exhibit marked sp^2 character and are significantly shorter than expected for a Tc—amine bond. The average Tc—N distance of about 1.913 Å, significantly shorter than a Tc—N (amine bond with about 2.088–2.2259 Å), suggests multiple-bond character. This is in agreement with the relatively low wavenumber of the Tc=O stretch between 908 cm^{-1} and 923 cm^{-1}, which is at the lower end of the frequency scale usually observed for terminal oxo complexes. The lipophilicity of these complexes rises steadily with the number of methyl groups present in the ligand, and the complex with six Me-group complexes is now used to prepare an important radiopharmaceutical for brain imaging (see Section 5.2.3.1.1).

The effect of the backbone ring size has been studied thoroughly, from amine–oxime which has no amine–amine hydrocarbon backbone, to (**118**) which forms a 13-membered macrocycle, and to pentao2 with a pentylene backbone which forms an 18-membered macrocycle. Interestingly, the change from a propylene backbone in (**117**) (pnao2) to the butylene backbone (bnao2) causes a significant change in the type of product. Whereas for pnao2 deprotonation of the amines takes place, that is not the case for bnao2; the two amine donors remain protonated forms, resulting in a neutral and highly lipophilic $[O{=}Tc{=}O]^{+}$ derivative. This structural formulation was obvious from $\nu_{O=Tc=O}$, which is at 790 cm^{-1}. X-ray structure analyses confirmed the structure of the ligands, proving backbone ring size greater than six obviously behave comparably to aliphatic diamines (see earlier in this section).[269] It has been suggested that the electronic properties of the ligands *cis* to the oxo group are the primary factor in determining whether the $[Tc{=}O]^{3+}$ or $[O{=}Tc{=}O]^{+}$ core will be obtained.[56,270]

For the complexes with the $[Tc{=}O]^{3+}$ core the amine ligands are deprotonated, partially neutralizing the charge of the Tc^{V} center. When the amines are neutral, an additional oxo group is required to compensate the remaining charge on the Tc center. For the amine–oxime ligands, the length of the hydrocarbon backbone dictated preference for the oxo-core over the other. The bidentate ligand ao has steric constraints and the mono-oxo complex $[TcO(ao)_2]$ forms.

The reaction of octaethylporphyrin (H_2oep, (**120**)) with $[TcO_4]^{-}$ in glacial acetic acid gave the first porphyrin complex of technetium in a higher oxidation state. On the basis of spectroscopic and mass spectroscopic data, it is formulated as the cationic species $[TcO(oep)][CH_3COO]$ (**121**). The compound is soluble in nonpolar organic solvents and, despite the highly lipophilic substituents on the porphyrin framework, its description as a salt seems somewhat doubtful.[271]

The only complex of Tc^{V} containing two phenanthroline ligands is $[TcOCl(phen)_2]^{2+}$ (**122**), which is obtained either electrochemically by controlled potential cathodic reduction or by reduction of $[TcO_4]^{-}$ with dithionite in the presence of phenanthroline. Its formulation as a mono-oxo species is suggested by the Tc═O stretch at 895 cm^{-1} in the IR. From the observation that all protons in the phenanthroline ligands are nonequivalent, chloride must be *cis* to the oxo group.[272]

Reaction of $[TcO_4]^{-}$ with $K[HB(pz)_3]$ in 3M HCl in the presence of $K[BH_4]$ as a reducing agent gives the complex $[TcOCl_2\{HB(pz)_3\}]$ (**123**) in 60% yield as a light green solid. The structure is distorted octahedral, with the three nitrogens occupying one face and the other comprising the terminal oxo- and two chloride ligands. The Tc—N bond *trans* to the oxo-ligand is significantly lengthened (2.259(4) Å), indicating a very weak binding interaction. In structural respects, this complex resembles strongly the previously mentioned $[TcOCl(phen)_2]$.[272] (Scheme 26)

(iv) Mixed NO donor ligands

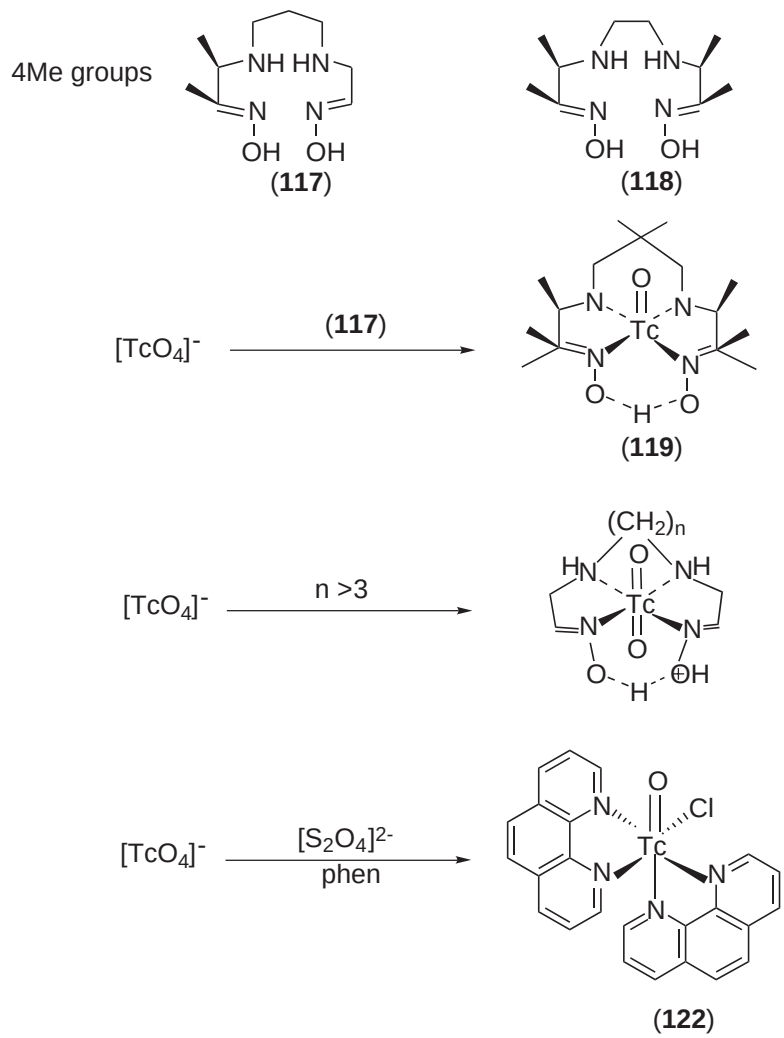
A wide variety of five- and six-coordinate $[Tc{=}O]^{3+}$ complexes with N,O ligands such as hydroxyquinolines, polyamino-polycarboxylates, or Schiff-base ligands have been prepared.

The unique seven-coordinate complex $[TcO(EDTA)]^{-}$ is obtained by reaction of $[TcOCl_4]^{-}$ with H_4EDTA in anhydrous dmso. The X-ray crystal structure confirmed pentagonal-bipyramidal geometry, with the oxo group and the two nitrogen donors bound in the equatorial plane.[274] All other structurally characterized technetium complexes with polyamino-polycarboxylates are in oxidation state IV.

The exchange of one nitrogen for an oxygen donor in a tetradentate ligand is exemplified by the reaction of the versatile starting material $[TcO(eg)_2]^{-}$ (**74**) with a pyrrole-based ligand N-{2(1H-pyrrolylmethyl)}N′-(4-pentene-3-one-2)ethane-1,2-diamin H_3ped (**124**). The reaction in methanol in the presence of acetate as a base gives the neutral, square-pyramidal, orange-red complex [TcO(ped)] (**125**) in which the ligand is triply deprotonated, including deprotonation at the pyrrole ring, and provides only the second example of a Tc–pyrrole species.[275] Because of its significant brain uptake, $[^{99m}TcO(ped)]$ has been considered as a potential brain perfusion agent.

The utility of $[TcOCl_4]^{-}$ in Tc^{V} chemistry is demonstrated by the first synthesis of 8-hydroxyquinoline (8-Hox, (**126**)) complexes of technetium in 1984. Ligand (**126**) is usually one of the first choices to explore the coordination chemistry of an element, but it was as late as 1984 when the first complex with Tc^{V} was prepared. It was known that the reaction of $[^{99m}TcO_4]^{-}$ with 8-Hox leads to complexes with high brain uptake, and it was therefore important to define the structure of the active species. This sequence of events is very typical for technetium chemistry. Nuclear medicinal experiments indentify a ^{99m}Tc species with useful biological behavior, which prompts investigations into the basic coordination chemistry to identify the structure of the Tc

species present. The reaction of $[TcOCl_4]^-$ with 8-Hox, 5,7-Cl_2-8-Hox, 5,7-Br_2-8-Hox, 5-NO_2-8-Hox, and 2-Me-8-Hox in methanol readily yields the complexes $[TcO(R\text{-}8\text{-}ox)_2Cl]$ (**127**) (R═H) in about 90% yield. The compounds are dark red-brown and precipitate directly from the methanolic solution. Since these neutral complexes were considered as potential radiopharmaceuticals, stability investigations were performed. The chloride or bromide ligands are readily substituted in methanol by $[CH_3O]^-$. The process is first order with a relatively low rate constant, suggesting that the chloride is *cis* rather than *trans* to the oxo-ligand. These kinetic findings were later confirmed by an X-ray structure determination. The bromide ligand exchanges about 100 times faster than chloride, indicating that the reaction mechanism can involve a *cis–trans* isomerization of the complex with subsequent rapid exchange of the *trans* labilized halide.[277] The X-ray crystal structure of the complex with 2-Me-8-ox as a ligand confirms the mechanistic findings. The structure has a distorted octahedral geometry, with one of the of the oxygen atoms of an 8-ox ligand located *trans* to the terminal oxo group. The distortion from the octahedron is primarily caused by the steric requirements of the oxygen donors of the deprotonated hydroxy group and the acute bite angles of the bidentate ligands. Interestingly, the Tc—O bond distance to the oxygen donor *trans* to the terminal oxo group is comparable to the one *trans* to the nitrogen ligand atom (average 1.96 Å). All other distances are within the expected range.[277]



Scheme 26

The electrochemistry of Tc^V complexes containing either two variously substituted bidentate 8-ox type ligands $[TcOCl(L_b)_2]$, one 8-ox ligand, and one bidentate Schiff-base ligand $[TcOCl(L_b)(L_a)]$, or one 8-ox ligand and one tridentate dianionic Schiff-base ligand such as

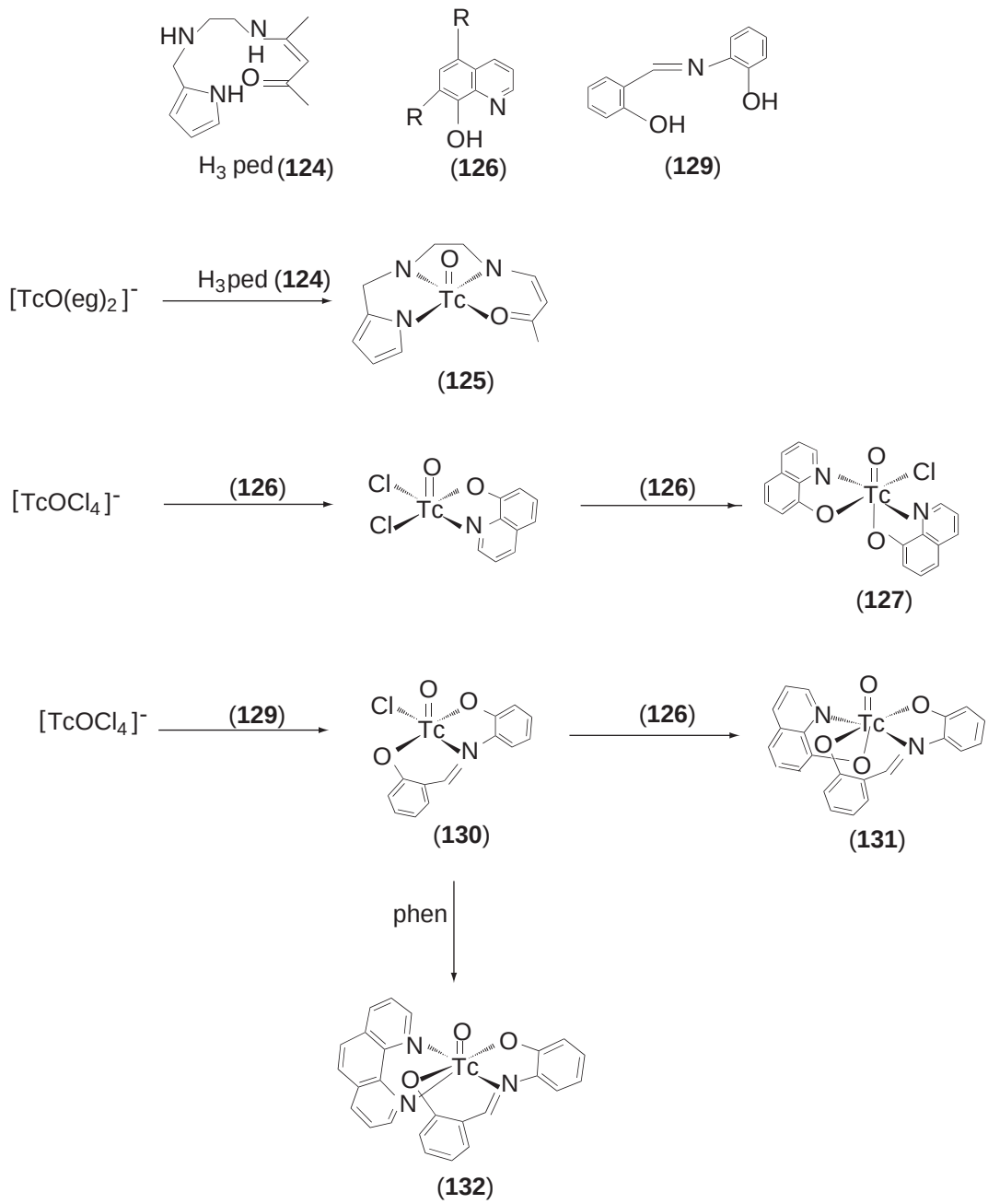
N-(2-oxidophenyl)salicylideneamine (H_2ophsal, (**129**)) [TcO(L_b)(L_t)], has been investigated in various solvents. These compounds are all prepared by stepwise substitution of chlorides in $[TcOCl_4]^-$ (see below).[277–279] For all the complexes, the deprotonated hydroxy function of 8-Hox is *trans* to the terminal oxo ligand. The Tc^V complexes are reduced to Tc^{IV} or Tc^{III} with loss of the ligand *cis* to the oxo group, generally a chloride. Loss of one ligand causes isomerization to a more stable complex, as evident from the irreversibility of the electrochemical series. It is assumed that in the isomers the site *trans* to oxo remains vacant.[280]

The complex containing one 8-ox and the tridentate ligand (**129**) is prepared by initial reaction of $[TcOCl_4]^-$ with (**129**) in methanol to give [TcOCl(ophsal)] (**130**) as a neutral complex, which was structurally characterized.[281] This five-coordinate precursor reacts further with (**126**) to give the six-coordinate, dark red, mixed-ligand complex [TcO(ophsal)(8-ox)] (**131**) in very good yields. The X-ray structure shows approximately octahedral geometry, with the tridentate ligand occupying three equatorial positions and the deprotonated oxygen of 8-ox *trans* to the oxo group.[279] Using a similar method, Tc^V complexes containing the TcO(N_2O_3) core could be obtained. The reaction of (**130**) with bidentate heterocyclic amines gave complexes of the general composition [TcO(ophsal)(L)] (**132**) (L = bipy, phen) in quantitative yield as dark green crystals. Although no X-ray data is available, it is evident from spectroscopic data that the ophsal ligand occupies three equatorial positions, with the aromatic amines in the fourth site in the plane and *trans* to the oxo group.[282] This chemistry illustrates a common strategy in technetium chemistry which has one substitution inert ligand and labile monodentate ligands. The substitution of the latter with various, less labile, polydentate ligands allows fine tuning properties of the complex for medical applications.

Reaction of ligands of the type 2,3-bis(2-pyridyl)pyrazin (bpp, (**133**)) and 2,3-bis(2-pyridyl)quinoxalin (dpq, (**134**)) with $[TcOCl_4]^-$ gives the complexes $[TcOCl_3(dpq)]$, $[TcOCl_2(OEt)(dpq)]$, and $[TcOCl_3(\mu\text{-bpp})TcOCl_2(OEt)]$ (X = Cl or OEt) in good yield. From IR data it was inferred that the chlorides are *cis* to the oxo ligand with the OEt group *trans*, as found for many other complexes. The structure of a complex with the related ligand 2,3-bis(pyridylbenzoquinoxaline (Hbbq (**135**)) with rhenium was elucidated. The complex $[TcOCl_2(bbq)]$ (**136**) shows the deprotonated hydroxy group *trans* to the terminal oxo ligand.[283] (Scheme 27)

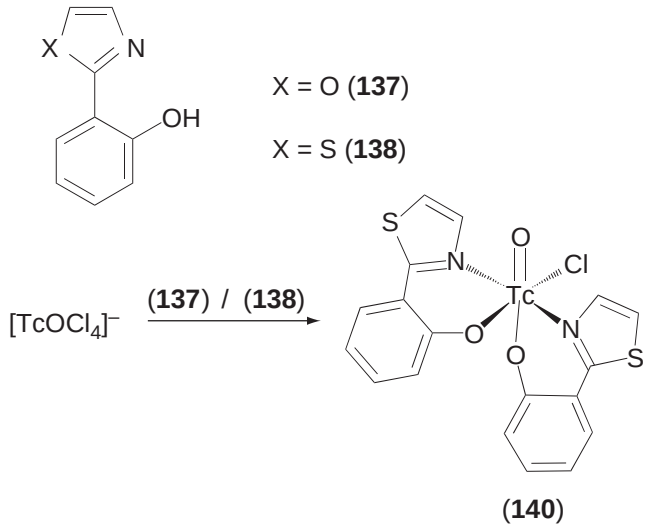
Interesting complexes with N,O ligands are formed with naturally occurring oxazolin and thioxazolin. These less common metal-binding species are found in siderophores. Bidentate ligand systems are produced by combination with phenol to give (2-(2′hydroxyphenyl)-2-oxazoline (Hoz, (**137**)) and (2-(2′hydroxyphenyl)-2-thiazoline (Hthoz, (**138**)). The interest in these ligands arose from (unsuccessful) attempts to prepare the homoleptic complexes $[TcL_3]^{n+}$. Although Tc^V complexes with bidentate Schiff-base-type ligands and (2-(2′hydroxyphenyl)-2-benzothiazolinato complexes have been reported,[277,278,284,285] compounds with (**137**) and (**138**) represent a new and interesting class of compounds. Reaction of $[TcOCl_4]^-$ with stochiometric amounts of the ligands Hoz and Hthoz under reflux gave the complexes $[TcOCl(L)_2]$ (L = oz (**139**), thoz (**140**)) in 60–80% yield as a dark red precipitate. The X-ray crystal structures show the deprotonated phenolate oxygen *trans* to the oxo group and the chloride ligand *cis*. For (**140**), the nitrogen rather than sulfur is bound. The bond distances to the oxygen donors *trans* and *cis* to the oxo group do not significantly differ, despite the strong *trans* influence of the oxo group.[286] (Scheme 28)

Examples of Tc^V-oxo complexes comprising one single, N,O-based, multidentate ligand are numerous. The radiopharmaceutical interest in these complexes arises from their high stability, the large number of possible variations in side chains and combinations of donor atoms, providing control of the overall physical properties of the complexes. Most of these ligands are of the Schiff-base type or reduced forms thereof. The first studies with the classical Schiff-base ligands $[(Hacac)_2en]$ (**141a**) $[H_2salen]$ (**141b**) and $[(Hsal)_2phen]$ (**141c**) were published in 1984. The reaction of $[TcOCl_4]^-$ with (**141b**) and (**141c**) gives the neutral, six-coordinate complexes [TcOCl(L)] (L = salen (**142**), $(sal)_2$phen) (**143**) as red-brown crystals in moderate yield. The same reaction with (**141a**), however, gives $[TcO(OH_2)(L)]Br$. Each complex exhibits an intense IR absorption in the region 900–980cm^{-1}, indicative of the presence of a mono-oxo species. The X-ray structures of the three complexes have been determined and show the chloride ligand *trans* to the oxo group, in contrast to the 8-hydroxyquinoline complexes. However, the comparable but sterically more flexible ligand Ph-sal forms six-coordinate $[TcO(Ph\text{-}sal)_2Cl]$ with phenoxide oxygen *trans* to the oxo group.[278] A sterically more flexible bidentate ligand adopts the thermodynamically favored coordination geometry, which is obviously not necessarily the case with the tetradentate Schiff-base-type ligands. Many of these complexes contain the $[O{=}Tc\text{-}OH_2]^{3+}$ unit, which is ubiquitous in $[Tc{=}O]^{3+}$ chemistry. In this complex, the Tc center lies about 0.39 Å above the basal plane, causing a lengthening of the Tc—OH_2 bond to 2.282(2) Å, vs. about 2.0 Å for a normal Tc—O distance.[287]



Scheme 27

Since the above complexes of Schiff-base ligands are rather lipophilic, the ligand framework was modified to achieve higher hydrophilicity. The ligand *N*,*N*′-ethylene-bis(phenoxyacetamide (H_4epa, (**144**)) reacts with $[TcOCl_4]^-$ in MeOH and in the presence of glycol to give the anionic complex $[TcO(epa)]^-$ (**145**) in moderate yield. The complex was shown by X-ray diffraction to be five-coordinate, and the two amide nitrogens and the hydroxy groups are deprotonated.[288] Interestingly, in contrast to technetium the analogous reactions with rhenium, based on spectroscopy, give μ-oxo-bridged dimers containing the $[O{=}Re{-}O{-}Re{=}O]^{4+}$ group.[289] If insufficient electron density is transferred to the metal center by the ligands, technetium also forms complexes with a $M_2O_3^{4+}$ core. Since the amido nitrogens are good donors and the oxygens are formally negatively charged, the proposed behavior is unexpected. The formation of the $[O{=}Tc{-}O{-}Tc{=}O]^{4+}$ group in the context of (reduced) Schiff-base-type ligands was confirmed



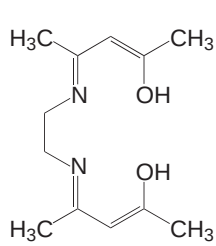
(140)

Scheme 28

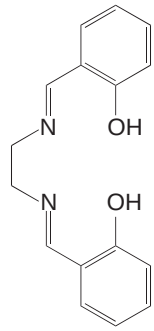
later. The ligand *N*,*N*′-bis(2-hydroxy-benzyl)-1,3-diamino-2-(4-nitrobenzyl)propane ($(Hsal)_2pda$, (**146**)) reacts with $[TcO(eg)_2]^-$, prepared *in situ*, to give the corresponding dinuclear complex $[O{=}TcL{-}O{-}LTc{=}O]^\circ$ (**147**) complex in good yield. Remarkably, the same reaction without initial preparation of the glycolato intermediate leads to the formation of insoluble polymeric material, with the dinuclear complex formed only in low yields. Obviously, the less reactive complex $[TcO(eg)_2]^-$ prevents the formation of complexes with more than one ligand bound to the same metal, and that prevents the formation of oligomeric species. The formation of oxo-bridged species seems to be typical for this class of ligand and has been observed for other complexes as well.[290,291] It is believed that species containing $[O{=}Tc{-}OH_2]^{3+}$ or $[O{=}Tc{-}OH]^{2+}$ groups are direct intermediates *en route* to the μ-O-bridged dinuclear species.[54,292] The bridging oxygen in this case is located on a crystallographic center of symmetry. The Tc centers are displaced by 0.117 Å out of the basal plane, significantly less than in the complexes with the $[O{=}Tc{-}OH_2]^{3+}$ group (*vide supra*). (Scheme 29).

An interesting example of a complex comprising the $[TcO(N_4O)]$ core is produced from the reaction between $[TcOCl_4]^-$ and the tridentate N,O ligand (N-salicylidene-D-glucosamine) (H_2glusal, (**148**)). In the presence of excess (**148**), the six-coordinate neutral complex $[TcO(gluca)(sal)]^\circ$ forms, which was structurally characterized. The salicylaldehyde obviously results from the hydrolysis of the original tridentate Schiff-base ligand. In the structure of $[TcO(gluca)(sal)]^\circ$ (**149**), the aldehyde oxygen is located *trans* to the terminal oxo group, which is electronically surprising but might simply be the result of the stereochemistry of the hydrolytic process. This represents the first example of a glucose complex of technetium.[293]

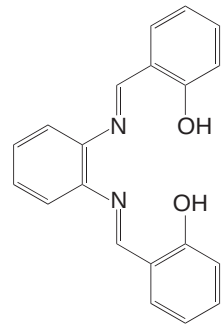
The reaction of $[TcOCl_4]^-$ with tridentate, Schiff-base ligands such as *N*-(8-quinolyl)salicylideneimine (Hqsi, (**150**)), based on an N_2O donor set, has been reported. The mechanism of the reaction of (**150**) with $[TcOCl_4]^-$ was studied in detail. In aprotic, dry solvents it is assumed that intermediate $[TcOCl_3(Hqsi)]^\circ$ forms first through coordination of the two nitrogen donors, but then quickly deprotonates to the final green product $[TcOCl_2(qsi)]^\circ$ (**151**). In the intermediate, the phenolato oxygen is probably *trans* to the oxo group, while one pyridine nitrogen remains uncoordinated. Upon addition of methanol to the green solution of the neutral complex, a red species forms, which is anionic and probably the mono-alcoholato compound $[TcOCl_2(OR)(L^1)]$, in which the potentially tridentate Schiff base is only bidentate. The same intermediate is also observed when the reaction is performed directly in alcoholic solutions. In aprotic solvents, the neutral complex $[TcOCl_2(L^1)]$ has the same configuration in solution as in the solid state, as confirmed by ^{1}H NMR. The reason for the unusual configuration seems to be a consequence of the high Lewis acidity of the $[Tc{=}O]^{3+}$ center, which can better be satisfied by three anionic ligands.[294] Complexes exhibiting the same configuration of a nitrogen donor *trans* to the oxo ligand are rare and only a few examples have been described.[261,273]



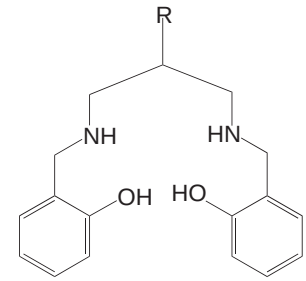
(**141**)



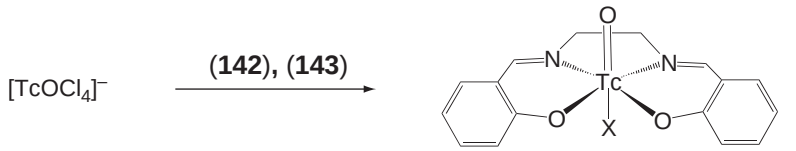
(**142**)



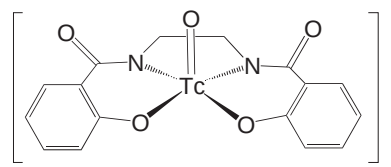
(**143**)



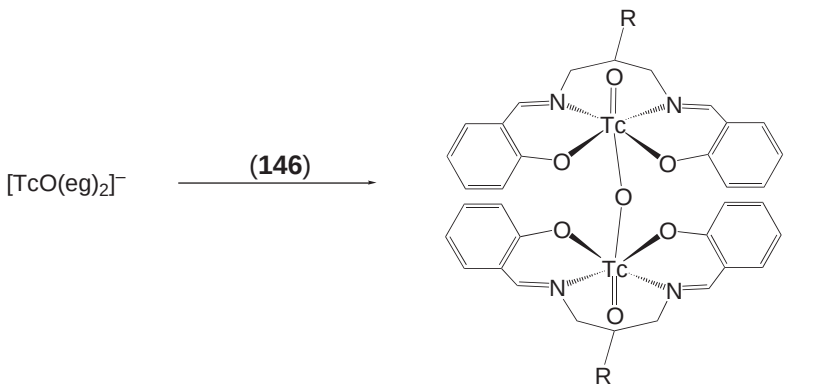
(**146**)



(**144**)



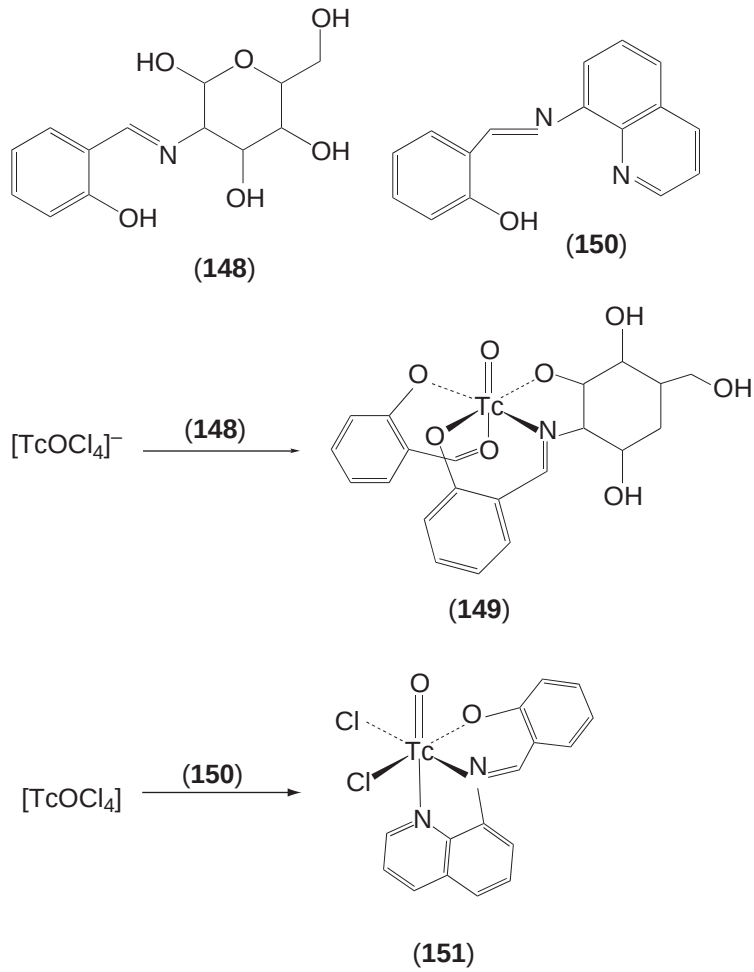
(**145**)



Scheme 29

The reaction of different types of tridentate N_2O ligands with $[TcOCl_4]^-$ in methanol at room temperature gives the corresponding, deep red, six-coordinate complexes $[TcOCl_2(L^1)]$ by ligand exchange. Interestingly, in the reaction of a tridentate Schiff-base ligand with mixed ONX donor set (X = O or S), five- and six-coordinate complexes were obtained.[281,295,296] The structure shows strongly distorted octahedral coordination, with the tridentate ligands in the equatorial plane and the terminal oxo-ligand in the *trans* position with respect to the central nitrogen donor of the Schiff-base ligand. The two chloride ligands are *trans*.

In addition, a variety of other Tc^V complexes with heterocyclic N,O[282] and other ligands and of salicylidine Schiff-base ligands with amino acids have been reported.[297,298] (Scheme 30)



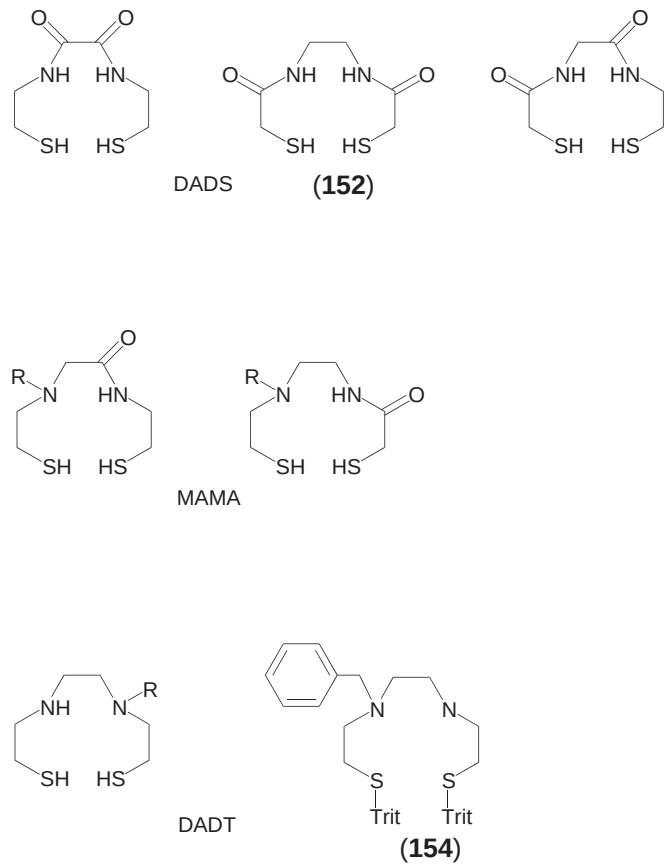
Scheme 30

(v) Mixed NS-donor ligands

Oxotechnetium(V) complexes with mixed N,S ligands are probably the most intensively studied class of complex in technetium chemistry. Complexes with tetradentate N,S ligands of various types efficiently stabilize the $[Tc{=}O]^{3+}$ core. A combination of nitrogen and sulfur donor stabilizes the formal Tc^{V} center very well. In ligands with an N_2S_2 donor set, both amido and amino nitrogens are used. Coordination of either type usually leads to deprotonation and the formation of neutral or even negatively charged complexes.

One of the earliest systems to be studied was the diamido-dithiol (dads) ligands. The preparations were performed with $[S_2O_4]^{2-}$ directly from $[TcO_4]^{-}$. Symmetrical tetradentate diamido-dithiols are preferred over bidentate variants, providing the same set of donor atoms, since geometrical isomerism is not possible.[299] One of the resulting complexes $[TcO(ema)]^{-}$ (**153**), with the ligand (*N*,*N*′-ethylenebis(2-mercaptoacetamide) (H_4ema, (**152**)), showed rapid clearance from the kidney and, significantly, the complex anion was excreted unchanged from animals.[300,301] Keeping the basic "diamido-dithiol" coordination framework intact, the location of the amido oxygen was varied and the corresponding complexes studied. (Scheme 31).

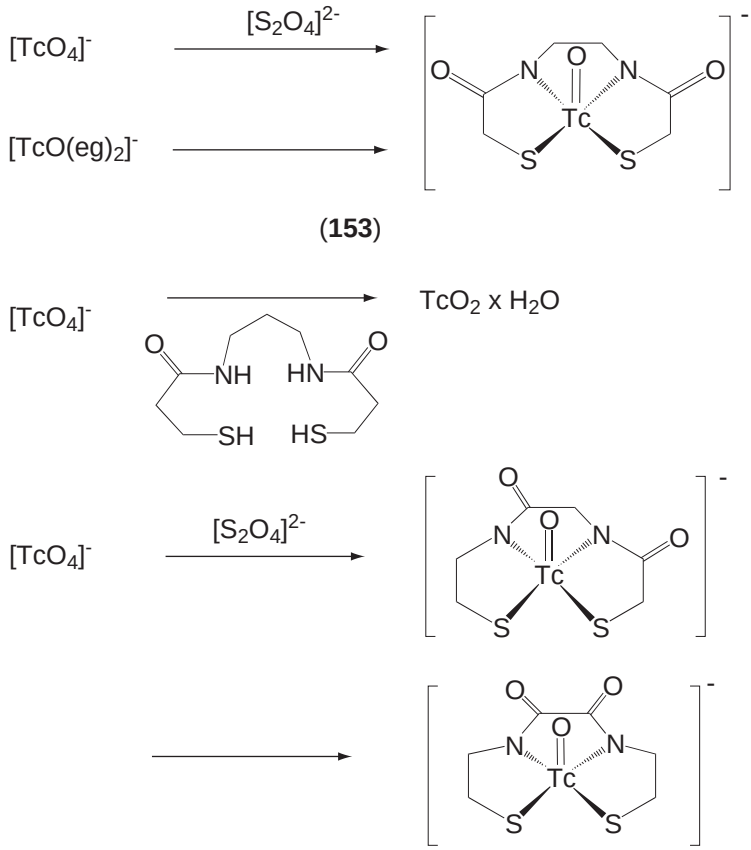
Complexes of the general composition $[TcO(dads)]^{-}$ can be prepared by several methods. Reduction of $[TcO_4]^{-}$ with $[S_2O_4]^{2-}$ in the presence of the ligand under strongly alkaline conditions produces the complexes in almost quantitative yield. Heating is sometimes required, but if the dithiols are not protected (as benzoyl esters or similar), the reactions also occur under ambient conditions. An alternative method consists of the *in situ* preparation of $[TcO(eg)_2]^{-}$, which is subsequently substituted with the tetradentate ligand, again under strongly alkaline conditions.



Scheme 31

The strongly alkaline conditions are required in order to deprotonate the amide protons. Reaction at pH 7.4 resulted in the quantitative formation of TcO_2. Most N_2S_2 complexes with Tc^V can conveniently be prepared by this route. The X-ray crystal structure of (**153**) confirms the pentacoordination of the technetium. The structure is, as expected, a square pyramid with the Tc atom located about 0.771 Å above the basal plane.[300] The configuration of (**153**) with three five-membered rings seems to be thermodynamically the most favored. A number of complexes based on the same type of coordinating framework, but with different backbone chain lengths and groups, have systematically been produced with the described synthetic procedure.[299,300,302,303]

By permuting the amide groups, a number of dads analogues have been prepared.[302] The kinetic stability of all the complexes with dads-type ligands is remarkable. It should be noted in particular that changing the number of methylene groups in the backbone and correspondingly the chelate ring sizes from, e.g., 5,5,5 to 5,7,5, or the position of the two carbonyl groups, did not affect the stability or the rate of formation of the complexes at all. The chemistry of such ligands is summarized in Scheme 32. This allows a very flexible design and backbone derivatization for the systematic study of radiotracers. All these complexes are stable for hours at from pH 0 to pH 14 and are, in general, resistant to electrochemical oxidation or reduction at biologically accessible potentials. No ligand exchange with other chelating agents occurs under mild conditions. It has to be emphasized that the presence of the apical oxygen atom makes the methylene protons in the complexes diastereotopic. Interestingly, the protons in a methylene group adjacent to an amido function undergo highly stereoselective deprotonation/protonation reactions, which can be followed by means of NMR spectroscopy, where in D_2O the original AB quartet collapses over time to give one single singlet. A plausible explanation for this stereoselective exchange requires deprotonation and redeuteration from the same side.[299,302] Complexes in which an alkyl-spaced carboxylate is attached to the NN backbone have also been prepared. Two chelate-ring epimers result on complex formation, since the carboxylate group can have syn and anti orientations. The compounds $[PPh_4][TcO(L)]$ have been isolated and characterized by spectroscopic and analytical methods.[304] (Scheme 32).



Scheme 32

A radiopharmaceutically inspired extension of the versatile dads system consists of the replacement of one of the amido nitrogens by an aliphatic amine nitrogen. These ligands are referred to as "mama" (monoamino-monoamido-dithiol, Scheme 31) in the following section. This alternative combination is particularly useful if the ligand is to be linked to biomolecules, which can be achieved by alkylation at the aliphatic amine functionality. In comparison to the complexes with dads ligands, the lipophilicity is expected to be higher since the complexes are neutral, but still less than for ligands based on the diamino-dithiol set of donors (dadt). A number of such complexes have been prepared and studied in detail. The *N*-benzylated ligands Bn-mama are used in a form with the thiolates protected by the trityl group (**154**). Deprotection and subsequent reaction with $[TcOCl_4]^-$ in methanol gave a 5:1 mixture of the syn and anti isomers [TcO(Bn-mama)] (**155**), which were separated by flash chromatography and structurally characterized.[305] In both isomers the Tc atom is located about 0.75 Å above the best least-squares fit for the basal plane. The order of the tertiary amine nitrogen-to-Tc bond is low, with a Tc—N bond length of about 2.182(5) Å. The syn isomer is favored for steric reasons, which explains its presence in higher yield. The syn isomer extends the bulky aromatic ring away from the bridging methylene group under the Re(Tc)═O bond, in order to minimize the interactions of the aromatic ring with the rest of the complex. A number of targeting biomolecules have been derivatized with mama-type ligands and these have been successfully labeled with ^{99m}Tc. Some examples are discussed in Section 5.2.3.1.2.

More recently, a systematic study with mama-type-based N_2S_2 ligands exhibiting variable ring sizes and many different substituents in the backbones have been performed, based on a novel synthesis for some of these and NS_3-based ligands. The substitution pattern and length of the ligand backbone can be varied without affecting the coordination chemistry.[306]

Complete replacement of the amide nitrogens by amino nitrogens yields the very important class of dadt-type ligands (diamino-dithiols). These ligands give, in general, neutral and highly lipophilic complexes with the $[Tc{=}O]^{3+}$ core, as summarized in Scheme 33. Upon complexation one of the aliphatic amines and the two thiol groups are deprotonated, thus neutralizing the charge of the $[Tc{=}O]^{3+}$ center. These ligands form complexes of exceptionally high thermodynamic stability, and

have found applications as brain perfusion agents and for the imaging of brain receptor ligands. Of major importance in this context is the neutral complex [TcO(L,L-ecd)] with the ligand *N*,*N*′-1,2-ethylene-bis(L-cysteine)diethylester (H_3ecd, (**156**)), which was originally prepared by ligand exchange of the precursor $[TcO_2(py)_4]^+$.[307] The corresponding ^{99m}Tc complex [TcO(L,L-ecd)] (**157**) shows excellent retention in the brain, due to ester hydrolysis which produces an anionic complex that is trapped in the brain. The complex (**157**) is sold as a commercial radiopharmaceutical for the assessment of cerebral blood flow (Neurolite®, DuPont).

Another neutral diaminodithiolate complex which showed high pulmonary accumulation in rodents was synthesized directly by the reduction of $[TcO_4]^-$ with $[S_2O_4]^{2-}$ in a basic medium and in the presence of the ligand 4-N-methyl-2,9-dimethyl-4,7-diaza-2,9-decanedithiol (H_3edd, (**158**)). The complex [TcO(edd)] (**159**) with the methyl substituent on the nitrogen adopts the (thermodynamically favoured) syn conformation (79:21), but to a lower extent also the anti. Both conformers were confirmed by X-ray structure analysis.[308]

Racemic mixtures of dadt ligands with substituents such as *N*′-benzylpiperazinyl on the carbon backbone between the two nitrogen donors were reacted directly with $[TcO_4]^-$ in the presence of $[S_2O_4]^{2-}$, to yield mixtures of the corresponding syn and anti isomers. The syn form showed higher brain uptake and resided longer than the anti isomer,[309] but with a phenylpiperidine substituent the syn and anti forms showed the reverse uptake/excretion behavior.[310]

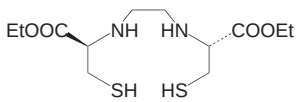
In the context of ligands related to dadt's, the ligand D-penicillamine (H_2D-pen, (**160**)) takes a special position. The complex $[TcO(D\text{-pen})_2]$ (**161**) can be prepared from $[TcOCl_4]^-$ and excess ligand under acidic conditions. The compound was found by X-ray structure determination to be six-coordinate.[90] The N,S atoms are located *cis* to each other and the charge is compensated by a carboxylate which coordinates *trans* to the oxo group. The bond length to this oxygen *trans* to the Tc=O bond is 2.214(4) Å, which is elongated as a result of the *trans* influence but is still relatively short in comparison to other complexes exhibiting the same features.[311,312] The Tc=O stretch was observed in the IR at 958 cm^{-1}. It was shown that neither Tc nor Re showed stereoselectivity for the D- or L-forms of penicillamine. The mixed complexes [TcO(D-pen)(L-pen)] exist as rapidly interconverting pairs of enantiomers. Racemization takes place with rates of 940 s^{-1} for technetium and 16.5 s^{-1} for rhenium, with energies of activation of 13.4 kcal mol^{-1} and 18.5 kcal mol^{-1}, respectively.[313]

The conditions for deprotonation of the amine nitrogens have been investigated with ligands of the dadt type $(HSCR_2CH_2NR'CH_2)_2$ (**162**) (R=Me, R′=H, Me) fully methylated at the α-carbon relative to thiol and/or at the aliphatic nitrogens giving neutral or cationic complexes. In the case of the fully methylated ligands, the cationic complexes $[TcO(L)]^{n+}$ (**163**) are formed, and with secondary amines present deprotonation took place at pH > 12.5 to yield the corresponding neutral complexes. Some of these complexes have been structurally characterized.[314] Other complexes of N_2S_2 ligands with tetraethylated ethylene and biphenyl backbones (**164**) have been prepared by the reaction of $[TcO_4]^-$ with tin(II) tartrate as a reducing agent. The structures of the complexes differ from one another in that for the complex with the ethylene backbone the remaining hydrogen is syn with the oxo-ligand, whereas in the case of the biphenyl backbone it is anti. The results of NMR investigations indicate that the conformations are retained in solution.[315]

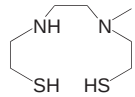
The conformationally restricted dadt-type ligand with piperazine in the backbone (H_3L (**165**)) has been prepared (with the aim of producing new cationic complexes for use as myocardial imaging agents). The cationic complex $[TcO(L^n)]^+$ (**166**) has been synthesized and structurally characterized.[316] A further example with a slightly different set of N_2S_2 donors provided by *N*,*N*′-ethylene-bis-(acetylacetone-thioiminato) ligand $\{HS(CR{=}CHCMe{=}NCH_2CH_2\text{-}\}_2$ (**167**). This tetradentate N_2S_2 chelator reacts rapidly with $[TcOCl_4]^-$ in methanol to form the neutral, six-coordinate species [TcOCl(L)] (**168**). Compared to a tetramine donor set, the imino groups are weak donors and the sixth position is occupied by chloride or by a water ligand. The X-ray crystal structure of the aqueous derivative confirms the presence of the $[O{=}Tc{-}OH_2]^+$ core with a Tc—OH_2 distance of 2.384(4) Å.[317]

In many cases thiols can act as both ligands and reducing agents. This is often the case with ^{99m}Tc under forcing conditions, but some cases with ^{99}Tc are also known. Based on an N_2S_2 ligand with two bidentate chelators, 2-benzimidazole-2′yl-ethanediol (Hbls) reacts with $[TcO_4]^-$ in $MeOH/H_2O$ to give $[TcO(bls)_2]^+$.[318] Ligand substitution of $[TcOCl_4]^-$ yields the same complex with one chloride coordinated *trans* to the terminal oxo substituent.[319] (Scheme 33).

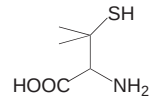
A further variation on this theme of significance in radiopharmaceutical chemistry was the development of various N_3S-type ligands. The archetypal ligand is designated MAG_3 (**169**) (mercapto-acetyl-glycine-glycine-glycine). This peptide-like ligand provides three amide and one



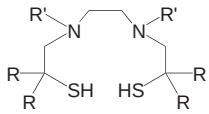
(**156**)



(**158**)

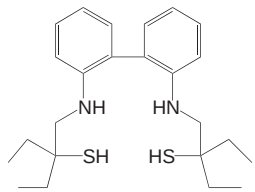


(**160**)

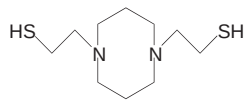


(**162**)

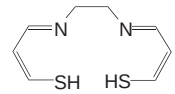
R' = H, Me



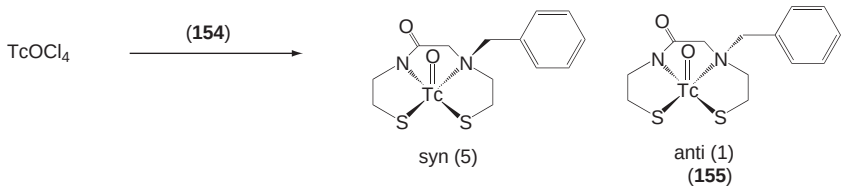
(**164**)



(**165**)



(**167**)



Scheme 33

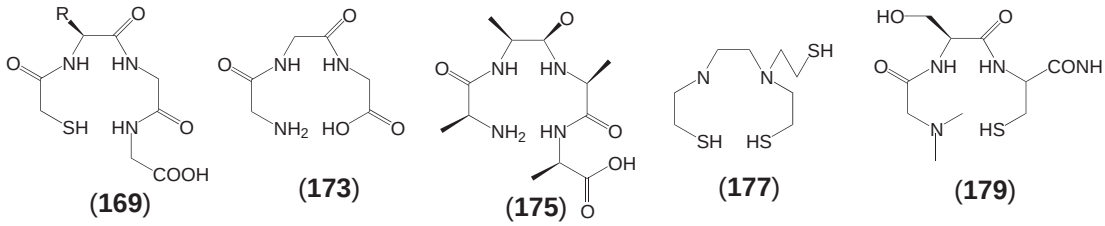
thiolate donors.[320] Complete deprotonation upon coordination gives the hydrophilic, five-coordinate, anionic Tc^{V} complex $[TcO(MAG_3)]^-$ (**170**). $[TcO(MAG_3)]^-$ can be prepared by the reaction of $[TcOCl_4]^-$ with free MAG_3 in methanol, and it was originally characterized by spectroscopic methods.[321] It can also be prepared directly from $[TcO_4]^-$ by reduction with $SnCl_2$. For both cases the thiol group can remain protected for the synthesis, since metal-mediated cleavage takes place to afford thiolato coordination. In the protected form, all the mentioned thiol ligands are much more stable than as free thiols. The structures of the complexes with a free acid or with a methylester group have been established by X-ray structure analysis.[322] The free acid structure shows the carboxylic acid to be distant from the Tc center, whereas two different structures of the corresponding methylester derivative show approximately parallel and perpendicular orientation, respectively.[323] It is assumed that the complexes are fluxional in solution.[324] The carboxylate group is not coordinated to the Tc center.[75] Under physiological conditions, the carboxylic acid is deprotonated to leave a "2−" charge on the complex. The resulting high hydrophilicity makes it a very versatile radiopharmaceutical for the assessment of renal function, and it is available commercially (TechneScan, MAG_3, Mallinckrodt). The free carboxylate group provides a coupling site for the N-terminus of a receptor-binding peptide. Variation of the biodistribution characteristics can be achieved by substituting one of the glycines in MAG_3 by another naturally occurring amino-acid.[324–327] Introduction of an alanine instead of the central glycine residue (MAAG, (**171**)) gives the syn conformation of the structurally analogous complex $[TcO(MAAG)]^-$ (**172**), with the same coordination sphere as $[TcO(MAG_3)]^-$.[328] Decreasing the number of available amido groups for coordination, as in the mercaptoacetyl-glycine-glycine (MAG_2, (**173**)) ligand, significantly diminishes the ability of the ligand to stabilize the $[Tc{=}O]^{3+}$ core. Nevertheless, reaction of Tc^{V}-gluconate with (**173**) in neutral, aqueous solution gives $[TcO(MAG_2)]$ (**174**) in 64% yield, and in alkaline media the yield is almost quantitative. To complete the coordination sphere the carboxylato group is engaged in coordination yielding an N_2SO ligand donor set, giving overall square-pyramidal geometry.[329] In the presence of excess ligand, additional, uncharacterized anionic species were found. It is assumed that these represent 2:1 and probably 4:1 complexes, as a consequence of the dominance of the thiol groups over other donors in coordination to the Tc^{V} center.

A unique reaction is found when a linear peptide ligand based on four coupled alanines $(L\text{-ala})_4$ (**175**) is used. In this case, tetradentate coordination is achieved and there is metal-mediated ring closure in $(l\text{-ala}_4)$, through amide formation between the terminal amino and carboxylato group and the complex $[TcO(cyc\text{-}ala_4)]^-$ (**176**) formed.[330] The ring closure reduces the number of potential coordinating atoms from five to four and provides additional macrocyclic stabilization. The methyl groups are syn in relation to the oxo core. This type of reaction is relatively rare, but does indicate a potential for analogous complexes and for the formation of cyclic peptides. It is remarkable, in particular, that attempts to get complexes directly with cyclic tetrapeptides were unsuccessful. Attempts to increase the denticity of N,S-based ligands, as in the $(l\text{-ala})_4$ ligand, often result in intramolecular reactions.

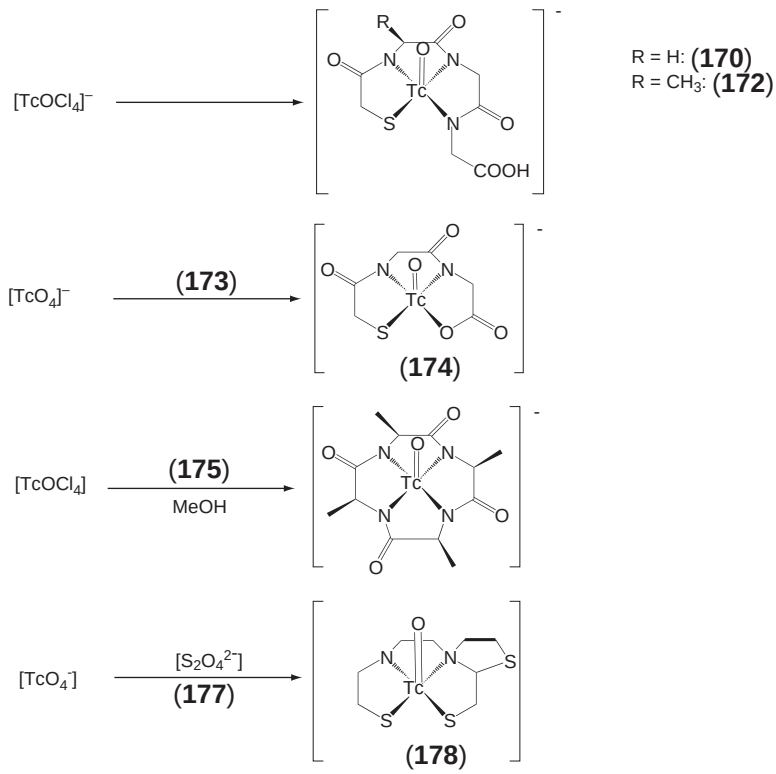
A further example of metal-mediated ring closure is provided by the mercaptoethyl N-derivatized ligand dadt (dadt-et, (**177**)) which is potentially a pentadentate ligand. Reduction of $[TcO_4]^-$ with $[S_2O_4]^{2-}$ in a water/ethanol mixture at r.t. did not influence the thermodynamically favored amide–amine dithiolato coordination, and the final neutral complex (**178**) displayed square-pyramidal structure with two thiolato, one deprotonated secondary amine, and an aliphatic tertiary amine as the donor atoms. Astonishingly, the third thiolato ligand was not involved in coordination, but underwent internal condensation which ultimately led to the formation of a thiazolidine ring in 70% yield. It was confirmed that the ring formation occurred during complex formation and was not present in the starting material as had been anticipated earlier.[331]

A variety of other amino-acid-based complexes for radiopharmaceutical purposes have been prepared. The ligand dimethyl-glycyl-L-seryl-cysteinyl-glycinamide (dmg-scg, (**179**)), contains an additional carboxylic group not required for coordination and which can be coupled to a targeting biomolecule. Reaction with $[TcO_4]^-$ in the presence of tin(II)gluconate gave the red, neutral complex $[TcO(dmg\text{-}scg)]^{\circ}$, which was spectroscopically characterized.[332] In a recent study in the context of combinatorial chemistry, this complex was activated at the carboxylic acid, coupled to bombesin and bound to a solid phase. The conjugate could be cleaved under drastic conditions, but could be isolated and was characterized by high-field NMR spectroscopy.[333]

The ligand (**179**) has also been used for conjugation of a Tuftsin receptor-binding peptide. The peptide conjugated to the complex is obtained as a red-orange solid by direct reduction of $[TcO_4]^-$ with Sn^{II} in pyridine. Column chromatography allowed purification, and characterization by 2-D NMR confirmed the structure. As expected, the serin $-CH_2OH$ side chain adopts both syn and anti conformation with respect to the Tc=O bond. The affinity for the Tuftsin receptor was retained.[334] (Scheme 34).



R = H: **(169)**
R = CH_3: **(171)**



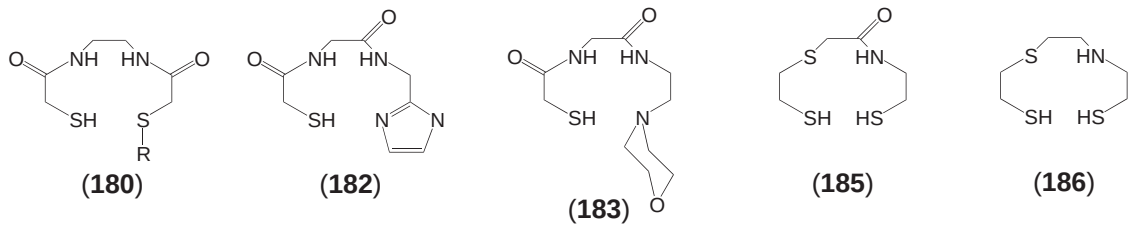
Scheme 34

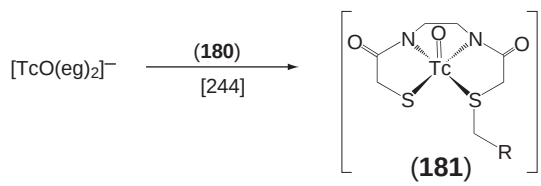
Tetradentate, N_2S_2-type ligands including thioether groups have been described. Based on previously mentioned work with *N*,*N*′-ethylene(2-mercaptoacetamide) (H_4ema, (**152**)) showing the ready accessibility of anionic Tc=O complexes, (**152**) was modified at one of the thiols to give a series of trianionic *S*-alkylated ligands (H_3ema-SR, (**180**)). These ligands react rapidly with $[TcOCl_4]^-$ or $[TcO(eg)_2]^-$ to give the corresponding neutral complexes [TcO(ema-SR)] (**181**), with a donor set consisting of a thiolato, two amido-, and one thioether group. Direct reduction of $[TcO_4]^-$ in the presence of the mono-*S*-alkylated ligand did not lead to the desired product, but exclusively to $TcO_2 \cdot H_2O$, probably as a consequence of the poorer donor ability of thioether relative to thiolate. The X-ray crystal structure of the complex [TcO(ema-morph)] has been determined and shows the expected square-pyramidal geometry.[335]

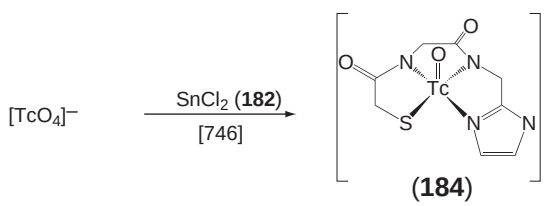
The coordination of thiolate protecting groups such as benzoyl, trityl, and others has been shown to deprotect upon reaction with Tc precursors under forcing conditions. This is synthetically useful, since the thiol ligands of the DADT or MAMA types are quite sensitive towards oxidation. The metal-mediated cleavage allows the use of protected and air-stable, double-protected ligands. The S–C cleavage reaction has also been applied to the preparation of no-carrier-added radiopharmaceuticals. In this approach, the ligand is bound via a cleavable thioether linkage to a solid phase. Coordination of the $[Tc{=}O]^{3+}$ group to this ligand leads to cleavage, and the noncoordinated ligand remains bound to the solid support and can be easily separated.[336,337]

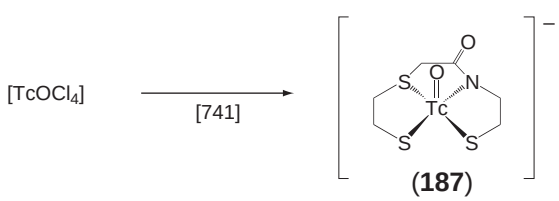
Cationic complexes of N_2S_2 ligands can be prepared if the amines are tertiary and therefore do not deprotonate upon coordination. Comparative studies with diamino-dithiol ligands which were not alkylated (H_4L^1) at the nitrogens, or alkylated by methyl and ethyl groups (H_2L^2), were performed by the reaction of $[TcOCl_4]^-$ with either H_4L^1 or H_2L^2. The cationic species $[TcO(H_2L^1)]^+$ or $[TcO(L^2)]^+$ are produced as orange-red solids. These complexes were analyzed spectroscopically and the charge confirmed by conductivity measurements. Above pH = 12.5 the nonalkylated complexes undergo mono-deprotonation to the corresponding neutral compounds $[TcO(HL^1)]$. This was confirmed by conductivity and by the ν(Tc=O), which shifts from 960 cm^{-1} to 890 cm^{-1} after deprotonation. As previously described, the alkyl groups in H_2L^2 are syn and anti with respect to the Tc=O moiety. This behavior is found with other complexes as well.[299,302,314,335,336,338,339] Complexes containing the $[Tc{\equiv}N]^{2+}$ core with these types of ligands have also been prepared (see Section 5.2.2.3.3(ii)).

Neutral complexes comprising the $[Tc{=}O]^{3+}$ core can not only be achieved by transforming one of the thiol groups into a thioether, but also by replacing –SH with an aromatic amine or a tertiary amine. The $N_2N^{ar}S$ ligands (**182**) and (**183**) were prepared. On the n.c.a. level with ^{99m}Tc, as well as with ^{99}Tc and Re, the corresponding complexes $[TcO(N_2N^{ar}S)]$ (**184**) formed in good yield. They were found to be stable when the terminal amine group was an aromatic nitrogen donor, but rather unstable when it was a tertiary amine group such as morrpholino.[340] Complexes containing an NS_3 donor set including one thioether group (**185**) and (**186**) and others were prepared, and $[TcO(NS_3)]$ (**187**) was structurally characterized with rhenium. Due to an elegant synthesis it was easily possible to vary the length of the backbones in the basic framework, as well as the position of the carbonyl group, and to investigate the corresponding Tc^V complexes.[306] (Scheme 35).









Scheme 35

(vi) Complexes of N,S ligands with mixed-ligand coordination

The [3 + 1] mixed-ligand concept for the preparation of neutral technetium and rhenium complexes with the $[M{=}O]^{3+}$ core offers a versatile route for the preparation of a wide variety of novel complexes for diagnostic or therapeutical radiopharmaceutical purposes. The concept is based on the utilization of one tridentate and one monodentate ligand. The mixed-ligand approach was originally designed for the preparation of new central nervous system (CNS) receptor imaging agents. By an appropriate combination of the tridentate and the monodentate ligand, the complexes $[TcO(L^1)(L^3)]$ are neutral and lipophilic and are thus ideal to traverse the blood brain barrier. Ligand L^1 is ideally a thiolate, whereas the tridentate ligand L^3 can be chosen from a wide variety of SXS or SXY systems, where X and/or Y represent nitrogen or sulfur and homologues. The ligand L^3 must be a bi-acid to achieve overall neutrality. The advantage of this mixed-ligand concept lies in the variety of possible mono- and tridentate ligands that can be obtained by relatively straightforward synthetic procedures.

Based on this concept, a wide variety of complexes based on the tridentate ligands $HS(CH_2)_nX(CH_2)_nSH$, in which X can be O,S or NR and $n = 2$, have been obtained and fully characterized.[227,229,230,341] They are stable towards dithiol challenge but are susceptible to glutathione exchange *in vivo*, which limits their range of application.[342–344]

In general, the complexes are prepared by successive addition of L^3 and L^1 ligands to a solution of $[TcOCl_4]^-$, or by simultaneous addition of both, or by a reduction/ligand-exchange reaction on a reduced $[TcO_4]^-$ solution containing preformed glucoheptonate or gluconate complexes.

(vii) Mixed X,P ligands

The fact that tertiary phosphines can be used as reducing agents for $[TcO_4]^-$ to yield Tc^V complexes without the need of additional reductants stimulated a systematic study of the coordination chemistry of Tc^V (and other oxidation states) with phosphorus-containing ligands. For potential practical radiopharmaceutical applications, the advantage of such a system is obvious. It has been reported that the reaction of (*o*-aminophenyl)diphenylphosphine (Happ, (**188**)) with $[TcO_4]^-$ in water gives different complexes, depending on the pH and solvents.[345] Although tertiary phosphines usually stabilize lower oxidation states, in particular +III and +II, combination with hard donor atoms can also result in the stabilization of Tc^V. The reaction of $[NBu_4][TcO_4]$ in methanol with three equivalents of (**188**) gives the neutral complex $[TcO(OR)(app)_2]$ (**189**), in which the two monodeprotonated app ligands lie in a plane. The compound with R = Me is significantly more sensitive towards decomposition than that with R = Et. If the reaction is performed in aprotic media, the Tc^{III} complex $[Tc(app)_3]$ (**190**) is the major product. The direct reaction of (**188**) with $[TcOCl_4]^-$ in aprotic solvents always leads to reduction and $[TcCl_2(app)_2]$ (**191**) is formed. The Tc=O stretching frequencies in complexes of the type (**189**) are observed at quite low wavenumbers (R = Me at 878 cm^{-1}, Re = Et at 857 cm^{-1}). This indicates a stronger Tc—OEt than Tc—OMe bond, in agreement with the higher basicity of the OEt group. The Tc=O bond length is 1.700 Å, which is significantly longer than that found for other Tc^V oxo-complexes and confirms the observations made from spectroscopic measurements. The X-ray structure analysis confirms that the N and P ligands lie in a plane which balances the charge density by a "push-pull" transfer from the π-donor amide to the π-acceptor phosphine.[346] The corresponding rhenium chemistry is remarkably different. Here the bidentate ligands are not only coplanar, as in the technetium case, but can also be orthogonal, with one deprotonated amine group *trans* to the oxo ligand. In addition, complexes with Cl^- instead of alkoxide have been characterized for rhenium, but not for technetium. Furthermore, the reaction of $[TcOCl_4]^-$ with the ligands produces only complexes in lower oxidation states, whereas analogous reactions with $[ReOCl_4]^-$ result in Re^V species. This is in accord with the general observation that Tc complexes reduce more easily then those of Re. If no strong π- or σ-donors are present, the Tc^V center undergoes reduction. As described later, replacement of oxo- by nitrido ligands causes enhanced stabilization of the Tc^V center, and substitution rather than reduction chemistry with tertiary phosphine-containing ligands is observed.

The coupling of two ligands of type (**188**) by a propylene bridge gave the novel ligand H_2dppd (**192**) (*N*,*N*′-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine). This tetradentate $H_2P_2N_2$ ligand reacts with $[TcO_4]^-$ by a reduction/substitution mechanism to give the six-coordinate neutral [TcO(X)(dppd)] (**193**).[347] The same reaction in acetonitrile in the presence of excess Cl^- gave the corresponding complex in which a chloride ligand *trans* to the oxo group completes the coordination sphere. The corresponding complexes with $X = OH^-$ or $O_2CCF_3^-$ could be obtained by ligand

exchange from X = OR. It is noteworthy that excess of the tetradentate ligand does not result in further reduction, in contrast to the behavior of the bidentate ligand (**188**) in complex (**189**) which undergoes reduction in HCl to give complex (**191**). This resistance to further reduction might be a consequence of the strong chelating effect provided by this tetradentate ligand.[348]

Another combination of N,P donors is represented by the capped (umbrella) ligands of the type 2-diphenylphosphino-*N*,*N*-bis(2-diphenylphosphinoethyl)ethaneamine (NP_3, (**194**)) or tris-2-diphenylphosphinoethylphosphine (PP_3, (**195**)). These ligands show a versatile chemistry with Tc. The reaction of $[TcO_4]^-$ in 32% HCl with a slight excess of (NP_3) gives orange, six-coordinate $[TcOCl_2(NP_3)]^+$ (**196**), based on spectroscopy and elemental analysis.[349] When $[TcCl_4(PPh_3)_2]$ is reacted with (**194**) or (**195**) the orange, cationic Tc^{III} complexes $[TcCl_2(NP_3)]^+$ and $[TcCl_2(PP_3)]^+$ are formed in good yields. Reaction of these ligands with $[TcNBr_2(PPh_3)_2]$ in EtOH under reflux gave pale yellow $[TcNBr_2(NP_3)]^+$ and off-white $[TcNBr_2(PP_3)]^+$, respectively (see Section 5.2.2.3.3(ii)).

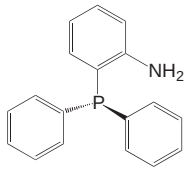
A bidentate, mixed P,S ligand is exemplified by 2-(diphenylphosphino)benzenethiol (Hpbt, (**197**)) which reacts with $[TcOCl_4]^-$ in CH_2Cl_2 at −80 °C in a 2:1 ratio to give six-coordinate $[TcOCl(pbt)_2]$ (**198**). This purple complex exhibits a strong Tc=O band at 940 cm^{-1}. When the reaction is performed in EtOH under reflux, reduction occurs and the blue-green Tc^{III} complex $[Tc(bdt)_3]$ formed in very good yield. The X-ray structure determinations showed that for Tc and for Re the [mer-P_3mer-S_3] geometry was formed exclusively.[350] The reaction with the nitrido precursor $[TcNBr_2(PPh_3)_2]$ in refluxing EtOH gave bright yellow $[TcN(pbt)_2]$ in good yield (see Section 5.2.2.3.3(ii)). Other complexes containing mixed P,N,O,S donor systems have also been described.[345,346,351]

The bidentate P, O donor ligand (*o*-hydroxyphenyl)diphenylphosphine (HPO, (**199**)) and the potentially tridentate ligand bis(*o*-hydroxyphenyl)-phenylphosphine (H_2PO_2, (**200**)) have been used to prepare both cationic and neutral Tc^V complexes. The Tc^V complexes *cis*-(P,P)-$[TcOCl(PO)_2]$ (**201**) or *cis*-(P,P)-$[TcO(PO_2)(HPO_2)]$ (**202**) are obtained by ligand metathesis from $[TcOCl_4]^-$ in ethanol under reflux or directly from $[TcO_4]^-$. It is perhaps surprising that no further reduction to the known Tc^{III} complex $[Tc(PO)_3]$ occurs.[351,352] The complex (**202**) can also be synthesized by reduction/ligand exchange from $[TcO_4]^-$, in moderate to good yields. One ligand is tridentate and the other bidentate, as shown by ^{1}H NMR. A singlet at 10 ppm is assigned to the hydroxyl proton in $[HPO_2]^-$, which forms a hydrogen bond to the terminal oxo ligand. Above 80 °C the complex decomposes in DMSO and the phosphineoxide is observed by ^{31}P NMR studies, indicating reduction to lower oxidation states. In contrast to the related ligand (**188**) (see above), even under reflux conditions no further reduction could be imposed with ligand (**200**).[352] From IR and ^{1}H NMR spectroscopic studies it is assumed that the two PO ligands in *cis*-(P,P)-$[TcOCl(PO)_2]$ are orthogonal, with one deprotonated OH group *trans* to the oxo group and the chloride ligand *cis*. This was confirmed by the X-ray structure of *cis*-(P,P)-$[TcOCl(PO)_2]$ and spectroscopic measurements. Reduction of $[TcO_4]^-$ in ethanol in the presence of the ligand as outlined above for the H_2PO_2 ligand and in the presence of conc. HCl gave the complex (**201**) in 91% yield. It should be emphasized that accurate control of the stoichiometry is required to prevent formation of the Tc^{III} oxidation state, which is known to be stabilized by a number of *ortho*-functionalized, triphenylphosphine-derived ligands.[345,346,351,353]

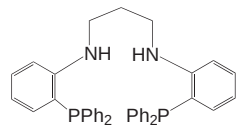
Technetium(V) complexes with exclusively phosphorus donors and the $[Tc{=}O]^{3+}$ core are obviously not stable. The lack of charge compensation leads to Tc^{III} compounds by further reduction, or to hydrolysis. Pure phosphorus coordination is then possible only if the $[O{=}Tc{=}O]^+$ core is present, as described in the following section (Scheme 36).

(viii) Tertiary phosphine and arsine complexes

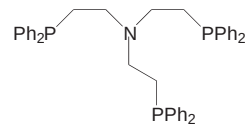
Oxo-complexes with tertiary phophorus donors alone are restricted to these containing the *trans* dioxogroup. The neutral σ-donating and weakly π-accepting phosphorus ligands in the equatorial plane are not able to neutralize the "3+" charge and to stabilize the $[Tc{=}O]^{3+}$ core. As described earlier (see Section 5.2.2.3.2(iv)) for macrocyclic amine ligands, deprotonation of coordinated water ultimately leads to formation of the $[O{=}Tc{=}O]^+$ core. Examples of complexes of the $[TcO_2]^+$ core are numerous: e.g., $[TcO_2(py)_4]^+$,[354,355] $[TcO_2(cyclam)]^+$,[253] or $[TcO_2$(1,4-dithia-8,11-diazacyclotetradecane)$]^+$.[356,357] The cationic nature of the $[TcO_2]^+$ core has attracted considerable attention in radiopharmaceutical chemistry in the context of developing a myocardial imaging agent. The reduction of $[TcO_4]^-$ with excess bis-(1,2-dimethylphosphino)ethane (dmpe) at room



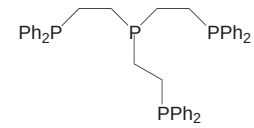
(**188**)



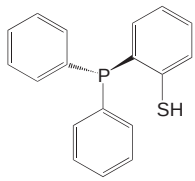
(**192**)



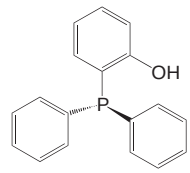
(**194**)



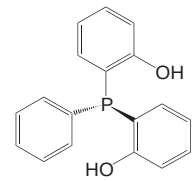
(**195**)



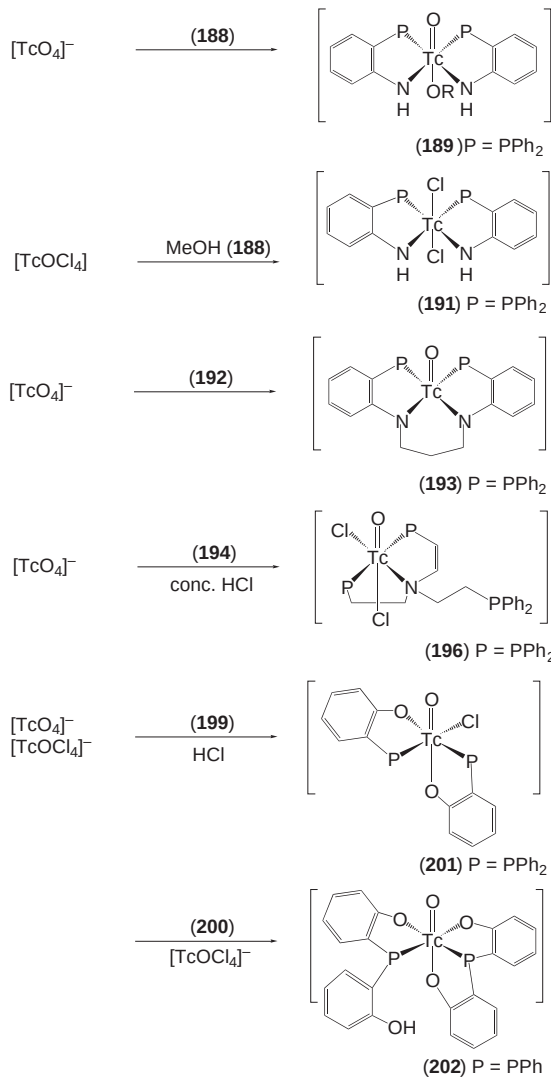
(**197**)



(**199**)



(**200**)



Scheme 36

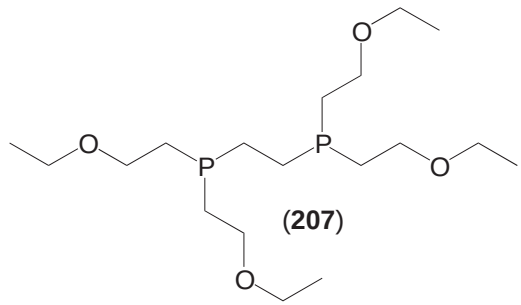
temperature in EtOH/H_2O and in the presence of a base rapidly gives the complex $[TcO_2(dmpe)_2]^+$ (**203**). This complex can be protonated under strongly acidic conditions to give the corresponding dicationic species, $[TcO(OH)(dmpe)_2]^{2+}$ (**204**). From spectrophotometric titrations, the pK_a was calculated to be about 0.8. The X-ray crystal structure of the $[CF_3SO_3]^-$ salt of this complex was elucidated. Because of disorder, it was not possible to distinguish between Tc═O and Tc—OH. The average bond distance to the two oxygen atoms is 1.795(3) Å, and from EXAFS studies the Tc═O distance is estimated to be in the range of 1.66 Å and the Tc—OH 1.96 Å, respectively.[358] The complex $[TcO_2(dmpe)_2]^+$ can be reduced stepwise to the Tc^{III} complex $[TcCl_2(dmpe)_2]^+$ (**205**) and finally the Tc^{I} species $[Tc(dmpe)_3]^+$ (**206**) under fairly rigorous conditions, which are, however, essentially comparable to those described for the direct syntheses of these complexes from $[^{99m}TcO_4]^-$.[258,359]

The bidentate phosphine ligand 1,2-bis[bis(2-ethoxyethyl)phosphino]ethane (tetrofosmin, (**207**)) reacts with $[TcO_4]^-$ to yield the complex *trans*-$[TcO_2(tetrofosmin)_2]^+$ (**208**) in high yield. The structure is close to octahedral and the two oxo groups are *trans*. This complex shows high myocardial uptake and retention and is commercially available (Myoview®, Amersham).[360]

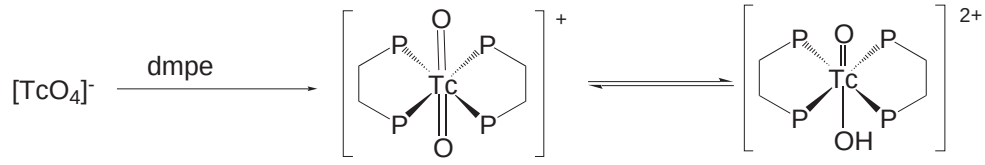
Useful and unexpected complexes are formed by reactions of monodentate aliphatic phosphines with $[TcO_4]^-$. With PR_3 (R = Et, Pr) the trigonal-bipyramidal, brown complexes $[TcO_2(PR_3)_3]^+$ (**209**) are produced, which are precipitated from solution as $[BPh_4]^-$ salts. This synthesis arose from attempts to prepare phenylimido complexes, which are usually available by reaction of $[TcO_4]^-$ with phosphines and then the hydrazine derivatives ($PhNHNHCOCH_3$). Instead, this new kind of cationic dioxo complex was found. With PMe_3, a mixture of products was produced. It is unusual in that the two oxo ligands and one P atom form the trigonal plane, whereas the apical positions are occupied by the other two phosphines. The $\nu_{Tc=O}$ is found at 850 cm^{-1}, which is intermediate between values typically found for *trans*-dioxo (ca. 800 cm^{-1}) and terminal mono-oxo (ca. 900 cm^{-1}) species. These complexes are a versatile starting material for further substitution reactions. In methanol and in the presence of pyridine, (**209**) coordinates two pyridine ligands with substitution of one phosphine, yielding yellow $[TcO_2(PR_3)_2(py)_2]^+$ (**210**) with *trans*-dioxo and *cis*,*cis* orientation of the ligands. The *trans* orientation of N and P is expected by analogy with similar complexes with bidentate N,P donors. Although the precursor (**209**) is not available with PMe_3, reaction of $[TcO_4]^-$ in the presence of PMe_3 and py gave $[TcO_2(PMe_3)_2(py)_2]^+$, which has the same structure as complex (**210**).[361] (Scheme 37).

A number of complexes containing the "$[O{=}Tc{-}O{-}Tc{=}O]^{4+}$" core have been reported, in addition to those described in Section 5.2.2.3.2. The reaction sequence leading to this type of dinuclear complex can be understood as a consequence of charge neutralization for complexes upon hydrolysis. In general, in a formally neutral complex of the type [TcOCl(L)], where L is a tetradentate ligand, the labile chloro ligand can be substituted by water. The induced acidity leads to deprotonation and the formation of a $[O{=}Tc{-}OH]^{2+}$ group, which undergoes dimerization and deprotonation and/or hydrolysis to yield the linear $[O{=}Tc{-}O{-}Tc{=}O]^{4+}$ core. This core seems to be very stable and is formed not only upon hydrolysis of a preformed Tc^{V} complex, but also by direct reduction of $[TcO_4]^-$ in aqueous media or in wet solvents in the presence of ligand. Generally a prerequisite for the formation of this class of compounds is the presence of a tetradentate ligand or bidentate ligands which can compensate two of the positive charges on the $[TcO]^{3+}$ core. This is nicely illustrated by $(sacac)_2enH_2$ (**211**), which reacts with $[TcOCl_4]^-$ in dry solvents to give $[TcOCl\{(sacac)_2en\}]$ (**212**), but in the presence of $[TcO(OH_2)\{(sacac)_2en\}]^+$ (**213**) is formed. Deprotonation and dimerization then gives the dimerized product $[\{O{=}TcL\}_2(\mu\text{-}O)]$ (**214**) (L = $(sacac)_2en$) in good yields.[362] Other tetradentate dianionic ligands which show this behavior include ONNO aminophenolato ligands derived from the reduction of Schiff-base complexes[290,363] and bidentate thioether ligands. Upon reaction of one equivalent of 3,6-dithiaoctane or 5,8-dithiadodecane (S^2) with $[TcOCl_4]^-$, the resulting intermediate is the five-coordinate complex $[TcOCl_2(S^2)]^+$ (**215**), which dimerizes in the presence of moisture to yield the dinuclear complex $[\{O{=}TcCl_2(S^2)\}_2(\mu\text{-}O)]$ (**216**).[225] In the case of rhenium, the dinuclear complex is formed directly from $[ReO_4]^-$ in acetone/5M HCl with Sn^{II} as a reducing agent.[226] A similar reaction occurs with aromatic diamines or triamines, such as terpy or bipy. The reaction of excess terpy with $[TcOCl_4]^-$ in refluxing ethanol gives the dinuclear complex $[\{O{=}TcCl(terpy)\}_2(\mu\text{-}O)]^{2+}$ (**217**), a rare example of a cationic dinuclear complex. This compound has been characterized by spectroscopic and analytical methods.[364] A limited number of other complexes containing the $[O{=}Tc{-}O{-}Tc{=}O]^{4+}$ core have also been described.[290,292,365–367]

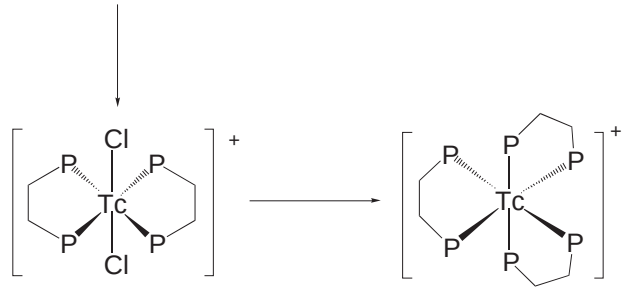
Cyano-complexes of Tc^{V} exhibit rather different chemistry. Ligand exchange of $[TcO_2(py)_4]^+$ (**110**) with a large excess of cyanide in aqueous solution yields bright yellow $[TcO_2(CN)_4]^{3-}$ (**218**). Other synthetic approaches give the same compound.[368] The complex has a $[O{=}Tc{=}O]^+$ core, despite the fact that negatively charged ligands do not generally favor deprotonation and formation of dioxo



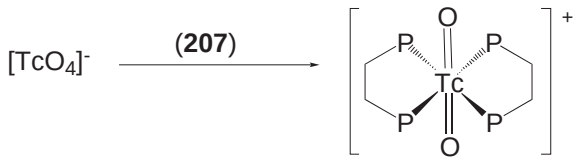
(**207**)



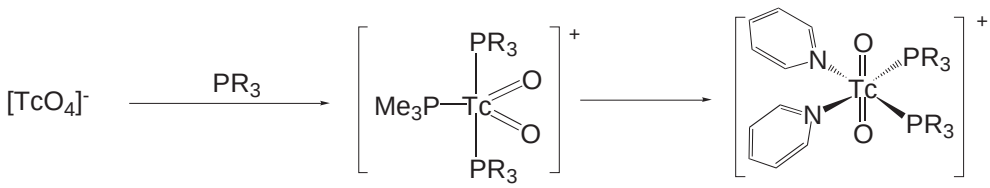
(**203**) (P = PMe_2) (**204**) (P = PMe_2)



(**205**) (P = PMe_2) (**206**) (P = PMe_2)



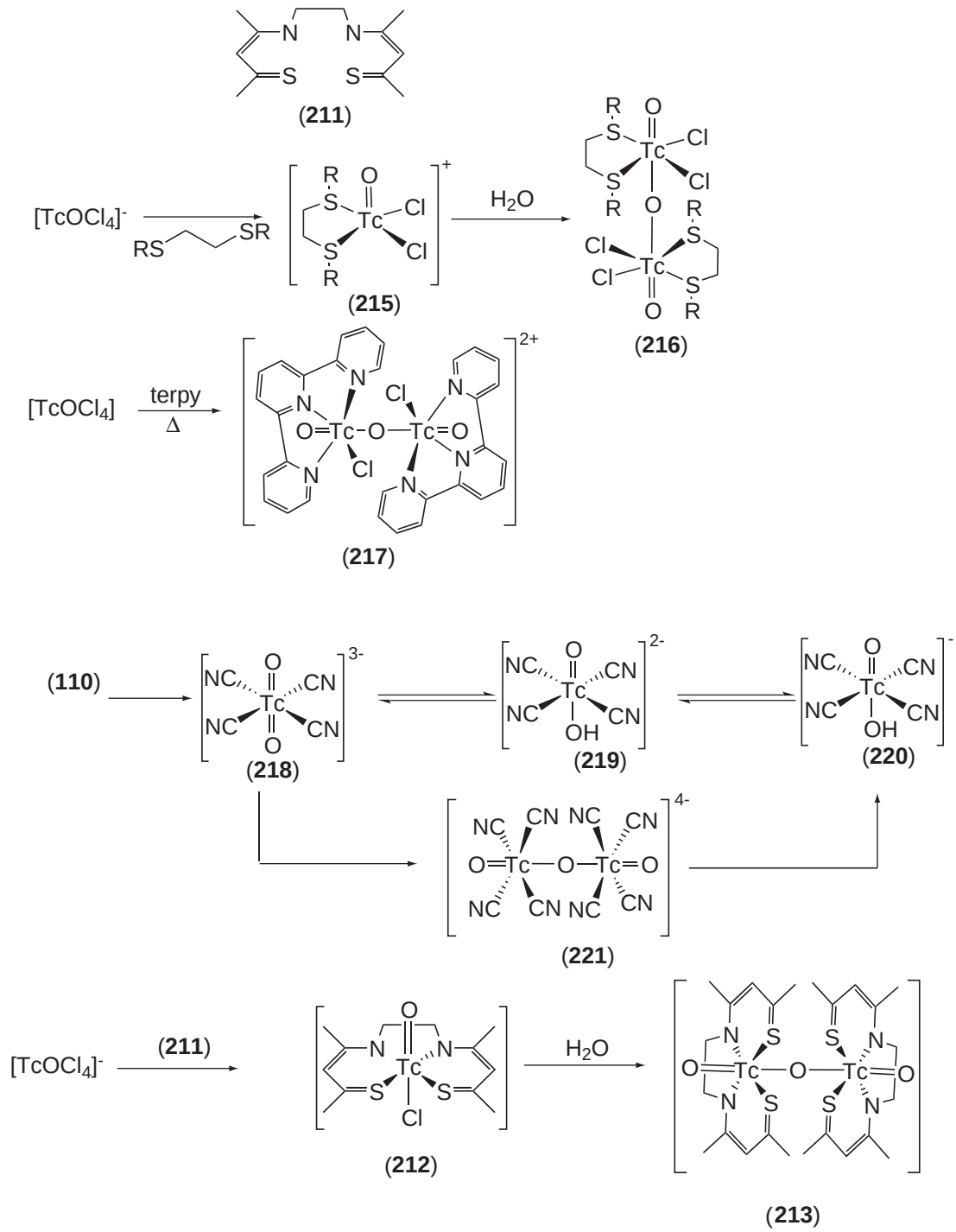
(**208**) (P = $P\{C_2H_4OC_2H_5\}_2$)



(**209**) (R = Et, Pr) (**210**) (R = Et, Pr)

Scheme 37

complexes. Cyanide, although a σ-donor, is also a π-acceptor. In fact, the complex $[TcO_2(CN)_4]^{3-}$ can be protonated in strong acids to give $[TcO(OH)(CN)_4]^{2-}$ (**219**) and blue $[TcO(OH_2)(CN)_4]^{-}$ (**220**). The pK_a value for (**220**) is about 2.9. The aquo ligand can be substituted by $[NCS]^{-}$, and the structurally characterized green complex $[TcO(NCS)(CN)_4]^{2-}$ is formed. As a consequence of the π-accepting properties of the cyanide ligands, the frequency of the ν(Tc═O) stretch is raised to 1,029 cm^{-1}.[355] The μ-O-bridged purple complex $[Tc_2O_3(CN)_8]^{4-}$ (**221**) forms as an intermediate *en route* to (**220**) and can be isolated in about 20% yield. (Scheme 38)



Scheme 38

A limited number of dinuclear complexes with bridging ligands other than oxo have been described. An interesting example is represented by the neutral complex [{$TcOCl_2(OEt)_2$}$_2$-(*m*-tppz)], in which tppz is 2,3,5,6-tetrakis(2-pyridyl)pyrazine. The complex is formed upon reaction of the ligand and $[TcOCl_4]^-$ in ethanol as a dark green precipitate. The IR spectrum shows two different ν(Tc═O) stretching bands, which suggests a mixture of complexes with different structures. It is claimed that one Tc center is seven-coordinate, whereas the other is six-coordinate.[369] No X-ray structures are available. The ligand 2,3-bis(2-pyridyl)pyrazine (bpp) reacts with $[TcOCl_4]^-$ to give an analogous mixture.[370]

The unique dinuclear complex $[(TcO)_2(edt)_3]$ (**222**) is formed when $[TcOCl_4]^-$ is reacted with 1.5 equivalents of H_2edt (**83**) or S-protected bis(acetamidomethyl)ethandithiol in methanol at room temperature for 1 h. It is remarkable that even these mild conditions were sufficient to deprotonate the ligand and form the novel sulfur-bridged complex in good yields. An X-ray structure determination suggested that the structure is best described as two square pyramids sharing one edge. Two sulfurs from two different edt ligands, but from the same square-pyramidal unit, bridge the two technetium centers. The coordination around the two metal centers is therefore different and two Tc═O stretches are observed, one at 953 cm^{-1} and the other at 946 cm^{-1}.[371] This dinuclear compound apparently is an intermediate *en route* to the final end product $[TcO(edt)_2]^-$ (**84**), so the direct reaction of (**83**) with $[TcOCl_4]^-$ under reflux conditions gave (**84**) in excellent yield. These reactions were described earlier, but the identity of the intermediate was not established at that time. Spectroscopic and analytical data suggest that 1,3-propanedithiol also gives a dinuclear intermediate complex with similar geometry.[217]

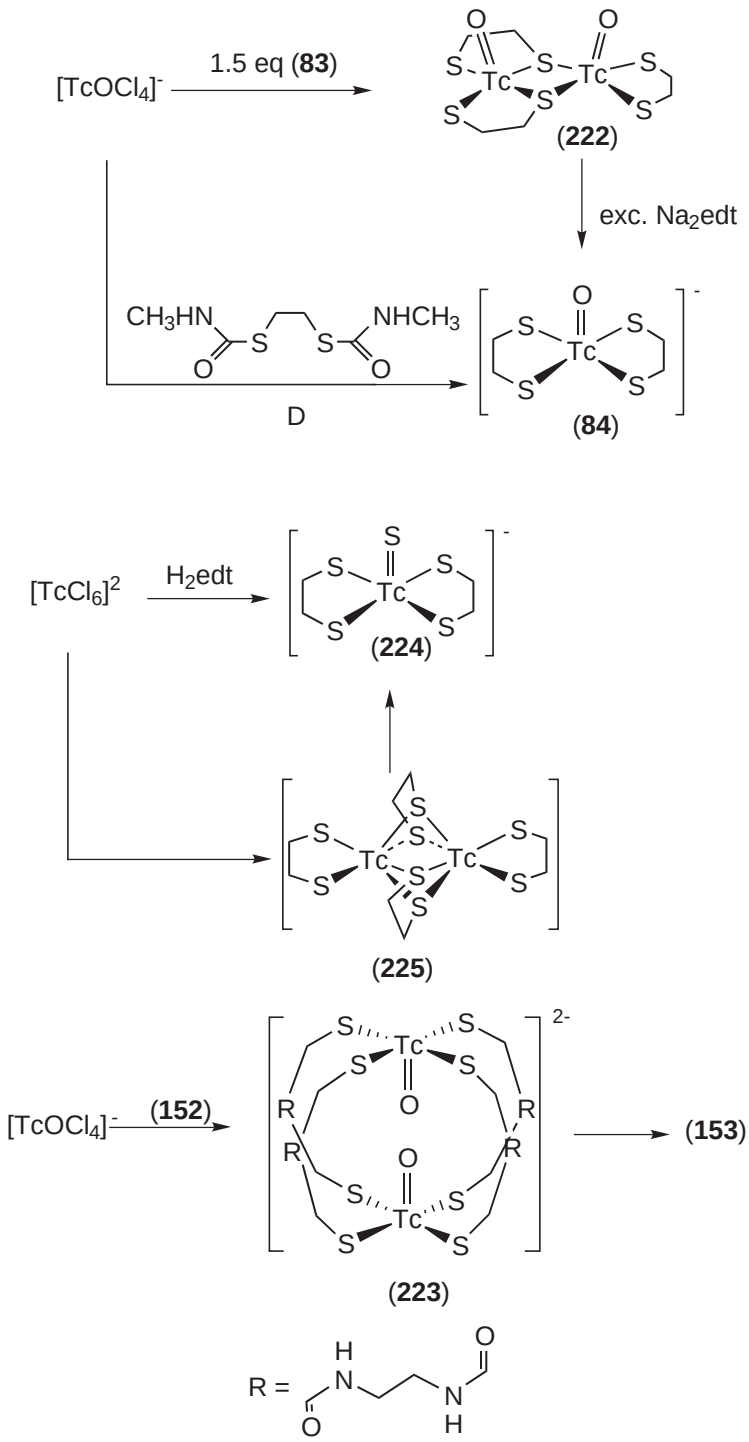
Another unusual, structurally characterized, dinuclear complex is formed using the ligand *N*,*N*′-ethylene-bis(2-mercaptoacetamide) (**152**). The blue, dinuclear complex $[Tc_2O_2(H_2ema)_4]^{2-}$ (**223**) forms from the reaction of the ligand with $[TcOCl_4]^-$ in alkaline methanolic solution, and crystals were obtained from aqueous MeOH as the hexahydrate of the complex. The four linear ligands coordinate via deprotonated thiolato groups to two different Tc centers, forming a cage-like structure. The amide groups remain protonated and are not involved in coordination, and thiolato groups only are bound to technetium. Interestingly, the oxo groups on the technetium point inside the cage to give a lantern-like structure (the bulbs being the oxo groups). Dipole–dipole interactions between the amide groups in the ligand and the terminal metal-oxo group might play a role in organizing the ligands, favoring the inclusion of the two oxo ligands inside the lantern and away from the solvent. The complex immediately decomposes to mononuclear $[TcO(ema)]^-$ in the presence of base in water or in organic solvents. This indicates that the mononuclear product is thermodynamically favored, as expected from chelate-effect considerations.[372] The dinuclear complex is clearly a kinetic intermediate, since no reasonable chelate stabilization is provided. The mononuclear complex $[TcO(ema)]^-$ (**153**) has been discussed earlier.

Technetium(V) complexes with terminal main groups other than oxo are very rare. The terminal $[M{=}S]^{3+}$ group is isoelectronic with $[M{=}O]^{3+}$, but as expected is much more sensitive towards hydrolysis. The Tc^V sulfido complexes $[TcS(edt)_2]^-$ (**224**) and $[TcSCl_2(HB(pz)_3)]$ are prepared by methods known from Mo or Re chemistry. Blood-red (**224**) is made from the Tc^{IV} complex $[TcCl_6]^{2-}$ (**69**) in the presence of a tenfold excess of (**83**), while the sulphido complex (**224**) is produced in 15% yield together with the novel, emerald-green Tc^{IV} complex $[Tc_2(edt)_4]$ (**225**) in 20 % yield. The structure of the latter is comparable to $[Tc_2(bdt)_4]$, which has been prepared directly from $[TcO_4]^-$.[373] Complex (**225**) is unstable in solution and readily converts back to the corresponding oxo complex. Since $[TcS(edt)_2]^-$ is stable in aqueous solution, it is clear that the ancillary dithiolate ligands are essential to stabilize the Tc═S group. The Tc═O IR band appears at 935 cm^{-1} in the oxo complex, compared to 520 cm^{-1} for ν(Tc═S) in the sulfido complex.[374] (Scheme 39).

5.2.2.3.3 Imido and nitrido complexes

(i) With monodentate ligands

The $[Tc{\equiv}N]^{2+/3+}$ core is second only to the $[Tc{=}O]^{3+}$ core in its importance for the coordination chemistry of technetium in the context of radiopharmaceutical applications. The nitrido ligand "N^{3-}" is isoelectronic with the oxo "O^{2-}" ligand and with the imido R—N^{2-} ligand. The highly negative charge makes the nitrido ligand a very powerful π-donor, well able to stabilize the



Scheme 39

oxidation states of technetium from +V up to +VII. The bonding with the metal comprises a σ-bond and two π-bonds overlapping with the d_{xz} and d_{yz} metal orbitals. The strong donating properties of the nitrido ligand transfer electron density to the metal center, and that is reflected in the coordination behavior which generally occurs with soft, "b-type" ligands. The chemistry of the $[Tc{\equiv}N]^{3+}$ core in the oxidation state +VI has been discussed in Section 5.2.2.2.2. The existence of the corresponding Tc^{V} complex $[TcNCl_4]^{2-}$ (**226**) has not been established[369], and coordination compounds containing the formal $[TcN]^{2+}$ core with technetium in the oxidation state +V are

generally obtained by two synthetic routes. One consists of ligand substitution on $[TcNCl_2(PPh_3)_2]$ (**227**), a general and useful precursor complex, and the other concerted reduction/ligand-substitution reactions with $[TcNCl_4]^-$ (**34**) or directly from $[TcO_4]^-$. In the latter case, (**34**) is probably formed *in situ* as an intermediate.[144,375,376] The complexes are characterized by a sharp IR $\nu_{(Tc\equiv N)}$ absorption band between 1,100 cm^{-1} and 1,000 cm^{-1}.

Although not isolated as a solid, the existence of $[TcNX_4]^{2-}$ was suggested by spectroelectrochemical and computational studies. The complexes $[Tc^{VI}NX_4]^-$ can be reversibly reduced at +0.21 V for Cl^- and at +0.32 V for Br^-, respectively (vs. SCE). This allowed the *in situ* electrochemical generation of the $[TcNX_4]^{2-}$ species and study of their spectroscopic properties. The Cl^- compound is reasonably stable at 218 K for 24 h, whereas the Br^- compound showed some decomposition. The Tc^{VI} compound is orange, whereas the Tc^V complex is essentially colorless, which is unusual for high-valent chloro and bromo complexes. Trends in redox potentials have been compared with the corresponding oxo compounds of Tc^V.[156]

The first two complexes containing the $[Tc^VN]^{2+}$ core to be synthesized were $[TcN(S_2CNEt_2)_2]$ and $[TcNCl_2(PPh_3)_2]$, by the reduction of $[TcO_4]^-$ with hydrazine hydrochloride in the presence of the appropriate coligands.[377,378] The other key starting materials, $[TcNCl_4]^-$ and $[TcNBr_4]^-$, are prepared by reduction of $[TcO_4]^-$ in concentrated HX with NaN_3 as the nitrogen source.[143] Starting from (**34**), the reaction with PPh_3 or $AsPh_3$ gives the five-coordinate complex (**227**) directly in high yield. The same reaction with sterically less bulky phosphines such as PMe_2Ph gives the six-coordinate complex $[TcNCl_2(PMe_2Ph)_3]$ (**229**), in which one chloride ligand is *trans* to the nitrido group.[379] In agreement with spectroscopic investigations, the P and Cl ligands are *trans* to each other. This structure is essentially identical to the one established by an X-ray analysis of the Re analogue.[380] Since all these complexes undergo fast ligand exchange, they represent very useful starting materials and a number of examples of the use of these precursors follows.

The complex $[TcNX_4]^-$ readily undergoes reduction/substitution during reaction with thiocyanate in aqueous acetonitrile. The six-coordinate Tc^V complex $[TcN(NCS)_4(NCCH_3)]^{2-}$ (**230**) forms, in which the acetonitrile ligand is most probably located *trans* to the nitrido group, as deduced from spectroscopic measurements. When recrystallized from acetonitrile/ethanol, the *trans*-aqua complex $[TcN(NCS)_4(OH_2)]^{2-}$ is formed and an X-ray structure showed that the thiocyanate ligands are N coordinated.[144,369,381] The halide ligands in (**34**) are generally easily exchanged for other anionic ligands. Therefore reaction of cyanide with $[TcNX_4]^-$ in acetonitrile/water produces the six-coordinate complex $[TcN(CN)_4(OH_2)]^{2-}$ (**231**), isolated as the $[AsPh_4]^+$ salt.[382] The Tc≡N bond is quite short at 1.596 Å, whereas the Tc—OH_2 bond, 2.559(9) Å, is very long, even taking into account the strong *trans* influence of the nitrido ligand. The $\nu_{Tc\equiv N}$ absorption occurs in the IR at 1,100 cm^{-1}. The short Tc≡N bond and the high Tc≡N stretch, in combination with the ν(CN) IR band at 2,112 cm^{-1}, clearly show that there is significant backbonding to the CN ligands, which stabilizes the Tc≡N bond. Ligand exchange of the bound water using large concentrations of N_3^- or CN^- or azide gave the six-coordinate complexes $[TcN(CN)_4(N_3)]^{3-}$ (**232**)[383] and $[TcN(CN)_5]^{3-}$ (**233**), respectively.[384] The latter complex and $[TcN(CN)_4Cl]^{3-}$ can also be prepared from $[TcN(tu)_4Cl]^+$ (**234**) in the presence of large amounts of KCN.[369] $[TcN(tu)_4Cl]^+$ can itself be prepared from (**34**) in acetonitrile in the presence of excess thiourea.[385] The complex (**234**) is readily soluble in water affording a strongly acidic solution, indicating substantial reactivity which merits more investigation.

The reaction of (**34**) in refluxing acetone in the presence of imidazole or pyridine gives the dicationic, five-coordinate complexes $[TcN(im)_4]^{2+}$ (**235**) and $[TcN(py)_4]^{2+}$ (**236**).[155] The high *trans* effect of the nitrido ligand in comparison to the oxo ligand is shown by the lack of any *trans* ligand in the nitrido species. The corresponding oxo complexes readily undergo coordination of water and subsequent double deprotonation to give the *trans* dioxo core.

An example of the versatility of (**227**) as a starting material is represented by the reaction with thiocyanate in water/EtOH under reflux. The complex $[TcN(NCS)_2(PPh_3)_2]$ (**237**) is formed in 69% yield, whereas the same reaction in the presence of acetonitrile gives the six-coordinate complex $[TcN(NCS)_2(NCCH_3)(PPh_3)_2]$ (**238**). The phosphine ligands are *trans* to each other and the acetonitrile ligand is *trans* to the nitrido group, exhibiting an exceptionally long Tc—N bond of 2.491(4) Å, indicative of potential lability. Recrystallization from $CHCl_3$ leads to complete loss of this ligand.[386] Interestingly, it is not possible to substitute more than the two chloride ligands in (**34**), but with other multidentate anions, as seen later in this section, the phosphines can readily be displaced by an appropriate choice of incoming ligand.

An essential feature of $[Tc\equiv N]^{2+}$ complexes is the Lewis basicity of the nitrido group, which can react with strong Lewis acids such as trivalent boron compounds. Recently the first nitrido bridges between technetium and boron were produced by an acid–base reaction between

$[TcNCl_2(PMe_2Ph)_3]$ (**229**) and BH_3 or BCl_2Ph. At low temperatures, the compounds $[Tc(NBCl_2Ph)Cl_2(PMe_2Ph)_3]$ (**239**) and $[Tc(NBH_3)Cl_2(PMe_2Ph)_3]$ (**240**) formed, and were both structurally characterized. The compounds are unstable at room temperature and the starting materials are reformed. The Tc≡N bond is only slightly longer (0.05 Å), whereas the Tc—Cl bonds are shorter by about 0.2 Å as a result of the diminished *trans* influence of the nitrido ligand on formation of the adduct. The source of the instability of the complexes is not obvious from the structural data, since the bond lengths are comparable to the corresponding rhenium complexes which are stable at room temperature.[387]

The reaction of 2-mercapto-methyltetrazolate (Hmmt) with (**34**) occurs with reduction to give the structurally characterized complex $[TcN(mmt)_4]^{2-}$ (**241**). The mmt ligands are coordinated via the deprotonated thiol groups.[388] (Scheme 40).

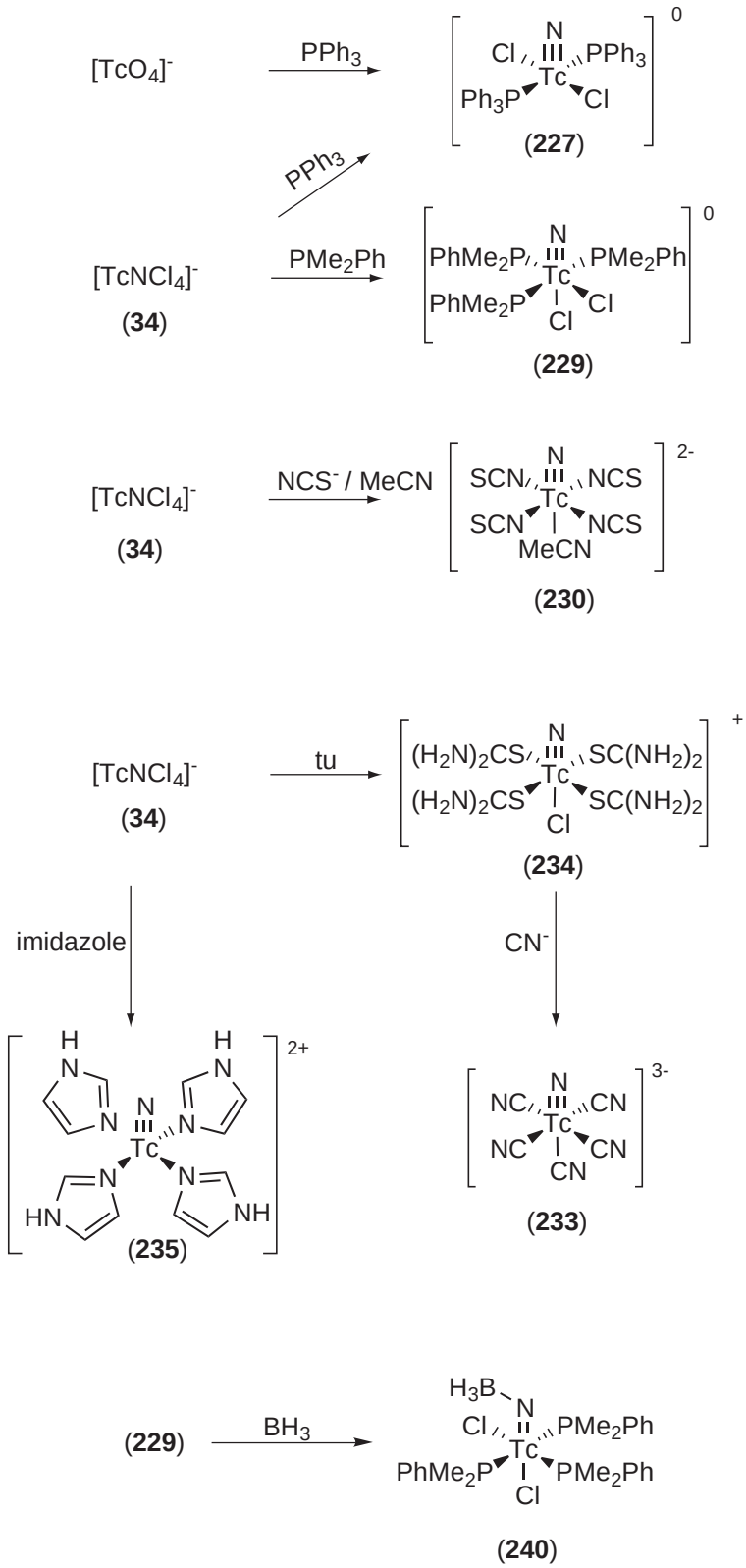
(ii) With polydentate ligands

The ease of phosphine replacement in $[TcNCl_2(PPh_3)_2]$ (**227**) is demonstrated by its reactions with a variety of sulfur-, selenium-, and phosphorus-containing ligands such as diphenyldithiophosphate, diisopropyldithiophosphate, diethyldiselenodithiocarbamate, maleonitrildithiolate (Hmndt), and with 1,2-diphenylphosphinoethane (dppe). Reaction with $[TcNCl_2(PPh_3)_2]$ in acetone/ethanol at room temperature gives in good yields the bis-substituted complexes such as $[TcN(mndt)_2]$ (**242**) or in general $[TcN(EE)_2]$, where EE represents a bidentate phosphorus, sulfur, selenium, or mixed S/Se ligand. Such facile substitution chemistry clearly demonstrates the potential of the Tc≡N core for use in radiopharmaceuticals.[389] Direct reaction of $[TcNX_4]^-$ with dicyanoethenedithiolate, pyridine, or imidazole gave the corresponding complexes with an S_4 or an N_4 donor set.[155] Use of the smaller, but more firmly bound, phosphine ligand PMe_2Ph in $[TcNCl_2(PMe_2Ph)_2]$ permits the substitution reaction with (mnt) to be performed stepwise. The monosubstituted complex $[TcN(mnt)(PMe_2Ph)_2]$ (**243**) is formed first, and with an additional equivalent of ligand the bis-substituted product (**242**) is formed in 60% yield. The monosubstituted complex was structurally characterized.[390] The same starting material was used for the preparation and structural characterization of complexes with dialkyldithiocarbamates (Het_2dtc) and *N*,*N*-dialkylthiocarbamoylbenzamidines (H_2Et_2tcb, (**244**)). Similarly, the six-coordinate, orange-yellow $[TcNCl(PMe_2Ph)_2(Et_2dtc)]$ (**245**) and $[TcN(PMe_2Ph)(Et_2dtc)_2]$ (**246**), yellow $[TcNCl(PMe_2Ph)_2(HEt_2tcb)]$ (**247**) can be prepared by stepwise ligand-exchange reactions from (**229**). Only the intermediate $[TcNCl(PMe_2Ph)_2(HEt_2tcb)]$ could be isolated during the reaction with *N*,*N*-diethylthiocarbamoylbenzamidine to yield finally the five-coordinate $[TcN(HEt_2tcb)_2]$ (**248**), the X-ray structure of which was elucidated.[391] (Scheme 41).

The reaction of $[TcNX_4]^-$ prepared *in situ* from $[TcO_4]^-$ and NaN_3 in conc HCl and/or ligand exchange with LiBr in acetonitrile and 8-quinolinethiol (8-Hqt, (**249**)) at room temperature gives complex $[TcN(8\text{-}qt)_2]$ (**250**) in good yield, and it was structurally characterized. The complex is five-coordinate, with *trans* S and N donors. Comparison of this structure with the similar complex $[TcOCl(2\text{-methyl-}8\text{-}ox)_2]$ is interesting.[368] The latter complex is six-coordinate, whereas the nitrido compound is five-coordinate. This structural change imposes stronger constraints on the structure of the former complex. The angles at the coordinating N of 8-qt in (**250**) are about 120°, as expected for the sp^2 nature of this donor, but deviate considerably (from 108–132°) for the oxo complex.[144]

Bidentate H(NS) (**253**) and tridentate H_2(ONS) (**251**)–(**252**) Schiff-base ligands, derived from S-methyl-dithiocarbazic acid (Hdtca) by reaction with ketones or salicylaldehyde, react with $[TcNCl_4]^-$ in the presence of PPh_3 to give the yellow to yellow-orange complexes of general formula $[TcN(ONS)(PPh_3)]$ (**254**), $[TcNCl(NS)(PPh_3)]$ (**255**), or $[TcN(NS)_2]$ (**256**), which can also be obtained by direct ligand-exchange reaction from $[TcNCl_2(PPh_3)_2]$. The reaction of $[TcNCl_2(PPh_3)_2]$ with a stoichiometric amount of the bidentate ligand H(NS) gave six-coordinate (**255**), which was also obtained from $[TcNCl_4]^-$ in the presence of the ligand and excess PPh_3. For both starting materials the disubstituted complex is formed only in the presence of excess ligand, giving the five-coordinate, yellow-orange (**256**), with S and N donors *trans*. Remarkably, there is no reaction of $[TcNCl_4]^-$ or $[TcNCl_2(PPh_3)_2]$ with other Schiff-base ligands with N,O donor sets, reflecting the relatively soft character of the $[Tc{\equiv}N]^{2+}$ core.[392] (Scheme 42).

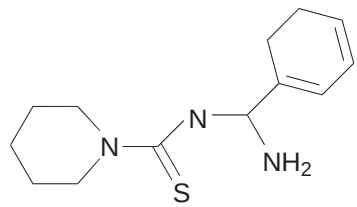
The use of *S*-methyl-2-methyldithiocarbazate $H_2NN(Me)C(S)SMe$ (H_2mdtc, (**257**)) as a source of the nitride ligand in $[Tc{\equiv}N]^{2+}$ radiopharmaceuticals has been developed. The reaction of $[TcOCl_4]^-$ in $EtOH/CH_2Cl_2$ with (**257**) produces the dark green complex $[TcO(Hmdtc)_2]^+$ (**258**).


[TcO4]-
PPh3
(227)
PPh3
[TcNCl4]-
(34)
PMe2Ph
(229)
[TcNCl4]-
(34)
NCS- / MeCN
(230)
[TcNCl4]-
(34)
tu
(234)
imidazole
CN-
(235)
(233)
(229)
BH3
(240)

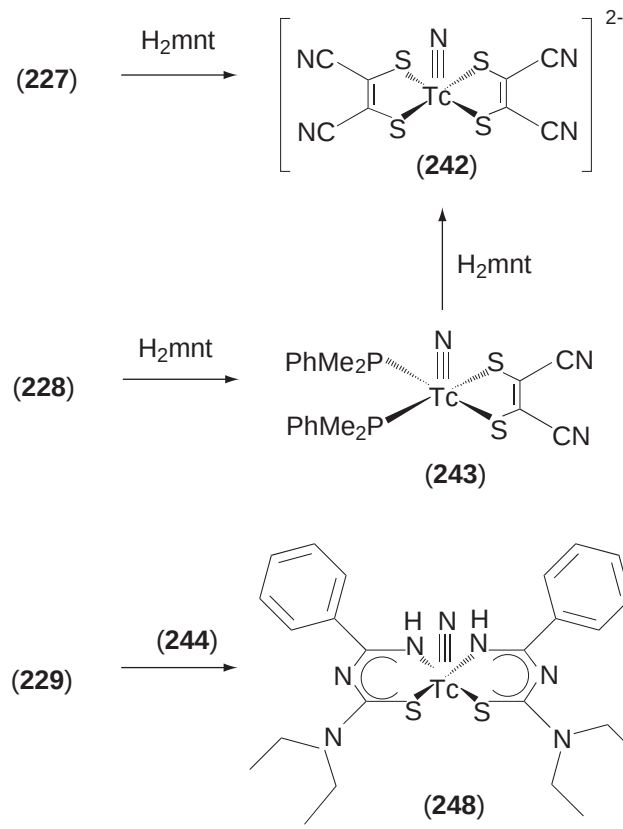
Scheme 40

The X-ray structure shows the Tc coordinated by a deprotonated $-NH_2$ group from the hydrazine and thione sulphur, with the N and S donors *cis* to each other. On subsequent treatment with PPh_3 and HCl, (**227**) is produced in high yield. When (**227**) is treated with (**257**) in the presence of NEt_3, the corresponding nitrido complex $[TcN(Hmdtc)_2]$ (**259**) is produced in very good yield. Addition of other coligands permits the facile syntheses of a wide range of Tc^V nitrido complexes.[393] These reactions elegantly demonstrate that hydrazine complexes of the $[Tc{=}O]^{3+}$ core can be transformed to the $[Tc{\equiv}N]^{2+}$ core in the presence of excess acid and a reducing agent—an important finding for the generation of similar complexes with ^{99m}Tc for radiopharmaceutical purposes.

The reaction of (**227**) with $E(CH_2CH_2PPh_2)_2$, where E = O or NPr, gives the structurally characterized, five-coordinate, pale yellow to yellow complexes $[TcNCl_2\{E(CH_2CH_2PPh_2)_2\}]$ (**260**) under mild conditions.[394] The two chloride ligands can be replaced by $[S_2CNEt_2]^-$ to give $[TcN(S_2CNEt_2)\{NPr(CH_2CH_2PPh_2)_2\}]$ (**261**).

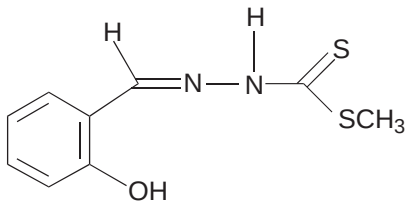


(**244**)

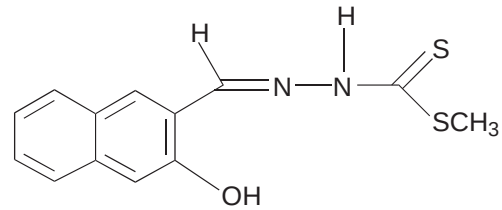


Scheme 41

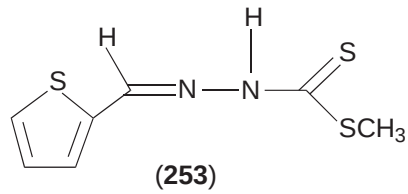
The bidentate, mixed N,P ligand (*o*-amino-phenyl)diphenylphosphine-N,P (H_2app, (**188**)) reacts with (**34**) or (**227**) to yield the six-coordinate cationic complex $[TcNCl(H_2app)_2]^+$ (**262**), in which the amines are not deprotonated. The X-ray crystal structure of this complex was elucidated, showing coordination of the two bidentate ligands with mutual *cis* P coordination.



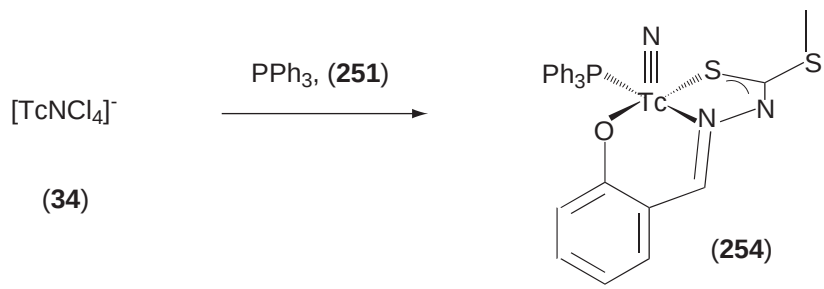
(**251**)

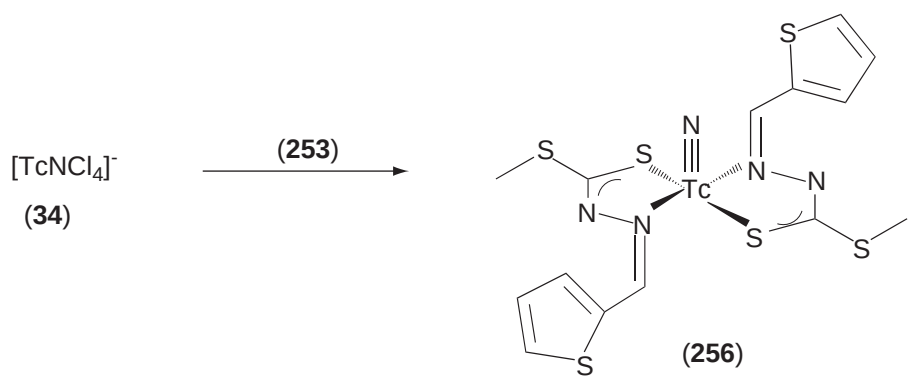


(**252**)



(**253**)





Scheme 42

It is interesting to note that in the reaction of (**188**) with $[TcOCl_4]^-$, the oxo group is replaced by a doubly deprotonated amino group. The mixed imido-amido Tc^V complex $[Tc(app)Cl_2(Happ)]$ (**263**) was synthesized and structurally characterized with Re. Neutral, mixed amino-phosphino ligands can stabilize the soft $[Tc{\equiv}N]^{2+}$ core in the expected way, whereas the harder $[Tc{=}O]^{3+}$ core imposes subsequent acid/base reactions. Stabilization is then mainly achieved by deprotonation, in order to compensate for the relatively high charge.[395]

A series of cationic complexes with tetradentate, umbrella-like NP_3 (**194**) and PP_3 (**195**) ligands have been prepared by the reaction of the ligands 2-diphenylphosphino-*N*,*N*′-bis(2-diphenylphosphinoethyl)ethaneamine (NP_3) and tris-2-diphenyphosphinoethylphosphine (PP_3) with $[TcNBr_4]^-$

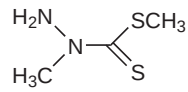
or $[TcNBr_2(PPh_3)_2]$ to give $[TcNBr(NP_3)]^+$ (**264**) and $[TcNBr(PP_3)]^+$ (**265**) in good yields. No X-ray crystal structures were reported. Electrochemical studies of these complexes show no reduction processes below −1.0 V. Oxidation occurred irreversibly at +0.86 V for the complex with the NP_3 ligand.[349]

The behavior of the $[Tc{\equiv}N]^{3+}$ core towards bidentate phosphino or amino ligands, or tetradentate N_2P_2 ligands, further systematizes the reactivity of $[TcNCl_4]^-$ (**34**) with these types of donor. The reaction of (**34**) with various diphosphine ligands, such as dmpe or dppe, gives the six-coordinate, cationic complexes $[TcNCl(PP)_2]^+$ in good yields. The structure of $[TcNCl(dmpe)_2]^+$ (**266**) was determined, showing the chloride *trans* to the nitrido ligand. This complex was erroneously described earlier as a five-coordinate species.[389] In the case of the sterically demanding dippe ligand $^iPr_2PCH_2CH_2P^iPr_2$ (**267**), a dinuclear, doubly chloro-bridged, orange complex $[\{TcNCl(\mu\text{-}Cl)(dippe)\}_2]$ (**268**) is formed, with only one dippe ligand coordinated to technetium. It seems that the phosphino ligands act as reducing agents in these syntheses. Unlike phosphines, nitrogen donors are generally not regarded as reducing agents. Depending on the solvent, the reaction of $[TcNX_4]^-$ with bipy or phen gave the red Tc^V complexes $[TcNBr(bipy)_2]^+$ (**269**) and $[TcNBr(phen)_2]^+$ (**270**), respectively. An X-ray structure shows that for (**269**), the Br^- ligand is located *cis* to the nitrido core and with a bipy N *trans*, although significant deviation from an octahedral geometry occurs. For steric reasons, the two bipy ligands cannot be coplanar. The Tc—N bond *trans* to nitrido is, expectedly, significantly longer than those in the *cis* position to it (mean 2.400 Å vs. 2.130 Å). The most unusual part of the structure is the unique presence of a $[TcBr_4]^{2-}$ counterion in the structure: a coordination compound which could not be synthesized as such so far. Reaction of (**34**) with the tetradentate N_2P_2 ligand *N*,*N*′-(2′-dimethylphosphinoethyl)-*N*,*N*′-(dimethylpropylene-diamine) gives the yellow, six-coordinate complex $[TcNCl(N_2P_2)]^+$.[396] The complexes $[TcNCl(dmpe)_2]^+$ and $[TcNCl(dppe)_2]^+$ can also be prepared from the already-mentioned thiourea precursor $[TcNCl(tu)_4]^+$, by ligand exchange at room temperature. The X-ray structures of both diphosphine complexes were reported. Due to the high lability of the thiourea ligands, the substitution reactions occurred under very mild conditions.[397] (Scheme 43)

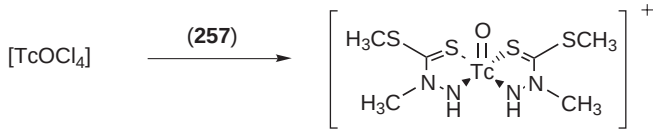
Ligand-exchange reactions of $[TcNCl_2(PPh_3)_2]$ with bidentate aliphatic amine ligands, such as 1,2-ethylenediamine or 1,3-propylenediamine, give the corresponding six-coordinate complexes $[TcNCl(NN)_2]^+$ (**271**). Analogously the tetradentate macrocyclic nitrogen ligand 1,5,8,12-tetraazadodecane cyclam (**105**) produces the corresponding complex $[TcNCl(cyclam)]^+$ (**272**) in good yields. Obviously the chloride ligand is required for charge compensation, although the strong *trans* influence of the nitrido ligand causes an extreme lengthening of the Tc—Cl bond to 2.7320 Å. It is noteworthy that with aliphatic diamines the chloride is usually found *trans* to the nitrido ligand, as there is no steric hindrance to both diamines as there is with bipy or phen. Similar structural differences are seen for complexes of bipy or phen with the $[TcO]^{3+}$ core.[398]

Neutral and monocationic complexes of $[Tc{\equiv}N]^{2+}$ with other tetra-azamacrocycles are synthesized by reaction of $[TcNCl_2(PPh_3)_2]$ or $[TcNCl_4]^-$ with 1,4,8,11-tetraazacyclotetradecane-5-one (cyclam-O, (**273**)), cyclam (N_4) or 1,4,8,11-tetraazacyclotetradecane-5,7-dione (cyclam-O_2, (**274**)). When the reaction is carried out directly with $[TcNCl_4]^-$, PPh_3 was required as a reducing agent. With cyclam six-coordinate (**272**) is formed, requiring coordination of one additional chloride for charge compensation. The potentially mono-anionic ligand (**273**) gave the five-coordinate cation $[TcN(cyclam\text{-}O)]^+$ (**275**), with one loosely bound water ligand *trans* to the nitrido ligand; whereas the dianionic ligand cyclam-O_2 gave the neutral complex $[TcN(cyclam\text{-}O_2]$ (**276**), again with one H_2O *trans* to nitrido.[399] The X-ray structures of all three complexes have been elucidated. This systematic study shows that the amide nitrogen atoms are generally deprotonated upon coordination to the $[TcN]^{2+}$ core, whereas the aliphatic amines are not, in contrast to Tc^V mono-oxo complexes where aliphatic amino groups are frequently deprotonated.

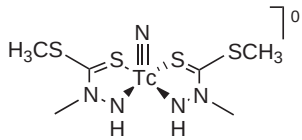
The different behavior of the $[Tc{\equiv}N]^{2+}$ compared to the $[Tc{=}O]^{3+}$ core is also shown by their different reactivities towards amine-oxime ligands of the H_3pnao_2 (**117**) type. $[TcNCl_2(PPh_3)_2]$ reacts with 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime (**117**) under mild conditions to yield the cationic complex $[TcN(OH_2)(H_2pnao_2)]^+$ (**277**) in good yield. In contrast to the corresponding complex with the $[Tc{=}O]^{3+}$ moiety, the amines are not deprotonated, but coordinate as normal aliphatic amines. The water ligand *trans* to the nitrido ligand displays a rather long bond distance of (2.481(4) Å).[400] In a systematic study, the propylene backbone was extended to butylene and pentylene respectively and gave analogous complexes. The same reaction with the $[Tc{=}O]^{3+}$ core led to a complex with a $[O{=}Tc{=}O]^+$ core and without amine deprotonation when the backbone was extended to pentylene (see Section 5.2.2.3.2(iv)). All the complexes exhibit similar structural features, with coordination via four neutral nitrogen donors and one water ligand *trans* to the nitrido group.[401] (Scheme 44).



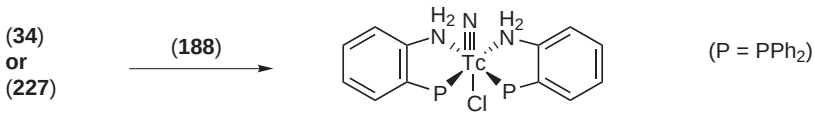
(**257**)



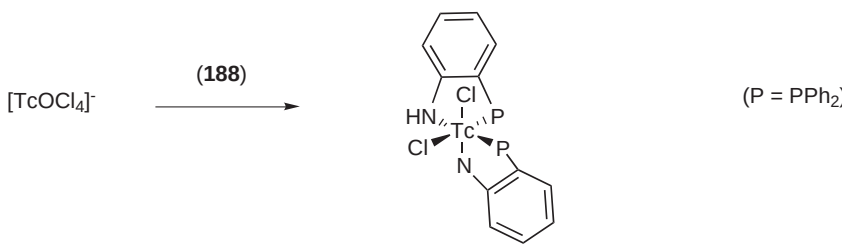
(**258**)



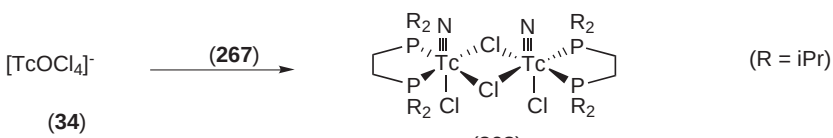
(**259**)



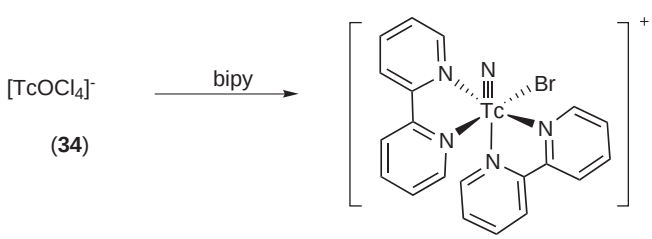
(**262**)



(**263**)

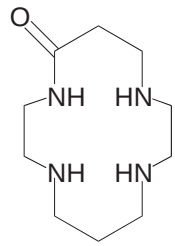


(**268**)

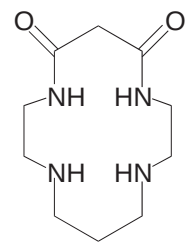


(**269**)

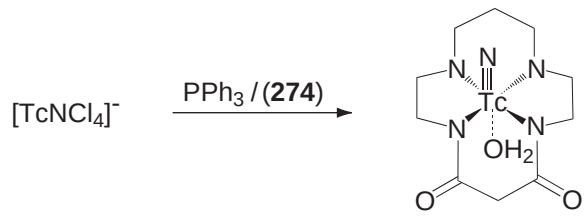
Scheme 43



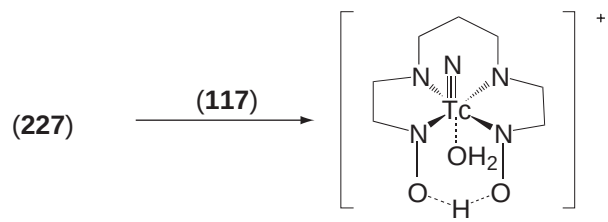
(**273**)



(**274**)



(**276**)



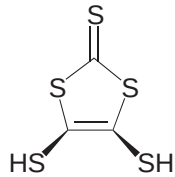
(**277**)

Scheme 44

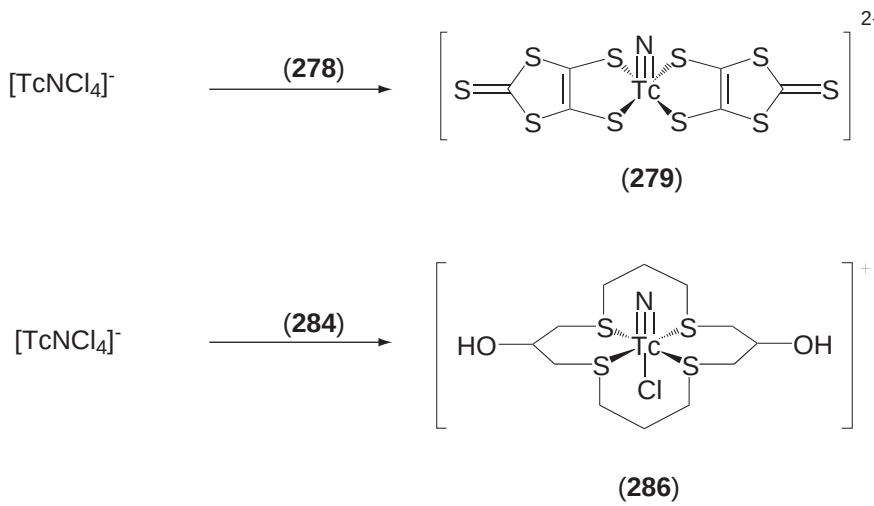
Reaction of (**34**) with the bidentate sulfur ligand isotrithionedithiol (H_2dmit, (**278**)) produced a dianionic complex. The reaction of (**278**) in which the thiol groups were deprotected *in situ* prior to the substitution reaction with $[TcNCl_4]^-$ in acetonitrile gave a 45% yield of $[TcN(dmit)_2]^{2-}$ (**279**) after a short reflux. The X-ray structure was determined. As observed with other pure thiolato ligands such as H_2mnt, no characterizable product is formed by direct substitution reaction with $[TcNCl_2(PPh_3)_2]$. The soft, neutral, and probably more strongly coordinating phosphines resist substitution by dianionic thiolato groups. The chlorides are less strongly bound and are easily replaced.[402]

In contrast, the mono-anionic bidentate ligand bis(diphenyl-thiophosphoryl)amide Na(dtp) (**280**) reacts with (**227**) with complete substitution of all the ligands except the nitride, and the complex $[TcN(dpt)_2]$ (**281**) forms in 85% yield after 30 minutes in MeOH under reflux. Direct reaction with $[TcNCl_4]^-$ gives the same compound in comparable yields. However, reaction of (**280**) with the alternative precursor $[TcNCl_2(PMe_2Ph)_2]$ gives the six-coordinate complex $[TcNCl(PMe_2Ph)_2(dpt)]$ (**282**), even with an excess of ligand. The X-ray crystal structure of (**282**) shows that the chloride is *trans* to the nitrido ligand, as is commonly encountered in this type of six-coordinate complex. Despite the fact that the ligand (**280**) stabilizes Tc^V efficiently, the reaction of $[TcNCl(PMe_2Ph)_2(dpt)]$ with Lewis acids to replace the remaining chloride, or with S_2Cl_2, leads to replacement of dpt and reduction to lower-oxidation-state complexes such as *trans*-$[Tc(NS)Cl_3(PMe_2Ph)_2]$ (**283**).[403]

A further difference from the $[Tc{=}O]^{3+}$ core is evident from reactions with macrocyclic thiacrowns. Whereas no complexes of $[Tc{=}O]^{3+}$ with pure thioether donors are known, $[TcNCl_4]^-$ reacts with 1,4,8,11-tetrathiacyclotetradecane (14-S-4) or (16-S-4-$(OH)_2$) (**284**) and (18-S-6) in acetone/MeOH solution to give the cationic, six-coordinate complexes $[TcNCl(14\text{-}S\text{-}4)]^+$ (**285**), $[TcNCl(16\text{-}S\text{-}4\text{-}(OH)_2)]^+$, and $[TcNCl(18\text{-}S\text{-}6)]^+$. The X-ray structures of all three complexes were determined, showing the tetradentate sulfur ligand to be in the plane and the chloride again *trans* to the nitrido group. This is a common structural feature in all these complexes, regardless of ring size or the presence of two additional sulfur donors in the last complex (Scheme 45).[404,405]



(**278**)



Scheme 45

Tetradentate N_2S_2 ligands have been used with both $[Tc{=}O]^{3+}$ and $[Tc{\equiv}N]^{2+}$ cores. Bis-aminethiols and aminoacids have been studied in detail due to their usefulness in the context of $[Tc{=}O]^{3+}$ chemistry. Various diaminodithiol ligands (dadt) of the type $\{HSCR_2(CH_2)_2NR'(CH_2)\}_2$, with R = Et or Me and R′ = Me, Et or H, react with (**227**) by simple ligand substitution under mild conditions to give complexes of the type $[TcN(N_2S_2)]$ (**286**).] The structures of two complexes with secondary and tertiary amines were elucidated.[314] For comparison, the same ligands were studied with $[TcOCl_4]^-$. It turned out that the products were the cationic species $[TcO(N_2S_2)]^+$ for all ligands without deprotonation at the secondary amines. However, the reaction of (**227**) with cysteinate ethylester (cys-OEt, (**287**)) gave the monosubstituted complex $[TcNCl(cys\text{-}OEt)(PPh_3)]$ (**288**), and the same complex was formed from $[TcNCl_4]^-$ in the presence of PPh_3.[406] The structure is square pyramidal, with the amino nitrogen and phosphine groups *trans*.

Studies with cysteine have been extended to derivatized amino acids. N_2S tridentate ligand systems (H_2aa-dtca, (**289**)) have been prepared by the combination of N-protected amino acids with *S*-methyl-2-methyldithiocarbazate. The reaction with $[TcOCl_4]^-$ under mild conditions gives the neutral, purple complexes [TcOCl(aa-dtca)] (**290**), in which the tridentate ligand is coordinated by deprotonated carbamate and carbazide groups and through the terminal thione sulfur. The reaction with $[TcNCl_2(PPh_3)_2]$ occurs under reflux and requires the presence of a strong base to

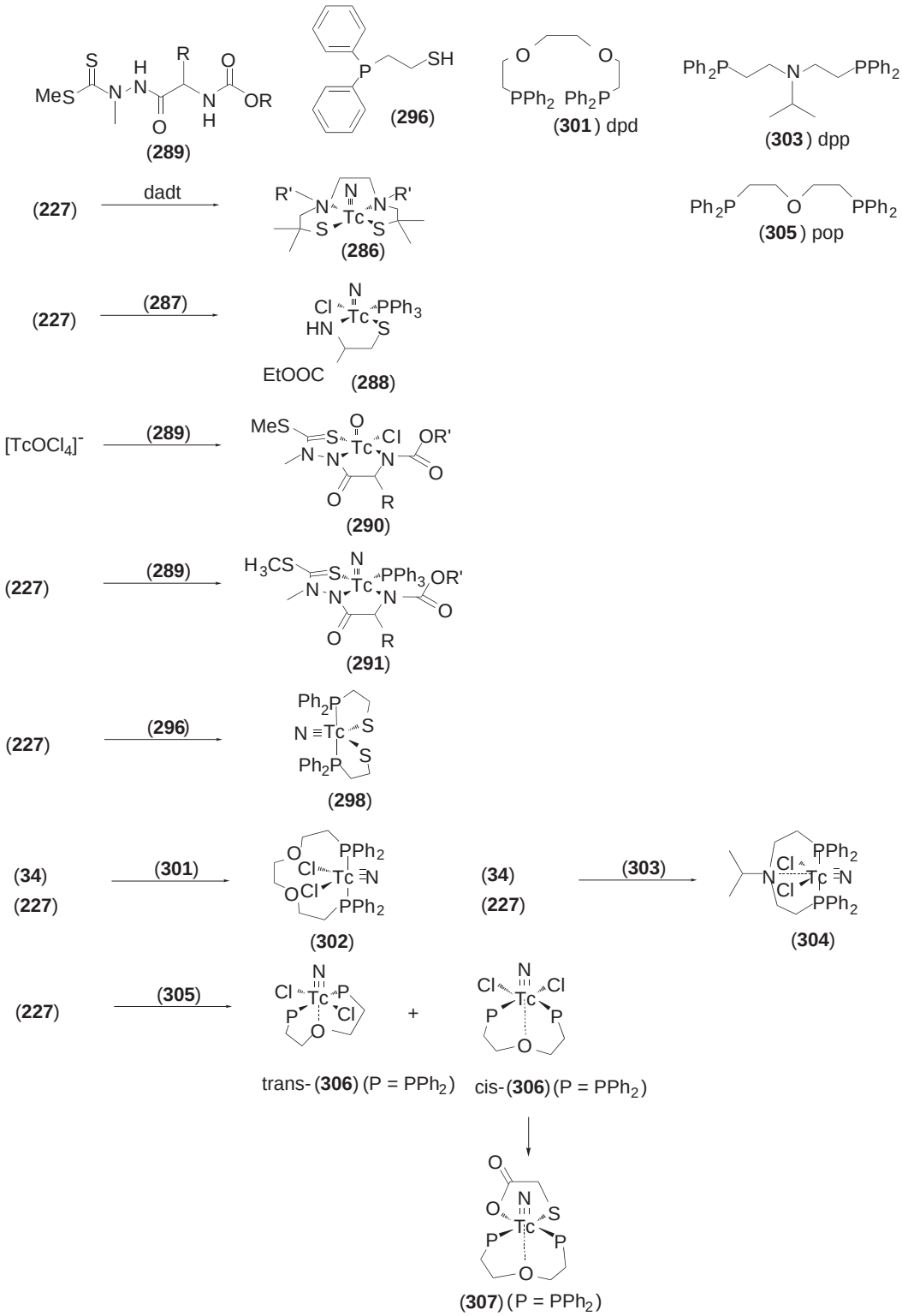
deprotonate the carbamate; the neutral, yellow complex [TcN(aa-dtca)(PPh_3)] is obtained and structurally characterized for aa = valine. In the case of the $[Tc{\equiv}N]^{2+}$, a phosphine ligand occupies the remaining coordination site, and a chloride in the case of $[Tc{=}O]^{3+}$. Both the oxo- and nitrido complexes have square-pyramidal structures. Complex (**290**) can also be synthesized in low yield from the Tc^{III} precursor [$TcCl_3(NCCH_3)(PPh_3)_2$] in the presence of O_2. Circular dichroism data showed considerable conformational variation for the complexes, which is attributed to a folded structure induced by conformational rigidity and stability of the complexes in solution.[407]

The reaction with the unsaturated N_2S_2 Schiff-base ligands *N*,*N*′-ethylene bis(thioacetonylideneimine) (H_2tai, (**292**)) and *N*,*N*′-ethylene bis(methyl-2-aminocyclopentene-1-dithiocarboxylate) (H_2apc, (**293**)) are of interest in the context of neutral, highly lipophilic brain perfusion agents. The neutral compounds [TcN(apc)] (**294**) and [TcN(tai)] (**295**) can be prepared from (**227**) in good yields. The X-ray crystal structures were elucidated.[362] The two structures are comparable, with the Tc lying about 0.6 Å above the basal plane. Both complexes show a quasi-reversible, one-electron oxidation wave at +1.04 V vs. SCE in CH_2Cl_2. Since these potentials are very similar to those of the free ligands, it was suggested that the oxidation process is ligand based. No cathodic response was observed, consistent with that the nitrido ligand acting as a strong π-donor. The sulfur ligands act as powerful π-acceptors in these complexes.[408]

A novel class of trigonal-bipyramidal Tc^{V}-nitrido complexes has been described. The bidentate, mixed P,S ligands of the type $R_2PCH_2CH_2SH$ Hpet, (**296**)) (R = phenyl, methoxypropyl), ($R_2'P(CH_2)_3SH$ (R′ = phenyl, tolyl) (Hppt, (**297**)) and Hpbt, (**197**)) afford the five-coordinate, disubstituted complexes [TcN$(PS)_2$], e.g., [TcN$(pet)_2$] (**298**), by reaction with (**227**) after 1 h under reflux in CH_2Cl_2. The complexes are formed in yields better than 90%, and were also formed in good yields when starting directly from $[TcNCl_4]^-$. With the same ligands and $[TcNCl_4]^-$ as starting material, reduction to Tc^{III} occurs, giving five-coordinate complexes of the type [$Tc(PS)_2$(S-P)] (**299**) or tris-substituted complexes of the type [$Tc(PS)_3$] (**300**), which is also formed from the reaction of $[TcO_4]^-$ with the corresponding ligands. The use of highly acidic solutions prevents the reduction, presumably since the thiols are now protonated and nonreducing. The X-ray crystal structures of several complexes have been elucidated and they exhibit similar features. In the trigonal-bipyramidal structure type, the equatorial positions are occupied by the nitrido and the two sulfur groups, and the axial sites by P donors. This is unusual in the sense that square-pyramidal geometry is usual for this set of donors, particularly where the coligands comprise four π-donors such as S^- and X^-. Since the phosphine-thiolato ligands have a mixed set of π-donor and π-acceptor ligands, the square-pyramidal structure is not maintained. The π-acceptors prefer *trans* positions, whereas the two π-donors are *cis*.[409] This class of neutral TcN complexes with mixed phosphino-thiolate ligands have been studied as potential myocardial imaging agents. Some show reasonable heart uptake, but they have short residence times and are therefore not convenient for clinical use.[410]

A trigonal-bipyramidal structure has also been found for the $[TcN]^{2+}$ core with a mixed P_2O_2 ligand. Reaction of $[TcNCl_4]^-$ or [$TcNCl_2(PPh_3)_2$] with 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (dpd, (**301**)) gave the structurally characterized complex [$TcNCl_2$(dpd)] (**302**), in which the two phosphorus atoms are *trans* and the nitride and the two chloride ligands form the equatorial plane. The two ether oxygens are noncoordinating. A similar trigonal-bipyramidal structure is also found for [$TcNCl_2$(dppp)] (**304**), formed with the tridentate P_2N ligand bis(diphenylphosphinoethyl)propylamine (dppp, (**303**)). The aliphatic amine nitrogen *trans* to the nitrido ligand is at a nonbonding distance of 2.70(1) Å, as expected for the high *trans* influence of nitride. However conversion to square-pyramidal geometry might be expected by the addition of chloride *trans* to nitrido, as observed for other complexes.[394]

More recently it has been proposed that changing the connectivity in [TcN$(PS)_2$] to [TcN$(P_2)(S_2)$] (**298**) would give asymmetric complexes with comparable stabilities. The reaction of $[Ph_2P(CH_2)_2]O$ (pop, (**305**)) with (**227**) gives the distorted pseudo-octahedral complex [$TcNCl_2$(pop)] (**306**), in which the two P donors are *trans*. The distance to the ether O is 2.500(4) Å and essentially nonbonding. For (**306**) both *cis* and *trans* isomers exist, and the reactivity of both was investigated towards bidentate OSH_2 ligands such as 2-mercaptoethanol or mercaptoacetic acid. The *trans* isomers were found to be almost inert towards substitution, whereas the *cis* isomers of (**306**) reacted readily, forming complexes of composition [TcN(PXP)(OS)] (**307**) (X = O,N).[411] The precursors of the type [$^{99m}TcNCl_2$(PXP)] can be used to label peptides at a high specific activity by replacement of the chlorides by an appropriate bifunctional ligand.[412] (Scheme 46)



Scheme 46

5.2.2.3.4 Imido complexes

Dianionic organoimido ligands (RN^{2-}) are isoelectronic with the oxo group, but complexes of technetium-containing imido ligands are comparatively rare. Although not yet employed in

radiopharmaceutical compounds, the organoimido core may well have future applications in technetium-based radiopharmaceuticals, since the R substituents can readily be varied, which should allow fine tuning of the properties of a potential radiopharmaceutical. In addition, the technetium(V) imido core is in some ways more stable than the corresponding oxo core. This is shown by the nonexistence of $[TcOCl_3(PPh_3)_2]$, whereas the isoelectronic imido analogue $[Tc(NR)Cl_3(PPh_3)_2]$ (**308**) is a very stable and useful compound. Thus, in many cases where the oxo complex does not exist, the corresponding organoimido complex does.

Organoimido-complexes are prepared by two general routes. The organoimido group can be introduced via a disubstituted organohydrazine such as 1-acetyl-2-phenylhydrazine (aph, (**309**)) with cleavage of the N—N bond, or via aromatic amines through double deprotonation. A less common method in technetium chemistry is the reaction of an oxo complex with arylisocyanates, which also generates organoimido complexes with the release of CO_2. Furthermore direct reaction of $[TcOCl_4]^-$ with aromatic amines may also yield Tc^V organoimido complexes.

The organoimido complex $[TcCl_3(NPh)(PPh_3)_2]$ (**308**) was synthesized from $[TcO_4]^-$ and (**309**) in the presence of excess PPh_3. The initial synthetic step must be carried out under alkaline conditions, since even $[NH_4]^+$ present as the counterion of $[TcO_4]^-$ is acidic enough to protonate (**309**) at the phenyl nitrogen and prevent imide formation. The reaction is thus performed initially under slightly alkaline conditions, followed by HX addition to give the complexes $[TcX_3(NR)(PPh_3)_2]$ (X = Cl, Br) in very good yields.[413–415] These complexes are golden brown for $X = Br^-$ and green-brown for $X = Cl^-$. An X-ray structure analysis showed a Tc—N—C angle of 171.8(4)°. The IR absorption due to ν(Tc=N) occurs at 1,090 cm^{-1}, a typical range for this structural unit. If a hydrazine derivate such as *N*-benzoylhydrazine is reacted with $[TcOCl_4]^-$ and PPh_3, a complex formulated as $[TcCl_3(NH)(PPh_3)_2]$ is formed as an intermediate, and then loses HCl to form the well-known nitrido complex $[TcNCl_2(PPh_3)_2]$ in excellent yields. [414]

An alternative route to imido-complexes starts directly from the Tc^V precursor $[TcOX_4]^-$. Reaction with PhNCO gave blue-black $[Tc(NPh)X_4]^-$ (**308a**) ($X = Cl^-$, Br^-) in essentially quantitative yield with loss of CO_2. These complexes are quite moisture sensitive, but are useful starting materials for substitution reactions. Reaction of $[TcOCl_4]^-$ with aromatic amines $ArNH_2$ and PPh_3 in alcohols gives the complex (**308**) directly. The X-ray crystal structure of the tolylimido complex has been elucidated and shows a Tc—N—C angle of 168° and a Tc—N distance of about 1.7 Å, typical for a TcN multiple bond. The same reaction in the presence of a bidentate phosphine ligand, dppe, produced the first cationic, purple, Tc^{IV} imido complex $[TcCl(NAr)(dppe)_2]^+$ (**310**).[416]

Reaction of $[TcOCl_4]^-$ with (**309**) in MeOH followed by dppe gives $[TcCl_3(NPh)(dppe)]$ (**311**) in relatively low yield. The X-ray crystal structure confirmed the formulation and the Tc—N—C angle is close to 180°, indicating that the imido ligand is formally donating four electrons. The low yield was expected, since the excess of dppe required to remove the terminal oxo group also produces the cationic complex $[TcCl(NAr)(dppe)_2]^+$ mentioned above, a complex that could indeed be isolated from the reaction mixture. The reaction of (**308**) with pyridine leads to the substitution of only one PPh_3 with pyridine, to give $[TcCl_3(NPh)(PPh_3)(py)]$ (**312**). Substitution of two PPh_3 did not occur as in the case of the rhenium analogue, probably due to the much milder conditions applied in the Tc reaction.[417]

The reaction of the neutral complex (**308**) with excess PMe_2Ph in refluxing MeOH gave the cationic complex $[TcCl_2(NPh)(PMe_2Ph)_3]^+$ (**313**), which has been structurally characterized. The Cl^- ligands are *cis* and one is *trans* to the organoimido group. The angle at the nitrogen atom is 178.8(2)° and the Tc—N bond length is 1.711(2) Å, consistent with a Tc—N triple bond. This simple substitution chemistry illustrates that there are parallels between nitrido and organoimido chemistry. Both form six-coordinate complexes with smaller tertiary phosphines, although the imido complexes are cationic.[418]

The reaction of (**308**) with thiophenols gives $[TcO(SPh)_4]^-$ (**89**) in better yields than by direct reaction with $[TcOCl_4]^-$. With the sterically more crowded 2,3,5,6-tetramethyl-benzenethiol (Htmbt, (**314**)), the Tc-organoimido core is retained and the complex $[Tc(NPh)(tmbt)_4]^-$ is formed and can be identified by mass spectrometry. Reaction with $\{P(C_6H_4\text{-}2\text{-}SH)_3\}$ (H_3PS_3, (**315**)) gives the five-coordinate Tc^{III} complex $[Tc(PS_3)(PPh_3)]$ (**316**).[415]

As already mentioned in Section 5.2.2.3.3(ii), the reaction of $[TcNCl_2(PPh_3)_2]$ with (*o*-aminophenyl)-diphenylphosphine (H_2app, (**188**)) produces the complex $[TcNCl(H_2app)_2]^+$ (**262**), whereas reaction with $[TcOCl_4]^-$ gives a mixed amido-imido complex $[TcCl_2(app)(Happ)]$ (**263**). The Tc—N imido bond length is longer than in the nonchelating imido complexes since the bond order is essentially two, which is also reflected in the Tc—N—C angle of ca. 137°.[295]

The Tc^{VII} complex $[Tc(NAr)_3I]$ (**28**) mentioned in Section 5.2.2.1.2 can be reduced with two equivalents of Na^0 to the unique, trigonal-planar, homoleptic Tc^V imido complex $[Tc(NAr)_3]^-$

(**317**).[171] The reactivity of this anionic complex towards main-group metals such as Hg and Au is fascinating. Reaction with Ph_3PAuCl produces $[(ArN)_3TcAu(PPh_3)]$ (**318**). The structure is a trigonal-based pyramid, with the Au in the apical site. The reaction with $HgBr_2$ results in the replacement of the two Br^- by (**317**) giving $[\{(NAr)_3Tc\}_2Hg]$ (**319**), which has a Tc—Hg—Tc angle of exactly 180°.[171] (Scheme 47).

5.2.2.3.5 Hydrazido, diazenido, and diazene complexes

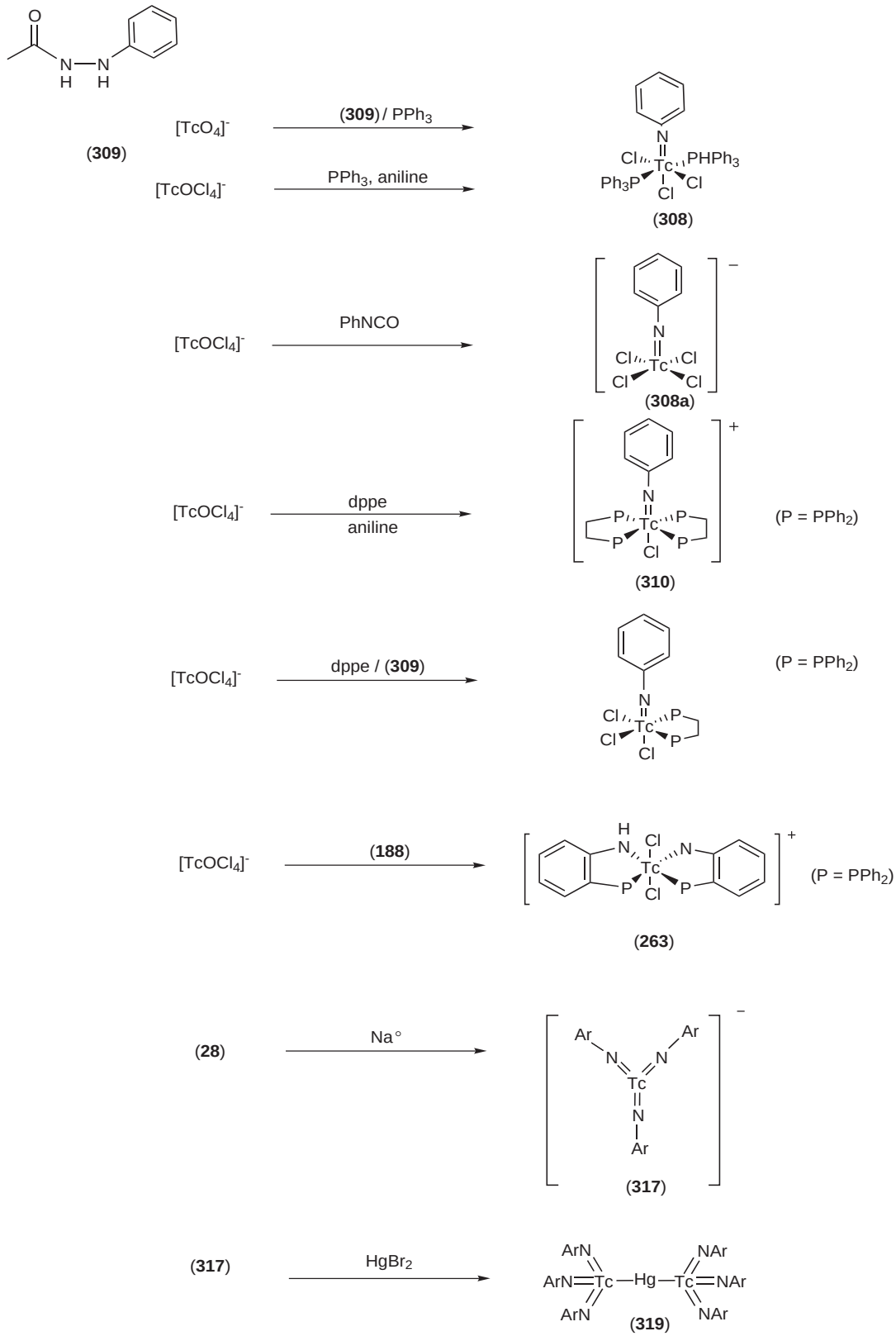
As is evident from the previous section, organohydrazines act as reducing agents and the oxidized hydrazine residue can also bind to the metal. Such ligands derived from organohydrazine precursors are in general referred to as organohydrazide ligands. This class of ligands includes the neutral hydrazino ligand (A), the anionic hydrazido (B), the neutral diazene (C), and the dianionic hydrazido (D) ligand. D is also referred to as the isodiazene ligand, and can be observed in both a linear (D) and bent (E) conformations. The diazenido ligand (F and G) is the most frequently observed species in this family and is also found in two conformations. As shown by the next section, organohydrazine ligands tend to react with high-valent technetium compounds to form a hydrazide ligand, which can be chelated when a further coordinating group is present in the organic residue. The assignment of oxidation state is not always unambiguous, and complexes containing monodentate or chelating organohydrazide ligands in any of the forms mentioned above will all be treated in the section below. A review of group 7 organohydrazide chemistry gives classifications of ligand types based on crystal structure data, which are helpful for assignment of metal oxidation states.[419] (Scheme 48).

The reaction of $[TcO_4]^-$ with aph (**309**) in MeOH in the presence of HBr and PMe_2Ph gives the phenyldiazenido complex $[Tc(NNPh)Br_2(PMe_2Ph)_3]$ (**320**) as an orange compound. The formation of the diazenido compound occurs with the cleavage of the N—$COCH_3$ bond in (**309**) and the PhN_2 fragment coordinates to the technetium center. Conventionally the diazenide ligand is regarded as being monoanionic, giving a formal oxidation state of three. The Tc—N—N angle is 172° and the Tc—N bond length 1.753(13) Å, indicating formal donation of three electrons and a Tc—N multiple bond.[420]

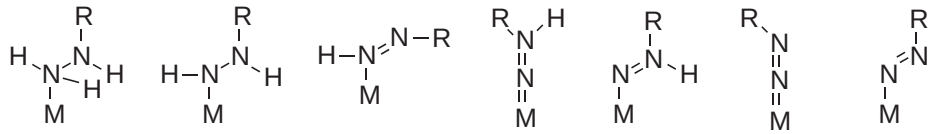
The reaction of *para*-substituted phenylhydrazines with $[TcO_4]^-$ and PPh_3 in EtOH under reflux in the presence of HCl produces the bis-substituted Tc^{III} diazenido complexes $[TcCl(NNC_6H_4\text{-}R)_2(PPh_3)_2]$ (**321**) (R=CH_3) in good yield. These compounds can also be prepared at room temperature by direct reaction of $[TcOCl_4]^-$ with the appropriate hydrazine.[416] The structure is essentially trigonal bipyramidal, with *trans* phosphines in the apical sites. If dppe is used instead of PPh_3 for the reaction of arylhydrazines $ArNHNH_2$ with $[TcOCl_4]^-$ or $[TcO_4]^-$, the six-coordinate, cationic complexes $[TcCl(NNAr)(dppe)_2]^+$ (**322**) are formed. The diazenido ligand is *trans* to chloride and the Tc—N—N angle is about 163°. This compares well with the bisubstituted complex in which the angles are 166° and 172°, respectively. Assuming that this bending counts for a single bond, the oxidation state could be considered in these complexes as +III rather than +V. Interestingly, with *p*-nitrophenyl-hydrazine, only the monosubstituted complex $[TcCl_2(NNC_6H_4\text{-}NO_2)(PPh_3)_2]$ (**323**) can be synthesized.[421]

The bright orange complex $[TcCl(NNC_6H_4Br)_2(PPh_3)_2]$ (**324**) has also been prepared by the reaction of $[TcCl_4(PPh_3)_2]$ with (*p*-bromophenyl)-hydrazine in methanol, in the presence of a base. These complexes are, as expected, isostructural with the chloro analogue. The structure is a trigonal bipyramid with the two phosphine ligands in apical positions, and depicts 166° and 170° angles for Tc—N—N. The bending can be ascribed to crystal-packing effects and is energetically not significant. Mono-anionic diazenido ligands would count for an oxidation state +III. Complexes with various substituents on phenyl have been prepared in a similar manner. The nitrogens of the diazenide ligands complexes (**324**) are basic. When exposed briefly to gaseous HCl, the red, six-coordinate, protonated complex $[TcCl_2(NNC_6H_4Br)(NNHC_6H_4Br)(PPh_3)_2]$ (**325**) is formed. Protonation takes place at the nitrogen adjacent to the phenyl ring. Longer exposure to HBr in benzene allows the isolation of the dark purple, doubly protonated, cationic hydrazido complex $[TcBr_2(NNC_6H_4Br)(NHNHC_6H_4Br)(PPh_3)_2]^+$ (**326**), in which the chlorides have been replaced by bromide.[422]

The bis(diazenido)technetium complex $[TcCl(NNC_6H_4\text{-}Cl)_2(PPh_3)_2]$ reacts with a variety of bi- and tetradentate ligands with loss of one diazenido ligand and formation of six-coordinate complexes. The reaction with $Na[S_2CNR_2]$ (dtc) gives $[Tc(NNR)(dtc)_2(PPh_3)]$ (**327**), and with dianionic tetradentate ligands such as H_2salen (**38**) the complex $[Tc(NNR)(salen)(PPh_3)]$ (**328**) is formed in good yield.


(309)
[TcO4]-
(309) / PPh3
[TcOCl4]-
PPh3, aniline
(308)
[TcOCl4]-
PhNCO
(308a)
[TcOCl4]-
dppe
aniline
(P = PPh2)
(310)
[TcOCl4]-
dppe / (309)
(P = PPh2)
[TcOCl4]-
(188)
(P = PPh2)
(263)
(28)
Na°
(317)
(317)
HgBr2
(319)

Scheme 47



(A) (B) (C) (D) (E) (F) (G)

Scheme 48

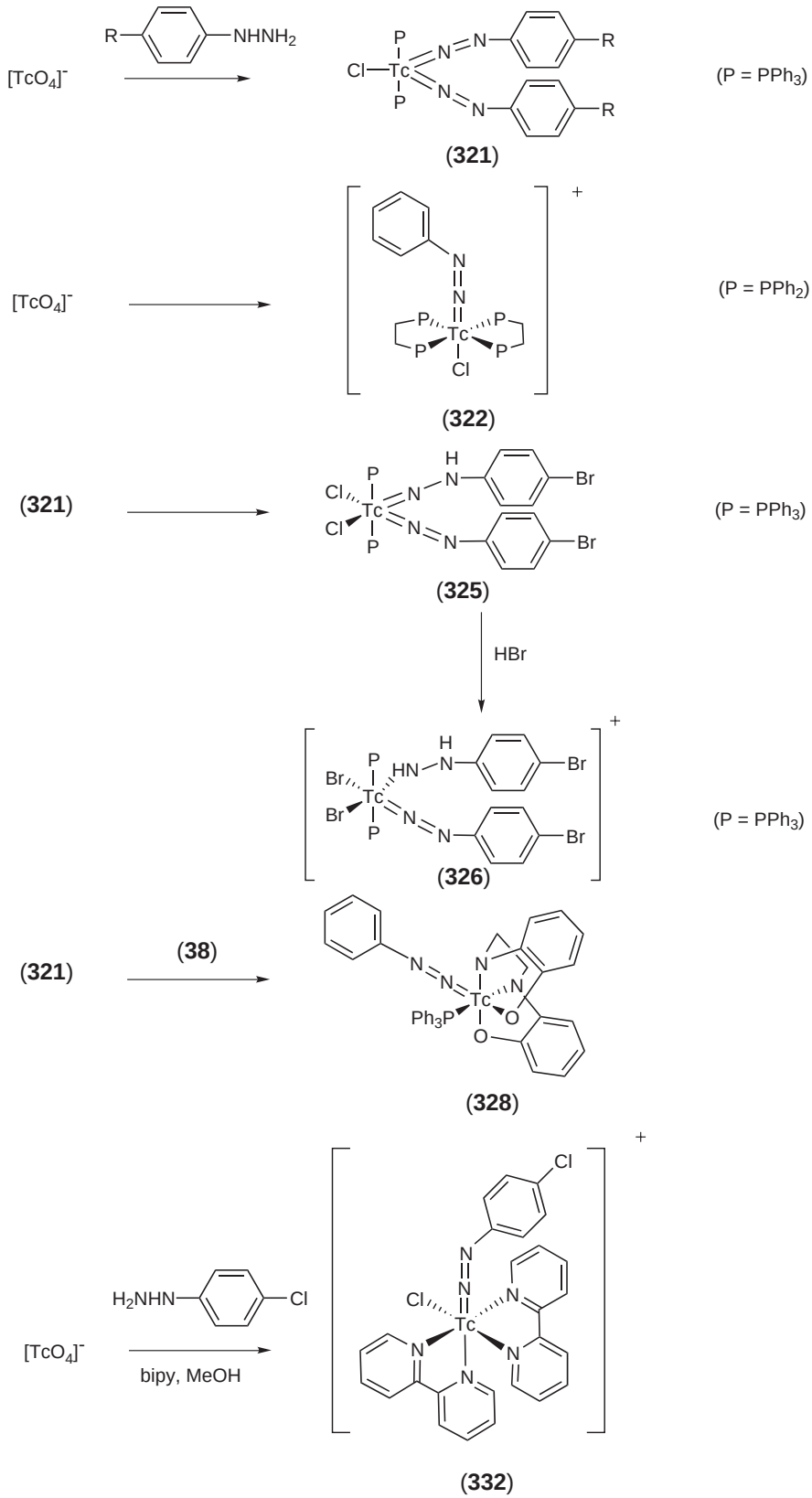
The X-ray crystal structure of the latter was elucidated, showing the PPh_3 and the diazenido ligand to be *cis*. Reaction with excess maltol (3-hydroxy-2-methyl-4H-pyran-4-one, Hma, (**78**)) in EtOH under reflux produces the 18-electron complex $[TcCl(NNR)(ma)(PPh_3)_2]$ (**329**). More elegantly, similar diazenido complexes were prepared directly from $[TcO_4]^-$ but in the absence of PPh_3. *In situ* reaction of a solution prepared from $[TcO_4]^-$ and phenylhydrazine with a range of ligands such as dithiocarbamate (dtc) gave the complex $[TcCl(NNR)_2(dtc)_2]$ (**330**), which is formally a Tc^V complex. Similarly, the reaction with (**78**) gave the cationic complex $[Tc(NNR)_2(ma)_2]^+$ (**331**), which is formulated as six-coordinate. Reaction with bipy gave the complex $[TcCl(NNR)(bipy)_2]^+$ (**332**). The complex ^1H NMR spectrum of (**322**) implies two inequivalent bipy ligands and hence a *cis* geometry. Interestingly, this shows that bipy can coordinate around the $[Tc(NNR)]^{2+}$ core when it is generated *in situ*. The complex $[TcCl(NNC_6H_4Cl)_2(PPh_3)_2]$ does not react at all with bipy, probably due to the sterically bulky PPh_3 ligands. The 4-Cl phenyl substituent was chosen because the unsubstituted phenyldiazenido complexes are inert to substitution, due to the polymeric character of the complex.[423] (Scheme 49).

A diazene complex derived from thiobenzoylhydrazine has been described. The reaction of thiobenzoylhydrazine (H_2tbh, (**333**)) with $[TcOCl_4]^-$ in methanol under reflux yields $[Tc(HNNCSPh)_2(S_2CNPh)]$ (**334**) as lustrous red crystals. The reaction proceeds by condensation to abstract the oxo ligand and the substitution of the chloride ligands. The persistent contamination of the starting material with dithiobenzoic acid explains the presence of this ligand in the final complex. The structure has been elucidated by X-ray crystal structure analysis. The Tc center exhibits distorted trigonal-prismatic geometry through ligation to the S donors of the bidentate thioacid group and the α-nitrogen and S donors of the chelating diazene ligands.[424]

Reaction with 1,1-substituted hydrazines has been described and produces isodiazene complexes. Thus, the reaction of $[TcOCl_4]^-$ with excess Ph_2NNH_2 (**335**) and PPh_3 in refluxing MeOH gave the six-coordinate complex $[Tc(NNPh_2)Cl_3(PPh_3)_2]$ (**336**). The X-ray structure shows a nearly linear Tc—N—N system. If the isodiazene ligand is regarded as being formally neutral, the oxidation state of the Tc is +III. In this structure, the two phosphines are *trans* and the Tc—N and the N—N bond distances support the formulation as a complex of neutral isodiazene.[425]

A number of complexes derived from chelating hydrazine derivatives such as 2-hydrazinopyridine (hypy, (**337**)) and hydralazine (hypyz, (**338**)) have been reported. The reaction of $[TcO_4]^-$ in acidic MeOH with (**338**) produced the homoleptic cationic complex $[Tc(HN{=}NC_8H_5N_2)_3]^+$. This complex can be described as a tris-organodiazene chelate complex in which the organohydrazine precursor has been formally oxidized.[426] The reaction of 2-hydrazinopyridine (**337**) with $[TcO_4]^-$ at room temperature gives the mixed organodiazene-organodiazenido complex $[TcCl_3(NNHpy)(HNNpy)]$ (**339**). The organodiazene (NHNpy) ligand forms a five-membered chelate system, whereas the organodiazenido ligand coordinates by the β-nitrogen. Assuming a monoanionic diazenido ligand, the formal oxidation state of the Tc is +IV.[427]

Chelating organodiazene complexes can also be obtained from Tc^{III} precursors. Reaction of $[TcCl_3(NCCH_3)(PPh_3)_2]$ with 2-hydrazino-4-(trifluoromethyl)pyrimidine ($CF_3C_4H_2N_2NHNH_2$) (H_2htfp, (**340**)) in refluxing MeOH leads to the substitution of one chloride and the acetonitrile ligand to produce the peach-tan-colored complex $[TcCl_2(htfp)(PPh_3)_2]$ (**341**) in moderate yield. The same complex can also be prepared directly from $[TcO_4]^-$ after initial reaction with the hydrazine and subsequent addition of HCl and PPh_3. The coordinated acetonitrile is lost during the process and the organohydrazine is oxidized to the organohydrazide ligands. From the X-ray crystal structure the two phosphines are *trans*, and the diazenido group is present as a chelating ligand. Interestingly, technetium and rhenium behave differently. Under the same reaction conditions but with rhenium, the complex $[ReCl_2(NNR)(HNNR)(PPh_3)]$ is produced, which contains both chelating diazenido and terminal diazene ligands. Both are uninegative and form a σ- and a π-bond to the metal center. The reason for these differences between Tc and Re is unknown.[428]


R
NHNH2
[TcO4]-
P
Cl
Tc
N
R
(P = PPh3)
(321)
[TcO4]-
(P = PPh2)
(322)
(321)
Cl
Br
(P = PPh3)
(325)
HBr
HN
(326)
(P = PPh3)
(321)
(38)
Ph3P
O
(328)
H2NHN
[TcO4]-
bipy, MeOH
(332)

Scheme 49

Introduction of benzenthiolato ligands leads to dinuclear species. Thus, reaction of $[TcCl_3(NNHpy)(HNNpy)]$ (**339**) (see above) with thiophenol gave the dinuclear complex $[Tc(SPh)_2(NNHpy)(NNpy)]_2$ (**342**) in excellent yields. Two of the thiolato ligands bridge the two Tc centers, with one terminal thiolate on each metal. The hydrazinopyridine-derived ligands, as in the precursor, are η^2-(diazene) and η^1(diazenido) bound.[429] An even more complex compound is obtained by further reaction with 2-pyridinethiol. A monomeric complex is formed in which one terminal benzenethiolato ligand, one chelating 2-pyridinethiolate, one η^1-diazenido ligand, and one η^2 diazene ligand are coordinated to the metal, giving a six-coordinate species which has been structurally characterized.[430]

An unusual compound is formed when $[TcOCl_4]^-$ is reacted with $Me_3SiNPPh_3$ (tms-np,(**343**)) in CH_2Cl_2. The neutral, yellow Tc^V complex $[TcNCl_2(NHPPh_3)_2]$ (**344**) is formed in 50% yield. Complex (**344**) is a nice example of a phosphoraneimineato complex. The formation of a terminal nitrido ligand from a phosphoraneiminate is unexpected, since the reverse reaction, the synthesis of phosphoraneiminato complexes from nitrido complexes and phosphines, is common for a number of transition metals. The nitrido ligand is an electrophile only in high oxidation states, but not if the oxidation state is reduced. The X-ray structure was obtained showing trigonal-bipyramidal structure, with the two phosphoranimine ligands *trans* to each other.[431] Phosphoraneimine complexes of Tc are very rare and only one example has been described, obtained by thermolysis of the salt $[Ph_3PNH_2][TcO_4]$.[432,433] (Scheme 50).

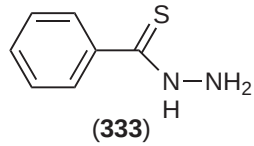
5.2.2.4 Oxidation State (IV)

Complexes of Tc^{IV} are relatively limited in number when compared to the neighboring oxidation states. Complexes in oxidation state +IV lie between those stabilized by π-donor ligands and those by π-acceptor ligands. Accordingly, carbonyl complexes in this oxidation state are unknown, as are complexes with terminal oxo or nitrido ligands. A frequent structural feature is the "$[Tc(\mu\text{-}O)_2Tc]^{4+}$" core. These coordination compounds virtually form their own class of Tc^{IV} complexes. The chemistry in water of this oxidation state is very limited. Tc^{IV} complexes which are water soluble tend to hydrolyze and to form $TcO_2 \cdot H_2O$, which is the most stable form of Tc^{IV}. This tendency can be suppressed only by the presence of hard, multidentate chelators such as edta and related polyamino-polycarboxylic acids. Usually, the complexes contain three unpaired electrons and the magnetic moments range between 3.5 B.M and 4.1 B.M. The dinuclear complexes, though, are in general diamagnetic, since the unpaired electrons participate in strong metal–metal triple bonds or there is a reduction in magnetic moment due to antiferromagnetic exchange between the metal centers.

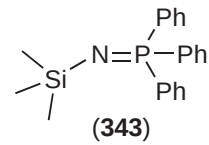
5.2.2.4.1 Halide and pseudohalide complexes

As mentioned earlier, chlorination of Tc metal with Cl_2 produces dark red $TcCl_4$ (**345**) as the major product.[92,434] The structure consists of polymeric chains in which the Tc centers are chloride bridged to give edge-sharing, distorted octahedra.[435] (**345**) is a possible starting material for Tc^{IV} chemistry, but because of the difficulty of its preparation it is rarely used. Reaction with Me_3SiBr exchanges the chloride for bromide and gives $TcBr_4$ (**346**). When black (**345**) or the mixture of $TcCl_4$ and Me_3SiBr is stirred in $NCCH_3$, yellow or red solutions are formed which contain the solvent species $[TcX_4(NCCH_3)_2]$ (**347**). The reaction of (**345**) in CH_2Cl_2 in the presence of 15-crown-5 afforded yellow-green crystals in 70% yield. An X-ray structure analysis confirmed that the crown is noncoordinating in this compound, but forms hydrogen bonds to an $[H_3O]^+$. The anion is six-coordinate $[TcCl_5(OH_2)]^-$ (**348**), in which the Tc—O distance is 2.08 Å.[436]

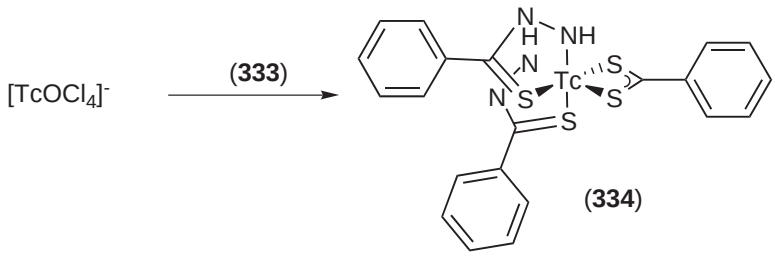
The most convenient starting materials for Tc^{IV} chemistry are the binary halide complexes $[TcX_6]^{2-}$ ($X = Cl^-$, (**69**); $X = Br^-$, (**71**); $X = I^-$, (**349**)) and less commonly $[TcO_4]^-$ or $[TcOCl_4]^-$. The complexes $[TcX_6]^{2-}$ are among the earliest compounds prepared in technetium chemistry. The complexes with $X = Cl^-$, Br^- and I^- can be prepared by several routes. The most convenient method consists of prolonged heating of $[TcO_4]^-$ under reflux in conc. HCl. Heating is required to ensure that the kinetic intermediate $[TcOCl_4]^-$ is completely converted to (**69**), which is then produced in quantitative yield.[434,437] An alternative procedure is reduction of $[TcO_4]^-$ in conc. HCl with KI. Recrystallization yields yellow crystals of $K_2[TcCl_6]$.[438,439] Reaction of $[TcO_4]^-$ in 11M HCl with KI as a reducing agent produces a red precipitate, which was shown to be (**349**). This complex is isostructural with (**69**).[440]



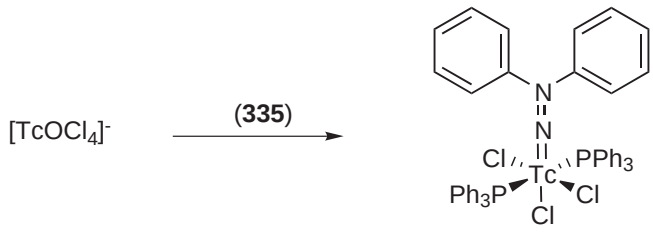
(**333**)



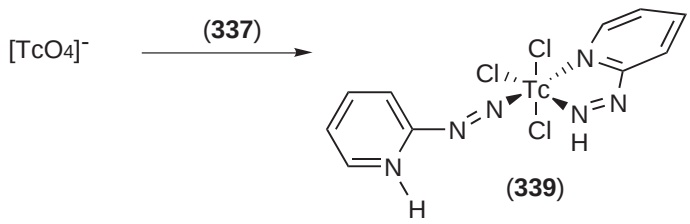
(**343**)



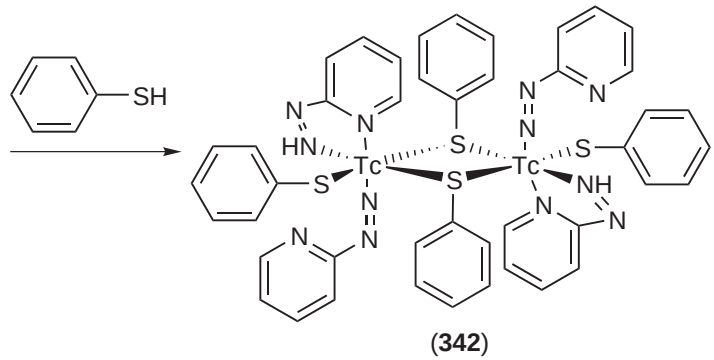
(**334**)



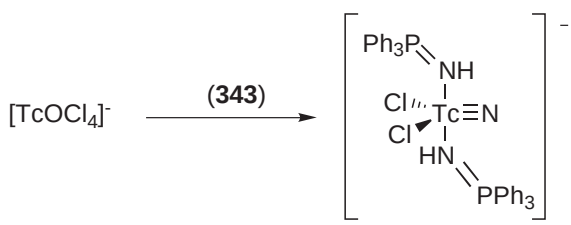
(**336**)



(**339**)



(**342**)



(**344**)

Scheme 50

The corresponding red species (**71**) is synthesized by the reaction of conc. HBr with $[TcO_4]^-$ or by ligand exchange of (**69**) with conc. HBr.[434,437,439] In the same way, deep purple $[TcI_6]^{2-}$ can be prepared by ligand exchange on $[TcX_6]^{2-}$ ($X = Cl^-$ or Br^-) with conc. HI or by the direct reaction of $[TcO_4]^-$ with dilute HI. In the presence of the appropriate cations, salts such as $Rb_2[TcI_6]$ can be obtained. Colorless $[TcF_6]^{2-}$ (**350**) is more difficult to prepare. Originally $K_2[TcF_6]$ was prepared by fusion of $K_2[TcBr_6]$ with excess KHF_2. After recrystallization, pale pink crystals of the pure complex are produced.[441] Alternatively, the reaction of $[TcF_6]$ in anhydrous HF with $[N_2H_6]F_2$ gave $[N_2H_6][TcF_6]$. The magnetic moment of this salt is 3.79 B.M., with a Weiss constant of $T = 52$ K.[182] A strong IR absorption at 545 cm^{-1} was assigned to ν_{Tc-F}. An alternative and high-yield route to (**350**) consists of the ligand-exchange reaction of (**71**) in 40% HF with AgF, with precipitation of AgBr during the exchange. A pale red compound formed in solution as an intermediate was tentatively identified as $[TcF_5(OH_2)]^-$, which is slowly substituted by a sixth fluoride ligand.[442] X-ray crystal structures are available for $[TcX_6]^{2-}$ with a number of counterions[443–445] for (**71**) and (**69**)[446] and for (**349**).[447]

The reactivity of the four hexahalogenotechnetate(IV) complexes is quite different. With the exception of (**350**), all the complexes readily undergo hydrolysis to brown-black precipitates of $TcO_2 \cdot H_2O$. $[TcF_6]^{2-}$, however, is resistant to hydrolysis. The ligand-field splittings for $[TcX_6]^{2-}$ are 28,400 cm^{-1} ($X = F^-$),[449] 24,400cm^{-1} ($X = Cl^-$),[450] 21,600 cm^{-1} ($X = Br^-$),[451] and 20,400 cm^{-1} ($X = I^-$).[452]

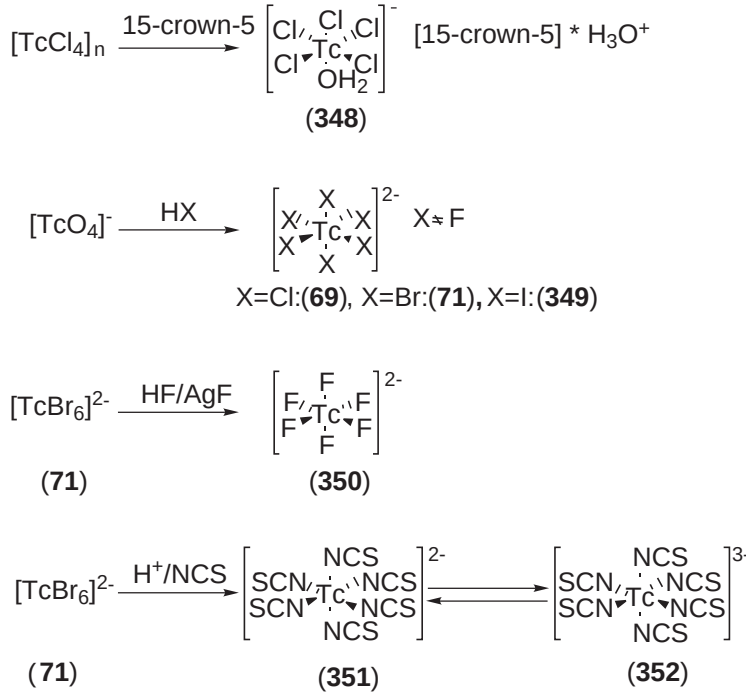
The cyclic voltammetry of these complexes reveals some interesting electrochemical properties. Due to the rapid hydrolysis of $[TcX_6]^{2-}$, electrochemical studies were performed in acetonitrile with $[NBu_4][BF_4]$ as support electrolyte. Irreversible oxidation waves were observed at +1.88 V ($X = Cl^-$) and +1.70 V vs. SCE for $X = Br^-$, respectively, and irreversible reductions occurred at −0.34 V and −0.27 V.[452] Spectroelectrochemical studies have been performed in acidic HX to suppress the irreversible formation of TcO_2. Under these conditions $[TcCl_6]^{2-}$ and $[TcBr_6]^{2-}$ undergo reversible electrochemical reductions. The experiments confirm the net reduction of Tc^{IV} to Tc^{III}. The halide ligands are considerably more labile on Tc^{III} than in the corresponding Tc^{IV} complexes, as shown by the strong dependence of redox potential on the X^- concentrations. This raises the possibility of preparing $[Tc(OH_2)_6]^{3+}$ electrochemically. This has not yet been achieved, but would merit more detailed investigation.[453]

A number of other partially hydrolyzed species have been described. The red species $K_2[TcCl_5(OH)]$ precipitates from solution during reduction of $K[TcO_4]$ by HCl/I[440] and yellow $Zn[TcCl_5(OH)]$ and $La_2[TcCl_5(OH)]_3$ are formed by reduction of the appropriate $[TcO_4]^-$ salts with HCl.[454,455] The chemistry in water is sometimes remarkably different for rhenium and technetium. For instance, the μ-oxo bridged rhenium(IV) complex $[\{ReBr_5(\mu\text{-}O)\}_2]$ is well established, but is unknown for Tc. On heating $[TcBr_6]^{2-}$ in CF_3COOH, dimeric $[Br_3Tc(\mu\text{-}Br)_3TcBr_3]^-$ is formed.[456]

In addition to the halogeno complexes of Tc^{IV}, complexes with isothiocyanate ligands are known and these complexes were used for many years for the quantitative spectroscopic determination of technetium.[457,458] A deep red-violet color is produced upon reaction of $[NCS]^-$ with $[TcO_4]^-$ in acidic solution, which was found to be the complex $[Tc(NCS)_6]^{2-}$ (**351**) ($\lambda_{max} = 500$ nm, $\varepsilon = 76{,}100$).[459,460] The same compound can also be prepared by ligand exchange, by the reaction of (**71**) with $[NCS]^-$ in MeOH under reflux. If $N_2H_4 \cdot H_2O$ is added to the reaction solution, the color changes immediately to deep yellow and the air-sensitive, yellow-orange Tc^{III} complex $[Tc(NCS)_6]^{3-}$ (**352**) forms. This compound shows a reversible, one-electron oxidation at +0.18 V vs. SCE. Reaction of (**352**) with either $(SCN)_2$ or NO gives (**351**) in quantitative yield. Voltametric studies with (**351**) show an irreversible oxidation wave at +1.6 V. Magnetic susceptibility measurements gave a magnetic moment of 4.1 B.M., consistent with a $^4A_{2g}$ ground state for this d^3 ion. The X-ray crystal structure of the Tc^{III} complex was determined and shows an almost perfect octahedral structure.[460] The X-ray crystal structure of the corresponding Tc^{IV} complex was elucidated some time later and the geometry again is octahedral, with the Tc^{IV} atom situated on a site of exact 4/m symmetry.[461] (Scheme 51)

5.2.2.5.2 Complexes with oxygen ligands

Mononuclear Tc^{IV} complexes with exclusively oxygen donor ligands are rare. In contrast to (**350**) and (**69**), (**71**) is very soluble in MeOH and the color of the solution changes gradually from dark red to almost colorless. The solution becomes very acidic which is interpreted in terms of the formation of methoxide complexes. Upon addition of $KOCH_3$ to the solution, pale greenish salts of composition $K_2[Tc(OCH_3)_6]$ (**353**) can be isolated. The complexes $[Tc(eg)_3]^{2-}$ (**354**) and $[Tc(butri)_2]^{2-}$ (**355**) (H_3butri = 1,2,4-butanetriol, (**356**)) are produced similarly. Reaction of (**71**)



Scheme 51

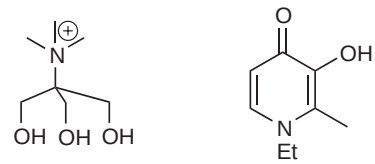
in methanol with the tripodal ligand tris(hydroxymethyl(trimethylammonium)methane iodide (H_3thmt, (**357**)) gave the structurally characterized zwitterionic complex [Tc(thmt)$_2$] (**358**), in which the trianionic core charge is compensated by two positive charges on the quaternary amines to give an overall neutral complex. This complex was reported to be stable in aqueous solution at pH > 4 for more than 24 h.[462]

Reaction of (**71**) with an aqueous solution of oxalic acid gives $[Tc(ox)_3]^{2-}$ (**359**) in good yield as pale yellow crystals. The use of oxalic acid, rather than a salt, was necessary in order to prevent the formation of TcO_2, as observed earlier in attempts to make this complex. In contrast to complexes of the form [Tc(L)$_3$], in which L represents a bidentate dithiolato ligand, (**359**) has a slightly distorted octahedral geometry. The twist angle between the triangular faces is 49°, which is close to that for optimal octahedral geometry.[128]

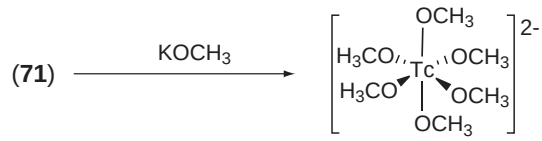
Another Tc^{IV} complex with exclusively oxygen donors is generated with N-substituted 3-hydroxy-4-pyridinone-based ligands such as 1-ethyl-2-methyl-3-hydroxy-4-pyridinone (Hmepp, (**360**)). The reaction of [NH_4][TcO_4] in EtOH/saline with (**360**) in the presence of $Na_2S_2O_4$ gives, after 16 h under reflux, the cationic complex $[Tc(mepp)_3]^+$ (**361**). This compound has also been prepared with ^{99m}Tc for radiopharmaceutical purposes. The compound shows two quasi-reversible waves at −0.74 V and +1.07 V vs. Ag/AgCl, which are tentatively assigned to the Tc^{IV}/Tc^{III} and Tc^{IV}/Tc^{V} couples. The large separation of the two redox waves indicates that the intermediate Tc^{IV} oxidation state is strongly stabilized by six O donors, and the conproportionation constant has been calculated to be 5.4×10^{30}.[463]

The reaction of acetylacetone (Hacac, (**362**)) with various Tc^{IV} starting materials yields complexes in different oxidation states, depending on the reaction conditions. The homoleptic Tc^{IV} complex $[Tc(acac)_3]^+$ (**363**) can be prepared by oxidation of [Tc(acac)$_3$] (**364**) with Fc^+.[464] The reaction of $[TcX_6]^{2-}$ or [$TcX_4(PPh_3)_2$] (**103**) with (**362**) yields various $[acac]^-$ complexes that could be isolated and characterized; examples are: [PPh_4][TcX_4(acac)] (**365**), [TcX_2(acac)$_2$] (**366**), and [$TcBr_3$(acac)(PPh_3)] (**367**).[465] The compounds are stable under acidic conditions, but are slowly hydrolyzed in base and obey the rate law $k[OH^-][TcX_2(acac)_2]$.[461]

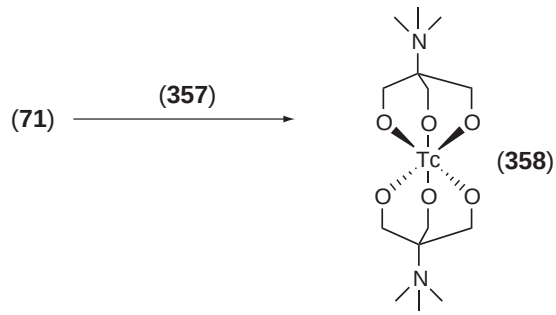
Somewhat analogous reactions occur with salicylaldehyde (Hsal, (**368**)). In (**368**) as a solvent for [PPh_4]$_2$[$TcCl_6$], the complex $[TcCl_4(sal)]^-$ (**369**) forms in good yield. The X-ray crystal structure confirms this formulation and the magnetic moment is 3.8 B.M.[466] The reaction of (**103**) with dmso gives [$TcCl_4$(dmso)$_2$] (**370**), in which the dmso is oxygen bound as concluded from spectroscopic data.[467] (Scheme 52).



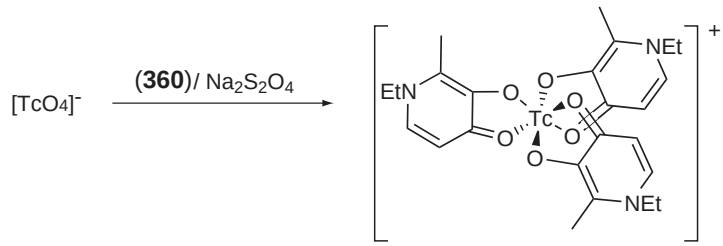
(**357**) (**360**)



(**71**)

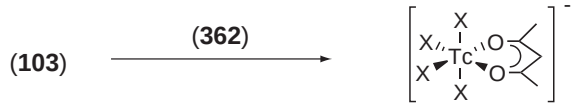


(**71**)



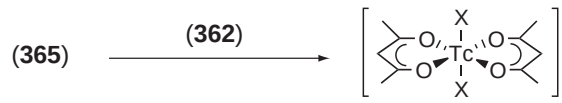
[TcO_4]$^-$

(**361**)



(**103**)

(**365**)



(**365**)

(**366**)

[$TcBr_4(PPh_3)_2$]

(**367**)

Scheme 52

5.2.2.4.3 Nitrogen ligands

Due to the high charge on the Tc^{IV} center, no homoleptic Tc^{IV} complexes containing exclusively nitrogen donors are known, and they are invariably combined with anionic donors such as halides or carboxylate. An early reaction was the direct combination of $TcCl_4$ (**345**) with bipy in EtOH to give the complex $[TcCl_2(bipy)_2]^{2+}$ (**371**), which precipitated out of the reaction solution after prolonged heating. Heating of $[TcCl_2(bipy)_2]Cl_2$ at 200 °C forms the thermodynamically favoured product $[TcCl_4(bipy)]$ (**372**).[189] Similarly, the pyridinium salt of (**69**) converts to $[TcCl_4(py)_2]$ (**373**) when heated to 300 °C under inert atmosphere to remove HCl. More directly, reaction of pyridine with $[TcCl_4(PPh_3)_2]$ in EtOH readily yielded (**373**), whereas prolonged heating forms the corresponding Tc^{III} complex mer-$[TcCl_3(py)_3]$ (**374**) in good yield. The reduction is caused by PPh_3, since a clear rate dependence on its concentration was found. Reaction with 4-methylpyridine or 3,5-dimethylpyridine proceeds analogously.[467] The complex (**373**) is described as being stable under both alkaline and acidic conditions. Its comparative insolubility in most of the common solvents is a surprising feature.[468]

The potential versatility of TcX_4 (X = Cl, Br) is shown in the reaction with acetonitrile, in which the polymeric structure is cleaved slowly and the complexes $[TcX_4(NCCH_3)_2]$ (**375**) are formed. Similar behavior is found for isocyanides, which form the neutral species $[TcX_4(CN\text{–}^tBu)_2]$ (**376**).[436]

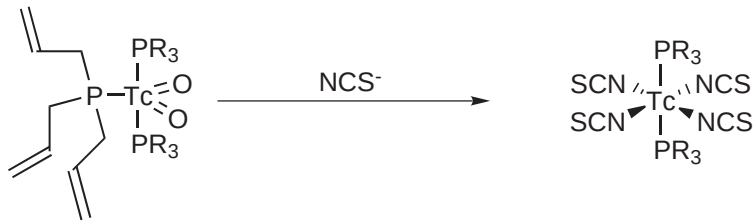
The Tc^V complex $[TcO_2(PC_3H_5)_3)_3]^+$ (**209**)[361] reacts with isothiocyanate in acidic MeOH/CH_2Cl_2 to give *trans*-$[Tc(NCS)_4(P(C_3H_5)_3)_2]$ (**377**). The *trans* configuration is deduced from ^1H NMR spectroscopy. Under slightly different reaction conditions or starting directly from $[TcO_4]^-$, a number of Tc^{II} complexes of the type $[Tc(NCS)_2(PR_3)_4]$ can be isolated and have been structurally characterized.[469]

Dinuclear asymmetric and μ-oxo-bridged complexes in which the two technetium atoms are in intimate electronic communication have been synthesized. The reaction of solutions of $[TcOCl_4]^-$ or $[TcCl_6]^{2-}$ with neat pyridines py-R (R = H, 2-Me, 3,5-Me_2) gave asymmetric complexes of the type $[Cl_2(py\text{-}R)_3Tc(\mu\text{-}O)TcCl_3(py\text{-}R)_2]$ (**378**), and disymmetric complexes $[Cl(py\text{-}R)_4Tc(\mu\text{-}O)TcCl_4(py\text{-}R)]$ (**379**) (R = 2-Me), which were prepared by direct reaction of $[TcO_4]^-$ with 2-methylpyridine with $NaBH_4$ as a reducing agent. All these mixed-valent species can also be obtained from other convenient starting materials, such as $[TcO_2(pic)_4]^+$, by heating under reflux in the appropriate neat pyridine. The complexes (**378**) and (**379**) (R = 2-Me) have been structurally characterized. They show an almost linear Tc—O—Tc bridging system. The mixed-valent, odd-electron compounds should exhibit a significant magnetic moment; however, because of strong antiferromagnetic coupling between molecules across the bridge, the magnetic moment is reduced. EPR spectra indicate that the single unpaired electron is located in a π-orbital involving both Tc and the bridging oxygen. Substantial π-bonding or strong antiferromagnetic coupling accounts for the pairing of the remaining 4*d* orbitals (Scheme 53)[470].

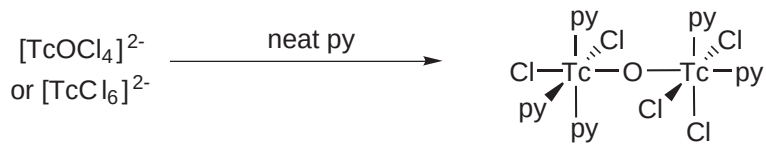
5.2.2.4.4 Sulfur ligands

Technetium(IV) complexes with pure sulfur donors are not very common, but the compounds with the ligands such as 1,2-dicyanoethenedithiol (H_2mnt, (**380**)) or benzene-1,2-dithiol (H_2bdt, (**63**)) are known. The reaction of $[TcBr_6]^{2-}$ in EtOH with three equivalents of (**380**) immediately gives a color change and the complex $[Tc(mnt)_3]^{2-}$ (**381**) can be precipitated in good yield by addition of $[AsPh_4]^+$. The structure of this complex is between trigonal prismatic and octahedral, as indicated by the corrected twist angle of 52°. The two triangular faces are almost parallel to one other.[373]

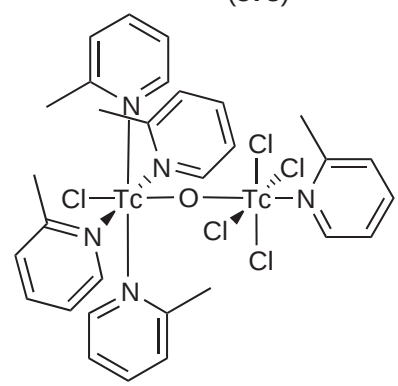
A number of reactions which give homoleptic Tc^{IV} sulfur-ligated complexes have been described, and occur by a concerted reduction/substitution mechanism from higher oxidation states. The reaction of $[TcOCl_4]^-$ with morpholino-dithiocarbamate (Hmodtc, (**382**)) results in reduction and loss of the oxo group and the unusual complex $[Tc(modtc)_4]$ (**383**) is produced.[471] The reaction of $[TcOCl_4]^-$ with 2-mercaptopyrimidine (Hmp, (**384**)) gives the structurally characterized complex $[TcCl_4(mp)]^-$ (**385**).[472] Direct reduction of $[TcO_4]^-$ with H_2bdt (**63**) forms a unique dinuclear species $[Tc_2(bdt)_4]$ (**386**). Each technetium center has trigonal-prismatic geometry with six sulfur donors, four of which are bridging the two Tc centers. Thus, two dithiolate ligands are terminal and two are bridging. The overall structure is best described as a rhombohedral prism. The Tc—Tc distance is 2.591(3) Å, which implies the possibility of a Tc—Tc multiple bond.[373,473] A similar complex has been described in Section 5.2.2.3.2. The complex $[Tc_2(edt)_4]$ (**225**), with the same overall geometry as $[Tc_2(bdt)_4]$, is available by reaction of (**69**) with Na_2[edt] (Scheme 54)[374].



(**209**) (**377**)



(**378**)



(**379**)

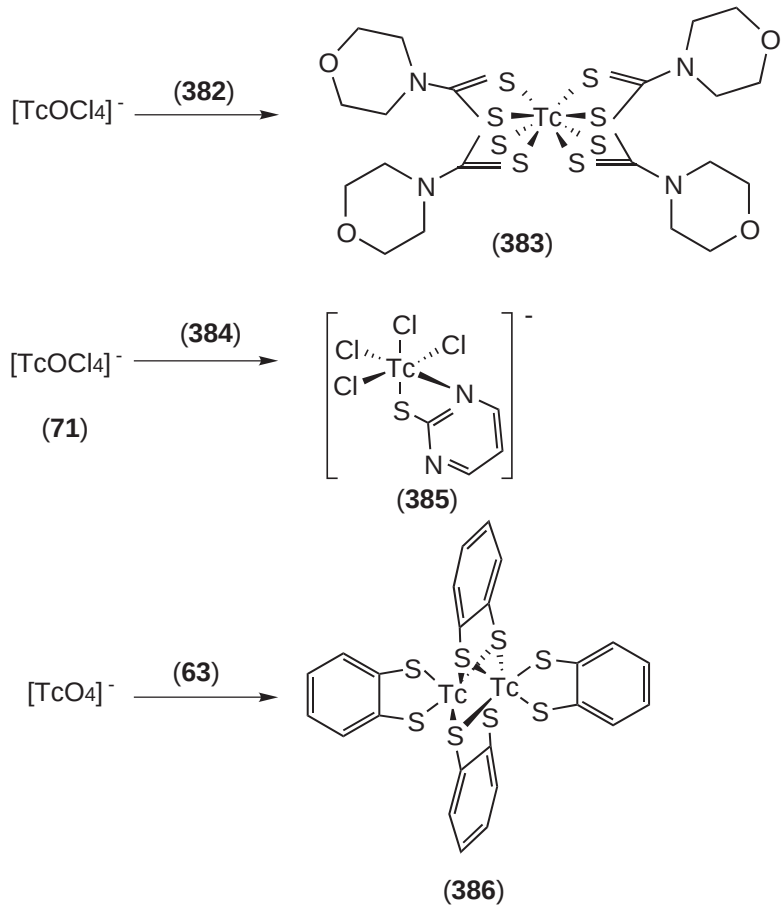
Scheme 53

5.2.2.4.5 Tertiary phosphine and arsine complexes

Mixed halide/tertiary phosphine complexes are important starting materials for Tc^{IV} chemistry. The two key compounds $[TcCl_4(PPh_3)_2]$ and $[TcCl_5(PPh_3)]^-$ can be obtained by the reaction of TcX_4 with the corresponding phosphine, or by direct reaction of $[TcO_4]^-$ with the phosphine in EtOH in the presence of HX.[474,475] A wide variety of such complexes have been described with X = Cl, Br, and different phosphine ligands PR_3. $[TcCl_4(PPh_3)_2]$ loses one phosphine ligand when reacted with HCl to yield $[TcCl_5(PPh_3)]^-$.[476] All the structurally characterized complexes have *trans* phosphine ligands.[476–480]

5.2.2.4.6 Mixed-donor-set polydentate ligands

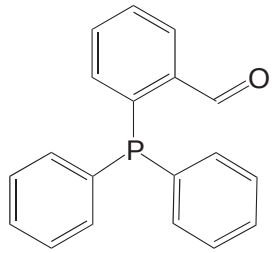
Technetium(IV) complexes of ligands with mixed donor sets are known, particularly with N,O and P,O ligands. A number of these are dinuclear and contain the "$[Tc(\mu\text{-}O)_2Tc]^{4+}$" group. An example of a mononuclear Tc^{IV} complex with a mixed P,O ligand is from the reaction of $[TcOCl_4]^-$ with the bidentate ligand *o*-(diphenylphosphino)benzaldehyde (dpb, (**387**)). At room temperature after 24 h, red-purple crystals of $[TcCl_2(Ph_2PCH(O)CH(O)CHPPh_2]$ (**388**) are obtained, in which a tetradentate P_2O_2 ligand is formed from the original bidentate PO system. Presumably the Tc center promotes the bimolecular reductive coupling of the two aldehydes to give the diolate system. The X-ray structure of this complex was determined and shows approximately octahedral geometry about Tc, with *cis*-chlorides which are each *trans* to a glycolato oxygen.[481]



Scheme 54

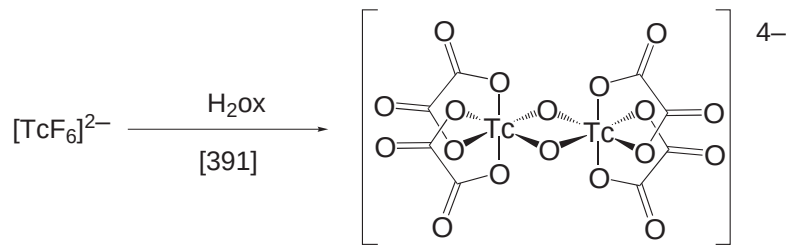
The nearly planar, four-membered ring of $[Tc(\mu\text{-}O)_2Tc]^{4+}$ is a structural feature that is sometimes found upon reaction of multidentate chelators with $[TcX_6]^{2-}$ directly in water. The first complex of this kind was prepared as red-brown crystals directly from $[TcO_4]^-$ in acidic solution and Na_2H_2edta (**389**), with $[HSO_3]^-$ as a reducing agent. An X-ray crystal structure was required to identify the complex unambiguously as $[(H_2edta)Tc(\mu\text{-}O)_2Tc(H_2edta)]$ (**390**). The Tc—Tc distance is very short at 2.33 Å, indicating a strong Tc—Tc interaction. An EHT calculation showed that the symmetry-matched *d* orbital is destabilized by the *p* orbitals of the bridging O ligands, and thus the normal orbital sequence for a metal—metal multiple bond is altered to $\sigma^2\pi^2\delta^2{*}\delta\pi{*}\sigma{*}$. This scheme explains the diamagnetism and the lengthening of the M—M bond from that expected for a triple bond, due to the occupation of antibonding orbitals.[161] With H_3nta (**391**), the complex $[(nta)Tc(\mu\text{-}O)_2Tc(nta)]^{2-}$ (**392**) was obtained by a similar synthetic procedure, and was also structurally characterized.[482] A variant on this procedure was chosen for the preparation of the corresponding oxalato complex $[(ox)_2Tc(\mu\text{-}O)_2Tc(ox)_2]^{4-}$ (**393**). The reaction of $[TcF_6]^{2-}$ for three days at 80 °C with oxalic acid gave the dimer complex (**393**) in 57% yield as dark red crystals. The color suggests a similar electronic structure to that proposed for the corresponding edta and nta complexes.[484]

A mixed-valent Tc^{III}/Tc^{IV} complex containing the $[Tc(\mu\text{-}O)_2Tc]^{4+}$ core has been prepared using 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate (H_3tcta, (**394**)). The reaction of $Na_2[TcO(eg)(tcta)]$ with $Na[BH_4]$ in water caused a color change from turquoise to deep golden, and then to blue. Column chromatographic separation gave the novel complex $[(tcta)Tc(\mu\text{-}O)_2Tc(tcta)]^{3-}$ (**395**), which has Tc^{III} and Tc^{IV} centers. Oxidation of this complex with $K_2[S_2O_8]$ gave the deep pink Tc^{IV}/Tc^{IV} complex $[(tcta)Tc(\mu\text{-}O)_2Tc(tcta)]^{2-}$ (**396**), which was precipitated as the Ba^{2+} salt. The structure of the Tc^{IV}/Tc^{IV} complex was determined by X-ray diffraction and confirmed the expected dimeric structure with the $[Tc(\mu\text{-}O)_2Tc]^{4+}$ core (Scheme 55)[484].



(**387**)

(**388**) (P = PPh_2)



(**393**)

Scheme 55

5.2.2.5 Oxidation State (III)

Complexes of technetium in the oxidation state +III are the second most numerous class of technetium complexes. The reason for this lies not only in the availability of convenient starting materials, but also in the fact that +III represents a reasonably stable oxidation state. Many cationic Tc^{III} complexes are water- and air stable, which makes them attractive candidates for radiopharmaceutical applications. However, no hexaquo-cation or other solvated Tc^{3+} cations have been described so far. The oxidation state +III can conveniently be achieved by reduction and stabilization with appropriate ligands. Since the Tc^{III} center with its d^4 electronic configuration is of more pronounced b-character, most of the fully characterized complexes are stabilized by ligands such as phosphines, arsines, and isocyanides. Tc^{III} is also the oxidation state in which organometallic complexes start to play an important role, and complexes with CO, isocyanides, or carbenes have all been described. In general, the structures are distorted octahedral, but the d^4 configuration allows expansion of the coordination number to seven, giving an 18-electron complex. Indeed, most of the seven-coordinate Tc complexes with cyanide are in oxidation state +III. In contrast to Re, Tc complexes containing the equivalent of the Re_3 triangular core are rare and no such complex has yet been described. Typical organometallic complexes in the oxidation state +III and lower will not be discussed here, except where reactions take place at the coordinated ligands. Two complexes containing Tc—C bonds will be covered, however, since they represent a fundamental class of Tc^{III} complexes.

The classical homoleptic cyanido complex of Tc^{III}, the seven-coordinate, yellow-orange complex $[Tc(CN)_7]^{4-}$ (**397**), is formed from $[TcI_6]^{2-}$ and an aqueous KCN solution after 24 h of heating under reflux. Careful exclusion of O_2 is required, otherwise appreciable amounts of cyano complexes in higher oxidation states are formed. The iodide acts as a reducing agent, since the

reaction of TcO_2 with cyanide gives the Tc^V compound $[TcO(CN)_5]^{2-}$. The reaction of $[TcO_2(py)_4]^+$ with cyanide produces $[TcO_2(CN)_5]^{2-}$. The ν(CN) IR bands in the Tc^{III} complex are at 2,089 cm^{-1} and 2,046 cm^{-1}, respectively. From IR and Raman spectroscopy it was possible to predict the structure to be pentagonal bipyramidal, which is in agreement with the X-ray crystal structure of the rhenium analogue.[368]

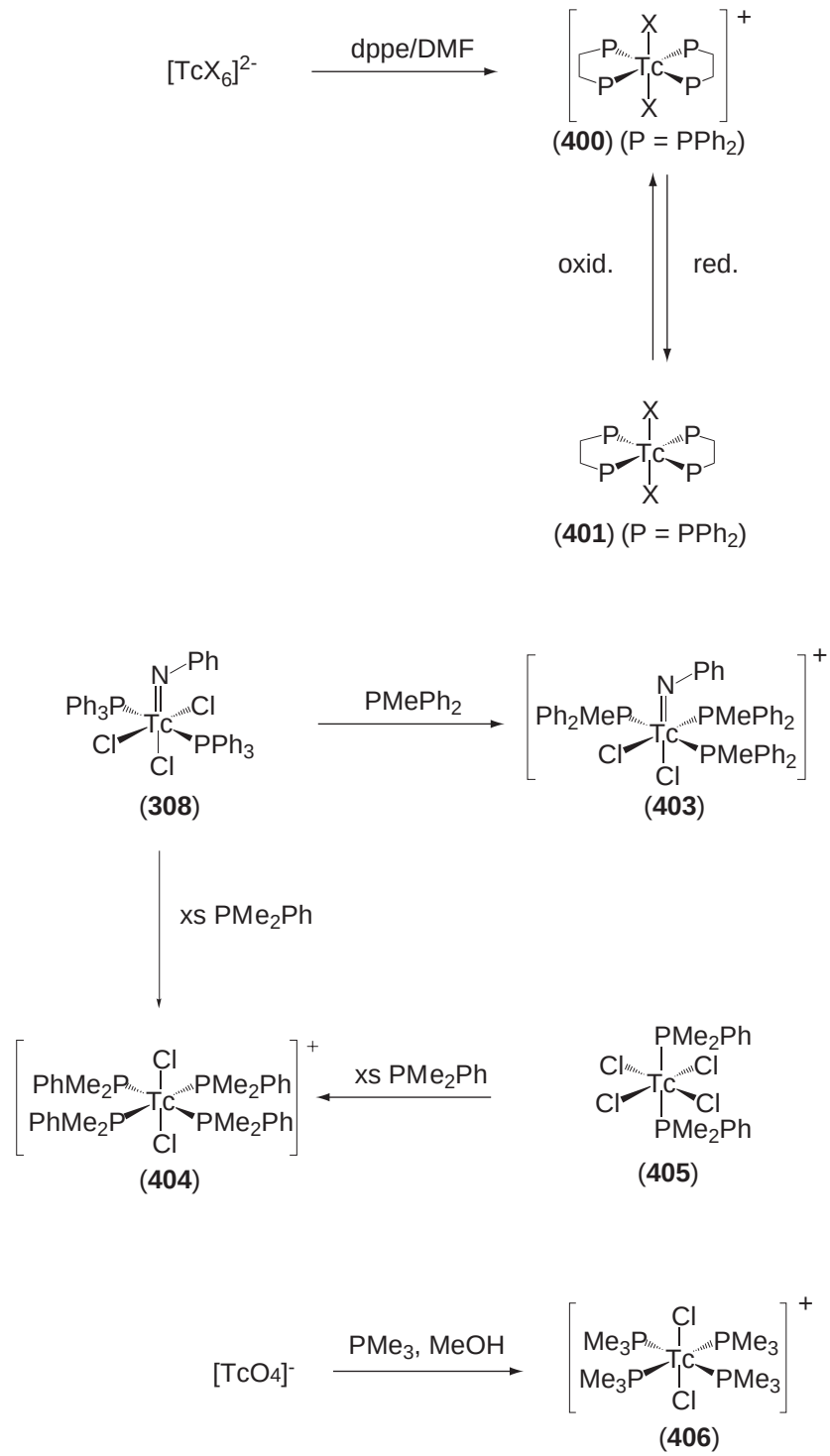
Another type of complex in which Tc—C bonds predominate is the seven-coordinate complex $[Tc(CNR)_6X]^{2+}$ (**398**) (R = variety of organic groups; X = Cl, Br). The compounds are easily prepared in good yield by reaction of the Tc^I complex $[Tc(CNR)_6]^+$[485] with Br_2 or Cl_2 in acetonitrile. Attempts to introduce a bipy ligand as well led to dealkylation of the isocyanide to give the seven-coordinate complex $[Tc(CNR)_5(CN)X]^+$ (**399**). Reductive coupling of the coordinated isocyanides was attempted, but the reduction of Tc^{III} to Tc^I was the only reaction.[486]

5.2.2.5.1 Tertiary phosphine and arsine ligands

Complexes with tertiary phosphines and arsines are ubiquitous in Tc^{III} chemistry. In general, the complexes comprise a maximum of four neutral phosphorus donors in combination with other anionic ligands. An important class are complexes of the general type $[Tc(PP)_2X_2]^+$, which can be prepared by several routes. The major interest in these compounds arose from the early observation that these cations accumulate in the myocardia of animals, and therefore show promise as heart-imaging agents with ^{99m}Tc. However, it turned out that there was no retention of these types of complex in the heart in humans, probably due to reduction of Tc^{III} to Tc^{II}. One synthetic route involves reaction of (**69**) in hot DMF in the presence of diphosphines such as dppe, dppb, depe, or dmpe. After several hours, reduction and substitution took place to afford the compounds $[Tc(PP)_2X_2]^+$ (**400**) in yields ranging from 30% to 60%. The compounds were purified chromatographically. A second method consists of the oxidation of the corresponding Tc^{II} complexes $[TcCl_2(dppe)_2]$ (**401**) with the appropriate halogens Cl_2 or Br_2 in $CHCl_3$ or CCl_4.[258] Alternatively, and more appropriately for radiopharmaceutical applications, the complexes can be prepared directly from $[TcO_4]^-$ in DMF in the presence of excess diphosphine ligand. The X-ray crystal structure of $[TcBr_2(dppe)_2]Br$ was determined and shows the expected *trans* configuration. Interestingly, the complex $[TcBr_2(dppe)_2]Br$ can be prepared by at least three different pathways, which indicates that this complex is very thermodynamically favoured. More forcing reaction conditions starting from Tc^{IV} or Tc^{VII} lead to the Tc^{II} complexes (**401**). Complexes of diarsines were prepared in the same way. The halides in the complexes can be substituted by other anions such as $[NCS]^-$. Interestingly, attempts to substitute the halides with $[CN]^-$ or $[N_3]^-$ caused its reduction to the divalent state, with no substitution occurring. The complexes exhibit a rich electrochemistry. The Tc^{III}/Tc^{II} and the Tc^{II}/Tc^I redox couples are fully reversible, and the potentials depend strongly on the coordinated anions and the type of diphosphine. The reduction potential for $[Tc(SCN)_2(dppe)_2]^{+/0}$ is +0.39 V vs. Ag/AgCl, whereas the same couple for $[TcCl_2(depe)_2]^{+/0}$ is −0.252 V. A linear relationship between E° and the energy of the halogen to technetium charge-transfer bands was found. The reduction of the diphos complexes is between 50 mV and 100 mV less negative compared to the analogous diars complexes.[258,487] A number of combined electrochemical and spectroelectrochemical studies have been performed on these complexes in various media and comparisons made with the corresponding rhenium compounds.[488–491] A linear relationship between the rhenium and the technetium complexes was shown for the M^{III}/M^{II} and M^{II}/M^I couples. A slope of about 1.04 mV and the intercept of 219 mV provide the average potential difference between analogous rhenium and technetium complexes.[491]

This chemistry has been extended to include complexes of monodentate phosphines. Compounds of the general type $[TcX_2(PR_3)_4]^+$ were obtained during attempts to find a new synthesis for $[TcCl_3(NPh)(PPh_3)_2]$ (**308**) (see Section 5.2.2.3.4) with less bulky phosphines. The reaction of $[TcO_4]^-$ with PPh_3, HCl and (**309**) gives (**308**).[414] A similar reaction with $PMePh_2$ instead of PPh_3 under the same conditions gave $[Tc(NPh)X_2(PMePh_2)_3]^+$ (**403**), as expected. For the less bulkier PMe_2Ph the organodiazenido complex $[Tc(NNPh)Br_3(PMe_2Ph)_2]$ (**402**) formed in 30% yield, together with the imido complex $[Tc(NPh)X_2(PMe_2Ph)_3]^+$ under the same conditions.[420] The latter complex has also been produced by ligand exchange of $[Tc(NPh)Cl_3(PPh_3)_2]$ with PMe_2Ph.[418] The access to $[TcX_2(PR_3)_4]^+$ resulted from studies to introduce even smaller phosphines, such as PMe_3. Attempts to exchange PPh_3 in (**308**) with PMe_2Ph or PR_3 (R = -Et, -Me) gave *trans*-$[TcX_2(PMe_2Ph)_4]^+$ (**404**). When the starting material $[TcCl_4(PMe_2Ph)_2]$ (**405**) (see Section 5.2.2.4.5) was treated with excess phosphine, (**404**) was produced in good yield. The complex *trans*-$[TcX_2(PMe_3)_4]^+$ (**406**) is also prepared as a yellow-orange precipitate by the same method, or alternatively by the direct reaction

of $[TcO_4]^-$ with PMe_3 in methanol after overnight reflux. The Tc^{III} complexes with both PMe_3 or PMe_2Ph are also available by reaction of excess PR_3 with $[TcCl_4(PR_3)_2]$ or $[TcCl_3(PR_3)_3]$. The structures of both (**406**) and (**404**) have been elucidated, showing all the chloride in mutual *trans* orientation.[492] These complexes with monodentate phosphine ligands are versatile starting materials for the development of Tc^{III} chemistry. (Scheme 56)



Scheme 56

Tc^{III} complexes with fewer than four phosphines are quite prominent as starting materials. It was found as early as 1976 that the reaction of $[TcO_4]^-$ with PMe_2Ph in the presence of HCl gave $[TcCl_3(PMe_2Ph)_3]$ (**407**) in good yield.[493] There is a *mer-mer* arrangement of ligands around the Tc, with a significantly longer Tc—Cl bond *trans* to P than *trans* to Cl. The reaction of $[TcOCl_4]^-$ with PMe_3 in acetonitrile gives $[TcCl_3(PMe_3)_3]$ (**408**), which also has *mer* conformation.[494] For (**407**) the coordination number can be increased to seven by reaction with small π-acceptor molecules such as CO. By bubbling CO through a solution of $[TcCl_3(PMe_2Ph)_3]$, one CO binds to produce the 18-electron complex $[TcCl_3(CO)(PMe_2Ph)_3]$ (**409**). This complex has approximately C_{3v} symmetry, with the C_3 axis lying along the Tc—C—O bonds, and can be described as having capped octahedral geometry.[495] The same complex is also formed from $[TcCl(CO)_2(PMe_2Ph)_3]$ (**410**) after prolonged stirring in $CHCl_3$ at room temperature.[496]

Attempts to prepare the analogous products with PPh_3 and $[TcOCl_4]^-$ in MeOH fail, probably due to the bulk of the phosphine, but the interesting complex $[TcCl_3(PPh_3)_2(DMF)]$ (**411**) is formed from the same reaction in DMF. The X-ray crystal structure showed that the phosphines are *trans* and that the DMF is coordinated via oxygen.[497] The same reaction in acetonitrile gives the related complex $[TcCl_3(PPh_3)_2(NCCH_3)]$ (**412**) and this compound can also be prepared by the reduction of $[TcCl_4(PPh_3)_2]$ with Zn metal in acetonitrile.[498,499] The complex precipitates as a bright orange powder directly from the solution and has a potentially rich chemistry. Reaction with CO replaces CH_3CN to yield the six-coordinate complex $[TcCl_3(PPh_3)_2(CO)]$ (**413**), which was structurally characterized.[500] There is no evidence for a seven-coordinate species. The ν(CO) is relatively high at 2,054 cm^{-1}, indicating minimal π-backbonding. Although seven-coordinate dicarbonyl complexes could be expected, no evidence for such a complex was found despite the existence of $[TcCl_3(CO)(PMe_2Ph)_3]$. This is probably due to the higher basicity of PMe_2Ph over PPh_3, which does not sufficiently enhance the electron density at the Tc^{III} center to stabilize a second strongly π-accepting ligand. With NO and (**412**), the complex $[TcCl_3(PPh_3)_2(NO)]$ (**414**) is formed as a green powder. The change in the formal oxidation state to Tc^{II} and the presence of one unpaired electron is verified by a ten-line esr pattern. The NO IR stretching frequency of 1,805 cm^{-1} is consistent with a linear, terminally bound NO ligand.[500]

5.2.2.5.2 Nitrogen and oxygen ligands

Many compounds are known which contain both nitrogen and additional donors such as monoanionic sulfur or oxygen, neutral phosphines, or combinations of these. There are few examples of complexes containing nitrogen and halide ligands only. Complexes of the general composition $[TcCl_3(Nhet)_3]$, where Nhet is an aromatic heterocycle, can be prepared by a variety of routes. Reaction of $[TcOCl_4]^-$ with 4-picoline (pic) using PPh_3 as a reducing agent gives $[TcCl_3(pic)_3]$ (**415**) in moderate yield as a yellow powder, and the corresponding pyridine complex $[TcCl_3(py)_3]$ (**374**) (see Section 5.2.2.4.3) can be prepared in the same way.[467] The X-ray crystal structure shows a meridional configuration for the three pic ligands. When PMe_2Ph was used as a reducing agent, the complex $[TcCl_3(PMe_2Ph)_2(pic)]$ (**416**) was produced. If a large excess of reducing agent is used, the mixed-valence species [Cl(pic)$_4$Tc—O—TcCl$_4$(pic)] (**379**) is formed (see Section 5.2.2.4.3). Electrochemical studies showed reversible reductions at −0.6 V (TcIII/TcII) and −1.74 V (Tc^{II}/Tc^{I}), respectively, for the pic complex.[501] Complexes of type (**379**) were also obtained by reaction of $[TcCl_4(PPh_3)_2]$ with a variety of heterocyclic amines in the presence of PPh_3 as reducing agent. The meridional geometry was concluded from ^{1}H NMR signals that are contact shifted due to the paramagnetism.[467]

The versatility of (**412**) as a starting material for accessing new, low-valent complexes of Tc is impressively demonstrated by its reactions with pyridine, tetramethylethylenediamine (tmeda, (**417**)), 4,4′-dimethyl-bipyridine (Me_2bipy), and terpyridine (terpy) in 1,2-dimethoxyethane. Orange-yellow $[TcCl_2(PPh_3)(py)_3]^+$ (**418**), purple $[TcCl_2(Me_2bpy)_2]^+$ (**419**), yellow $[TcCl_3(PPh_3)(tmeda)]$ (**420**), and black-green $[TcCl_3(terpy)]$ (**421**) are formed in good to quantitative yields. For the cationic compounds, one halide was precipitated with Tl^+. Reaction of (**418**) with neat pyridine substitutes PPh_3 and *trans*-$[TcCl_2(py)_4]^+$ (**422**) is formed. The structure of the complex *trans*-$[TcCl_2(py)_3(PPh_3)]^+$ has been elucidated. Substitution of the phosphines and halide ligand occurs much more easily for Tc than for the Re analogues.[502] Electrochemical data suggest that the synthesis of lower-valent analogues is possible, and that low-valent oxidation states of Tc can be stabilized with pyridine. Corresponding Tc^{II} and Tc^{I} complexes have indeed been prepared by Zn^0 reduction in neat aromatic amines (see Section 5.2.2.6.1).

Dinuclear μ-oxo complexes of Tc^{III} with aromatic amines have also been prepared. The reaction of $[TcOBr_4]^-$ in dmf with bipy gives, after 6–8 h heating under reflux, the complex $[\{TcBr(bipy)_2\}_2(\mu\text{-}O)]^{2+}$ (**423**) as purple crystals. Analogous complexes with phen or chloride were prepared similarly. The phen complex crystallizes with 6 to 9 waters of crystallisation. When $[\{TcCl(bipy)_2\}_2(\mu\text{-}O)]^{2+}$ (**423**) is eluted from an anion-exchange column in water, chloride is exchanged for $[OH]^-$ and $[\{Tc(OH)(bipy)_2\}_2(\mu\text{-}O)]^{2+}$ (**424**) is produced as an orange solid. The structures of $[\{TcBr(bipy)_2\}_2(\mu\text{-}O)]^{2+}$ and $[\{TcCl(phen)_2\}_2(\mu\text{-}O)]^{2+}$ were determined. The Tc—O—Tc axis is almost linear and the average Tc—O distance is 1.824(5) Å, intermediate between a double and a single bond, indicating significant π-bonding between the Tc atoms.[503]

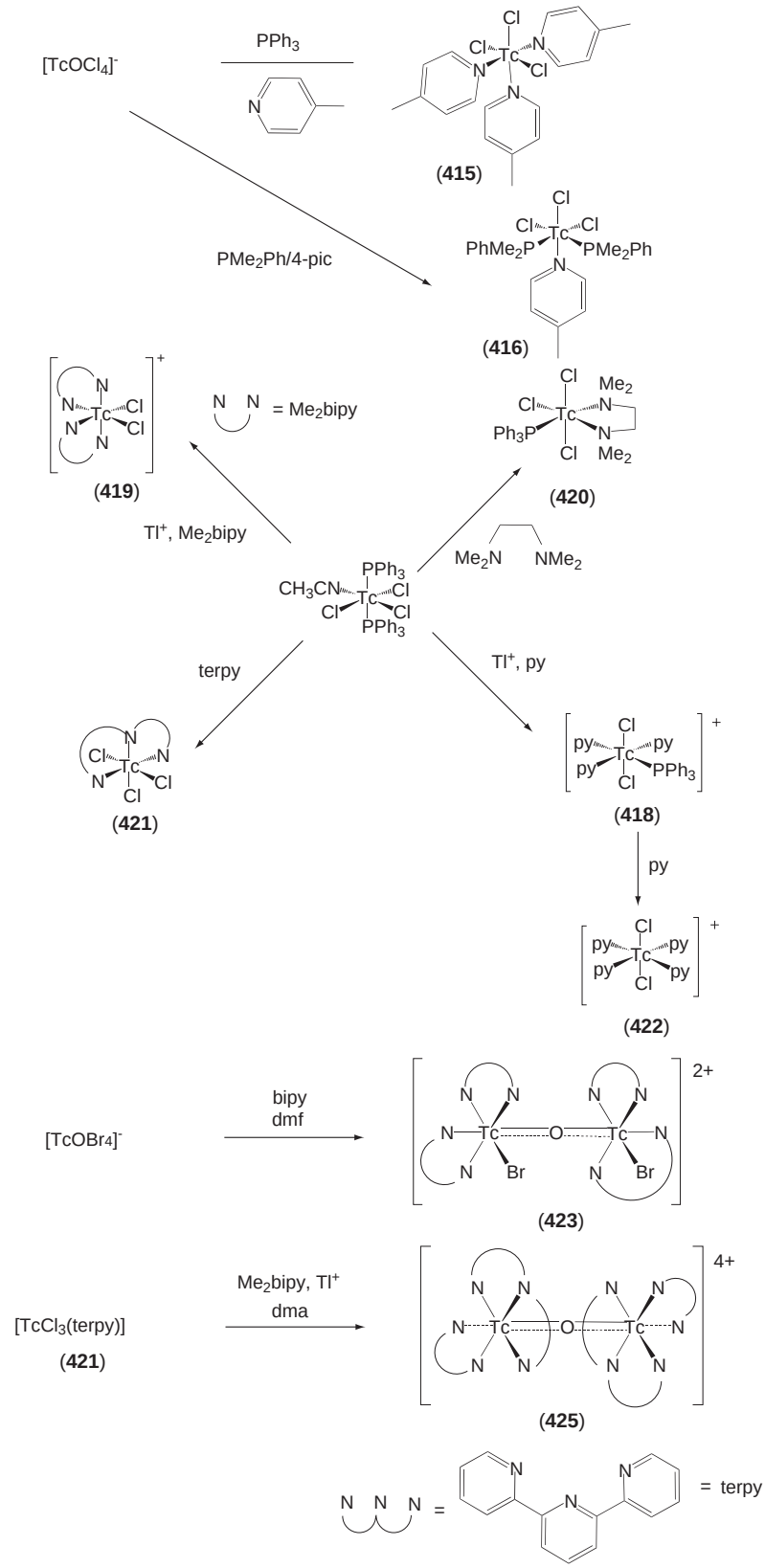
A similar complex $[\{Tc(terpy)(Me_2bipy)\}_2(\mu\text{-}O)]^{4+}$ (**425**) can be prepared as a purple solid in 45% yield from the reaction of (**421**) with TlO_2CCF_3 and Me_2bipy. Reduction with Zn dust in acetone gives the corresponding Tc^{II} complex $[\{Tc(terpy)(bipy)\}_2(\mu\text{-}O)]^{2+}$ (**426**) in 82% yield. The X-ray crystal structure of the Tc^{III} complex shows two identical N_5O coordination cores rotated by about 90° to each other. The Tc—O—Tc bond angle of 171.3° is almost identical to the complex described above. Cyclic voltammetry shows two reversible, one-electron reductions at −0.14 V and −0.39 V. The separation of the two couples by 0.25 V indicates that, unlike other oxo-bridged binuclear complexes, the two Tc atoms are not strongly coupled and the reductions occur in orbitals which are located to a significant extent on the Tc centres (Scheme 57)[504].

The reaction of (**407**) in refluxing ethanol with bidentate heterocyclic amines such as bipy or phen gives $[TcCl_2(bipy)(PMe_2Ph)_2]^+$ (**427**). As a consequence of the *trans* effect, the remaining chlorides are *cis*. The Cl *trans* to phosphorus and one additional phosphine have been substituted regioselectively. Analogous behavior occurs for PEt_2Ph and phen.[505]

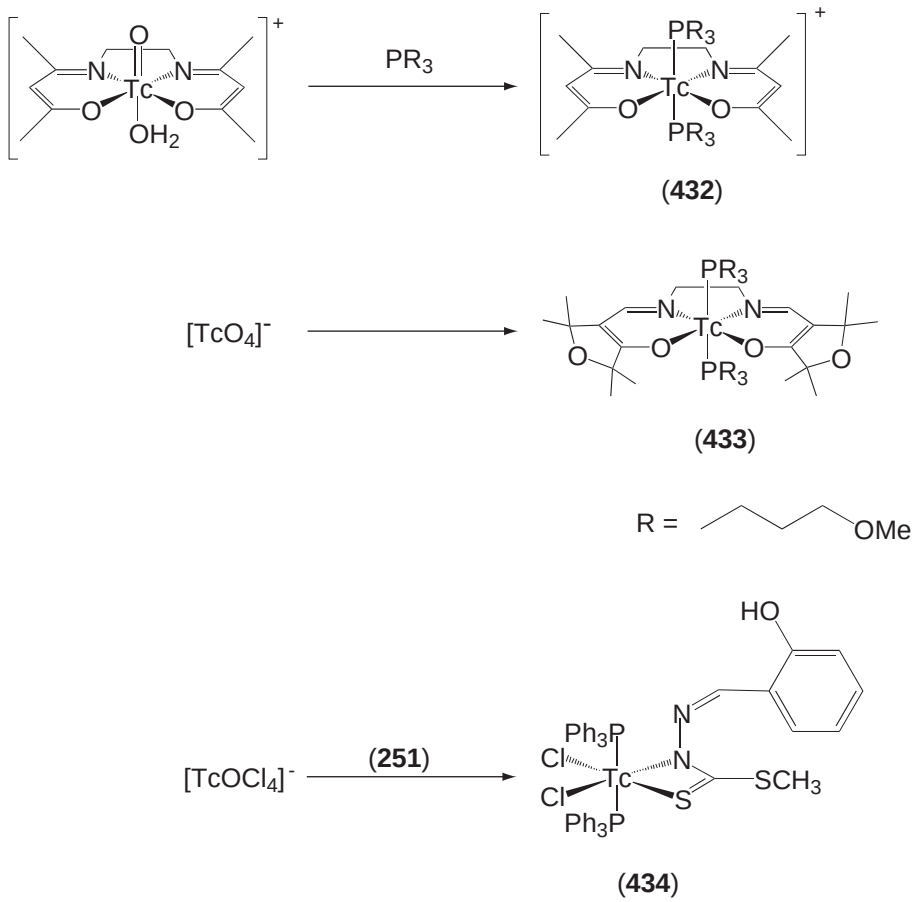
Attempts to prepare heterocyclic diamine complexes starting from the Tc^{IV} complex $[TcCl_4(PPh_3)_2]$ give only low yields of $[TcCl_3(bipy)(PPh_3)]$ (**428**). However, bipy complexes in other, lower oxidation states are also produced and are discussed in Section 6.6.1. When *mer*-$[TcCl_3(PMe_2Ph)_3]$ reacts in a nonpolar solvent such as toluene with bipy, phen, or bipyrimidine, it gives the neutral complexes *fac*-$[TcCl_3(PMe_2Ph)(NN)]$ (**429**) (NN = heterocyclic diamine). Reaction in a polar solvent, though, gives the cationic compounds $[TcCl_2(PMe_2Ph)_2(NN)]^+$ (**430**) in good yields. Depending on the solvent, different isomers are formed. These compounds have also been produced directly from $[TcO_4]^-$ and the appropriate diamine, using excess PMe_2Ph as a reducing agent. Longer refluxing times afford considerable amounts of the Tc^{II} complexes $[TcCl_2(PMe_2Ph)_2(NN)]$. The X-ray structure of $[TcCl_3(PMe_2Ph)(bipy)]$ confirmed the *fac*-geometry. The bipy ligand is *trans* to both chloride ligands.[467]

Tc^{III} complexes with Schiff-base-type ligands have been prepared by two different synthetic strategies. The Tc^V precursor $[TcO(\{acac\}_2en)(OH_2)]^+$ (**431**) reacts with three equivalents of various phosphines to give $[Tc(\{acac\}_2en)(PR_3)_2]^+$ (**432**) in very good yield. Alternatively, reaction of $[TcO_4]^-$ with the Schiff-base ligands (**141a**) or (**141b**) and phosphines produces the same compound, albeit in lower yields. The X-ray crystal structure shows the two phosphines to be *trans*. In the mechanism proposed, the first phosphine coordinates to the Tc^V center *trans* to the oxo group and a second reduces the Tc^V center, producing a phosphinoxide ligand which is then replaced by phosphine.[506] Other Schiff-base ligands have also been investigated. Extended spectroelectrochemical studies with these complexes have been performed.[489] Complexes with substituted $(acac)_2en$ ligands are of interest in the context of the search for new myocardial imaging agents. Variation of the substituents in the tetradentate ligand, as well as the phosphines, has been systematically studied and gives the series of "Q-compounds". Q12 has shown promise as a myocardial imaging agent.[506–509] Compounds of the general type $[Tc(N_2O_2)(PR_3)_2]^+$ are prepared for radiopharmaceutical applications as described above, or directly from $[^{99m}TcO_4]^-$ with Sn^{II} tartrate as a reducing agent. The structure of Q12 (**433**) is shown in Section 5.2.3.1.1.[510]

A range of complexes with tridentate, Schiff-base-type ligands (HNSO) such as (**251**), derived from *S*-methyl-dithiocarbazate, have been prepared (see also Section 5.2.2.3.3(ii)). This is illustrated by the two ligands *S*-methyl-3-(2′-hydroxy-1-naphthylmethylene)-dithiocarbazate (S^1dtca) and *S*-methyl-3-(2′-hydroxybenzylidene)-dithiocarbazate (S^2dtca), which react with $[TcOCl_4]^-$ to give the dark red and structurally characterized Tc^V complexes $[TcOCl(S^1dtca)]$ and $[TcOCl(S^2dtca)]$, respectively. These complexes are square pyramidal as expected, with doubly deprotonated tridentate ligands. The reaction with $[TcOCl_4]^-$ in the presence of the ligand (**251**), PPh_3, and HCl gave the dark red Tc^{III} complexes $[TcCl_2(S^1dtca)(PPh_3)_2]$ (**434**) in good yields. Not surprisingly, all attempts to reduce the Tc^V complex to Tc^{III} with PPh_3 as reductant gave no reaction, even under harsh conditions, demonstrating the excellent stability of the Tc^V complexes. The structure of the Tc^{III} complex shows bidentate coordination through N and deprotonated S, while the phenolic hydroxy group remains uncoordinated. The phosphines are *trans* (Scheme 58)[385].


[TcOCl4]-
PPh3
(415)
PMe2Ph/4-pic
(416)
(419)
N N = Me2bipy
(420)
Tl+, Me2bipy
Me2N NMe2
PPh3
CH3CN
Cl
Cl
PPh3
terpy
Tl+, py
(421)
(418)
py
(422)
[TcOBr4]-
bipy
dmf
2+
(423)
[TcCl3(terpy)]
(421)
Me2bipy, Tl+
dma
4+
(425)
N N N =
= terpy

Scheme 57



Scheme 58

A novel type of seven-coordinated Tc^{III} complex is obtained when dimethylglyoxime (Hdmg, (**435**)), in the presence of a boronic acid derivative such as an alkylboronic acid, is reacted with $[TcO_4]^-$ in the presence of Sn^{II} as a reducing agent. Alternatively, direct reduction/substitution from (**69**) or $[TcOCl_4]^-$ can be used. This produces red to orange tris-(dioximato) compounds of the type $[TcCl(dmg)_3(BR)]$ (**436**), with various R groups which are capped at one end by the boronic acid. These are abbreviated as BATO complexes (boron acid adducts of technetium dioximes). A chloride (or other monodentate anion) completes the coordination sphere. The single, hexadentate ligand consists of three bidentate dioxime groups joined through three covalent B—O bonds to a tetrahedral boron cap derived from methyl or butyl boronic acid. The six ligating nitrogen atoms form a distorted trigonal prism, with the two planes being almost parallel to each other. Distortion from the perfect prism arises from the presence of the seventh chloride ligand. This chloride is labile, as predicted by X-ray photoelectron spectroscopy, and can readily be exchanged for hydroxide or other mono-anions. The synthesis of a bis-capped complex by removal of the chloride as AgCl was not successful. The same type of BATO complex can also be synthesized with other diones, such as cyclohexanedione-dioxime (Hcdo, (**437**)).[511] These complexes are highly lipophilic and of potential use in radiopharmacy for imaging heart and brain perfusion. That the synthesis of these BATO complexes is probably templated is shown by preparation of the precursor $[TcCl(dmg)_3]$ (**438**) and its reaction with an alkyl boronic acid. Reaction of $[TcO_4]^-$ in the presence of Sn^{II} gives the complexes $[Tc(dioxime)_3(\mu\text{-}OH)(SnCl_3)]$ (**439**) in 97% yield. Here the seventh site is occupied by a hydroxy ligand that bridges to Sn^{IV}. The Sn^{IV} is hexacoordinate and bound to three chlorides and to two oxygens from two of the three dioxime ligands. Acidification of (**439**) with HCl removes the Sn cap to give the deep red-orange, seven-coordinate complex (**438**), which was also prepared directly from $[TcO_4]^-$ and (**435**) with PPh_3 as reducing agent. The ligand geometry around the Tc center is very similar to that with a boron cap. As in the BATO structure(s) there are two equivalent and one unique dioxime ligands,

which lie in a paddle-wheel array about the Tc. $[TcCl(dmg)_3]$ reacts rapidly with boronic acid to form the Tc^{III} BATO complexes (**436**). No bis capping was possible.[512] An unusual boron-capped Tc^{III} mixed imine-oxime complex has been produced from the reaction of $[TcCl_3(PPh_3)_2(NCCH_3)]$ with Hdmg and ethylboronic acid. This gives the red-violet complex $[TcCl(dmg)_2(bdi)(BR)]$ (bdi = butane-2,3-dione imine-oxime) in low yield. This synthesis is general and has been used to prepare several complexes with mixed imine-oxime ligands. It seems that the imine-oxime ligand is generated by reduction of Hdmg prior to coordination.[513]

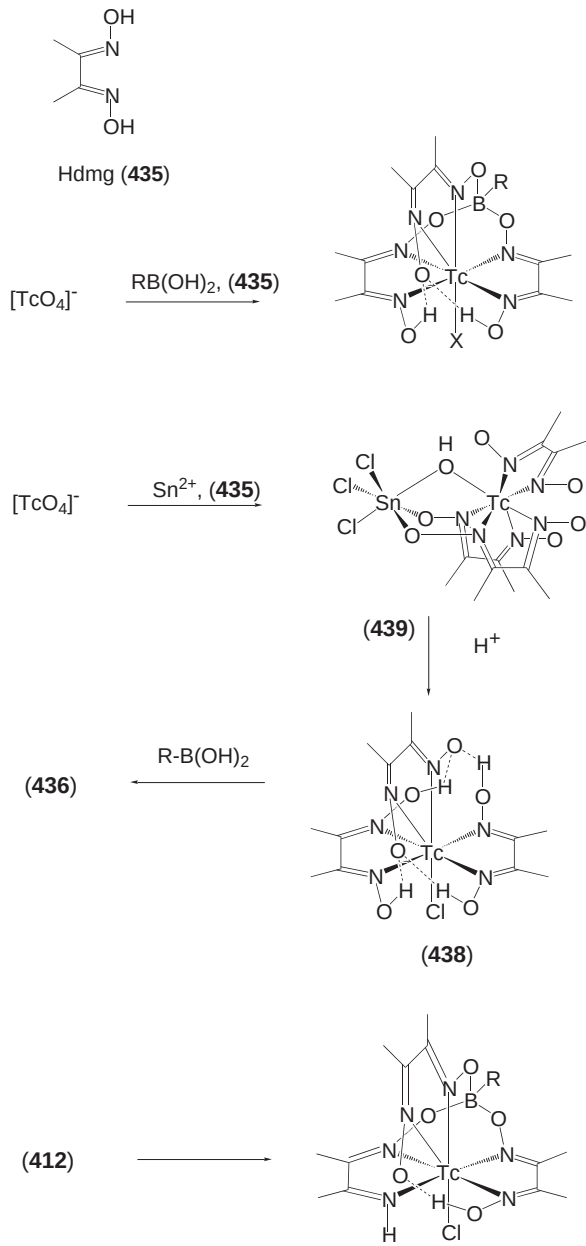
An interesting study with BATO compounds concerns the linkage isomerization of coordinated $[NCS]^-$ in $[Tc(NCS)(cdoh)_2(cdo)(BMe)]$ (**440**). Both a red, N-bond isothiocyanato complex $[Tc(NCS)(cdoh)_2(cdo)(BMe)]$ and the brown, S-bond thiocyanato complex $[Tc(SCN)(dmg)_3(BR)]$ (**441**) were isolated from the direct synthesis from $[TcO_4]^-$. The N-bound (**440**) was found to be thermodynamically more stable than the S-bound isomer (**441**) and the conversion was monitored elegantly by spectroscopic methods. The X-ray crystal structure of (**440**) was determined. The NCS^- and SCN^--substituted analogues exhibited $\nu_{C\equiv N}$ stretch at 2,114–2,124 cm^{-1} and at 2,055–2,079 cm^{-1}, respectively.[514] (Scheme 59).

Organohydrazines are good reducing agents, and the coordination chemistry of organohydrazides is of interest owing to their structural versatility. Some complexes of these have already been discussed in Section 5.2.2.3.5, since the oxidation state of the metal is not unambiguously clear. However, the examples that follow formally contain Tc^{III}. The reaction of (**412**) in refluxing methanol with hypy (**337**) gives pink $[TcCl_2(hypy)(PPh_3)_2]$ (**442**) in good yield. The structure of the corresponding Re complex was elucidated, showing a six-coordinate structure with bidentate chelating organodiazenido coordination. In a second Tc^{III} complex $[Tc(hypy)_2(PMe_2Ph)Cl)]^+$ (**443**), the hypy fragment coordinates in both mono- and bidentate fashion. One of the hypy ligands is of the neutral organodiazene type and the other is a mono-anionic, monodentate, linear diazenido ligand. The X-ray crystal structure of the rhenium complex was determined. This complex has special electronic characteristics that might be attributed to the π-system formed by the chelate, in which the lone pair of electrons is donated in the t_{2g} set of the metal, allowing the product to behave as a diamagnetic pseudo-M^I complex with diamagnetic behavior, as evidenced by sharp ^1H NMR signals.[515] The general behavior of organohydrazines is demonstrated by the reaction of $[TcOCl_4]^-$ with H_2NNPh_2 (**335**) and PPh_3 in refluxing MeOH to give the orange-yellow complex $[TcCl_3(NNPh_2)(PPh_3)_2]$ (**336**) (see Section 5.2.2.3.5). The corresponding methylphenyl-substituted isodiazene complexes have been prepared, but no structural data is available for comparison.[416]

A unique compound is produced from the reaction of $[Tc_2Cl_8]^{2-}$ (**444**) (see Section 5.2.2.5.5) with acetonitrile in the presence of HBF_4 Et_2O. One week of heating cleaves the Tc—Tc quadruple bond and the mononuclear complex $[TcCl_2(NCCH_3)_4]^+$ (**445**) is formed. The X-ray crystal structure confirms the *trans* locations of the two chlorides. Electrochemical studies of the complex showed a reversible, one-electron reduction to $[TcCl_2(NCCH_3)_4]^0$ at −0.62 V vs. ferrocene. A second, but irreversible, reduction occurred at −1.96 V. Irreversibility is probably due to the expulsion of either one or two Cl^- ligands.[516] A side product from this reaction was $[Tc_2(NCCH_3)_{10}]^{4+}$ (**446**) (see Section 5.2.2.5.5). The acetonitrile ligands are extremely labile. ^1H NMR in CD_3CN shows only the signal of free CH_3CN, and the potential of such complexes to provide access to other low-valent complexes is evident (Scheme 60).

5.2.2.5.3 *Oxygen ligands*

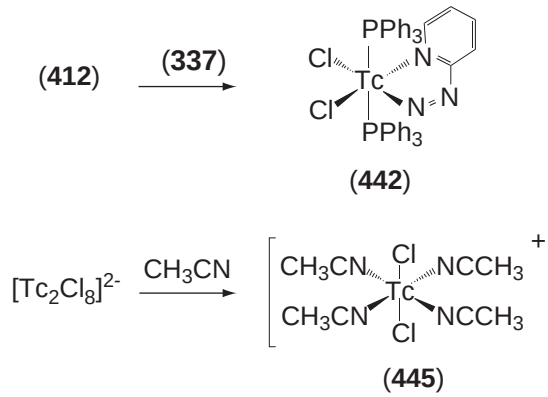
A number of Tc^{III} complexes containing oxygen ligands have already been mentioned in earlier sections. The examples discussed here comprise in general ligands derived of the acetylacetone (Hacac, (**362**)) type, with variations containing either two oxygen donors or one oxygen and one sulfur donor. Since these acac complexes are long established in coordination chemistry, complexes with Tc were produced quite early. The reduction/substitution of pentane-2,4-dione (Hacac) with *trans*-$[TcCl_4(PPh_3)_2]$ gave the first, orange-red acac complex of Tc^{III} $[TcCl(acac)_2(PPh_3)]$ (**447**). The array of four oxygens is nearly planar and the Cl^- and the phosphine are *trans*.[517,518] Direct reaction of several other Tc^{IV} precursors with neat (**362**) gave a number of other acac complexes of Tc^{IV} and Tc^{III}; thus $[TcX_6]^{2-}$ with (X = Cl, Br) gave the Tc^{IV} complexes $[Tc(acac)X_4]^-$ (**365**) after 2 h under reflux in pure ligand. Starting from $[TcX_4(PPh_3)_2]$, the complex $[TcX_3(acac)(PPh_3)]$ (**367**) is produced. The Tc^{III} complexes $[TcX_2(acac)(PPh_3)_2]$ (**448**) are obtained after 10 h reflux starting from $[TcX_6]^{2-}$ or $[TcX_4(PPh_3)_2]$. An extension of heating time to 12 h causes replacement of one



Scheme 59

more PPh_3 and one halide to give the bis-substituted complex (**447**); finally after 18 h heating complete substitution occurs and the violet, homoleptic acac complex [Tc(acac)$_3$] (**449**) is produced.[465] The X-ray crystal structure of [Tc(acac)$_3$] revealed an almost regular octahedral geometry about Tc.[519] The same complexes can also be synthesized by direct reaction of $[TcO_4]^-$ with (**362**) and with reducing agents such as $[S_2O_4]^{2-}$.[464] A variety of other homoleptic tris-diketonate complexes have been prepared with hexane, heptane, and octane backbones under similar conditions. The X-ray crystal structure of the hexane-2,4-dionato complex was also determined.[520] Ligand self-exchange reactions were performed with [Tc(acac)$_3$] and ^{14}C-labeled acacH ligand. The rate constant under pseudo-first-order conditions was 2.1×10^{-4} s^{-1} at 141 °C, and no catalysis by water was observed. The temperature dependence of the reaction gave $\Delta H^{\#} = 119$ kJ mol^{-1} and $\Delta S^{\#} = -27$ kJ mol^{-1}. Based on this data, an I_a mechanism was proposed via a seven-coordinate intermediate.[521]

Mixed β-diketonato complexes of the type [Tc(acac)$_2$(β-dik)] (**450**) have been obtained by CH_3CN substitution in $[Tc(acac)_2(NCCH_3)_2]^+$ (**451**). Under strongly acidic conditions in aceto-



Scheme 60

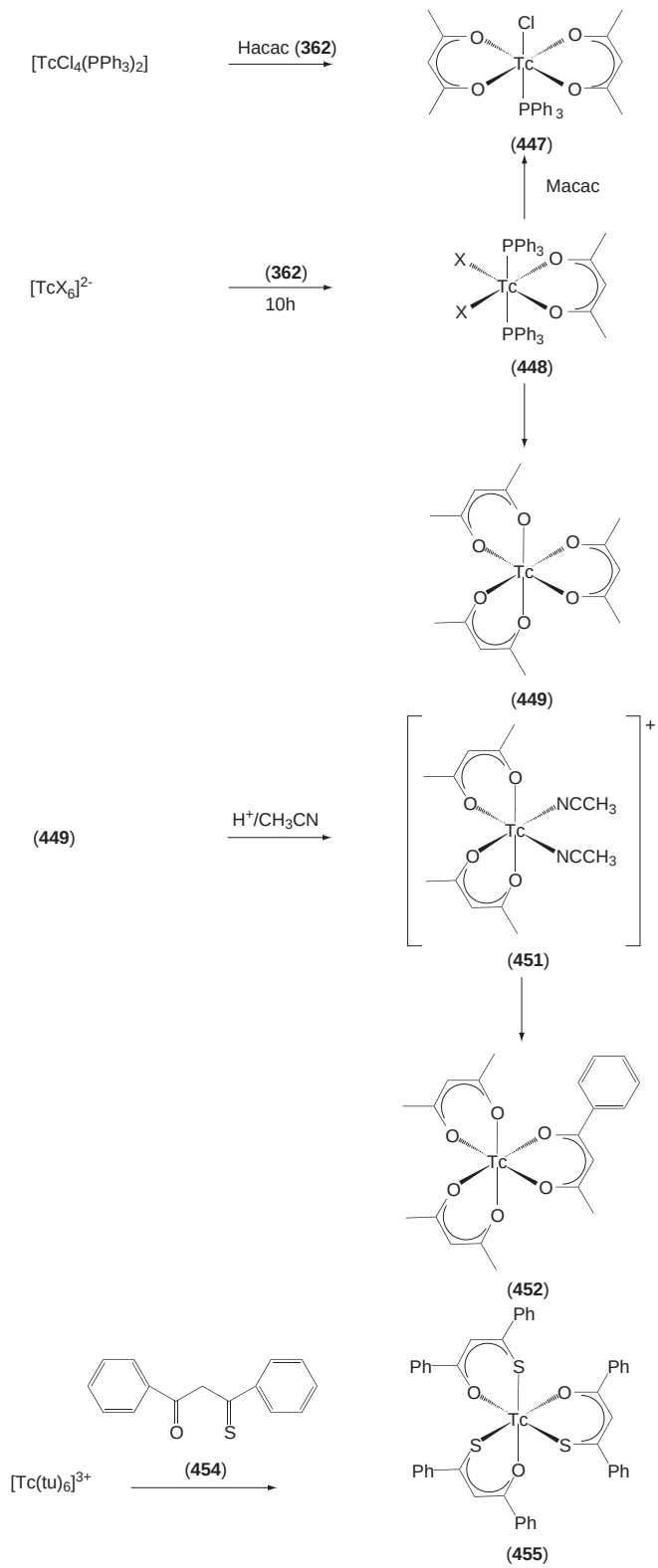
nitrile, one of the acac ligands in (**449**) is substituted and the cationic compound (**451**) is formed. These acetonitrile ligands can then be substituted by a variety of ligands such as benzoylacetone (Hbza), dipivaloylmethane (Hdpm), and others to form the neutral complexes $[Tc(acac)_2(bza)]$ (**452**) and $[Tc(acac)_2(dpm)]$ (**453**).[522] Complexes with some monothio-β-diketones have been also prepared. Reaction of the ligand monothio-dibenzoylmethane (Hmtm,(**454**)) with the Tc^{III} precursor $[Tc(tu)_6]^{3+}$ (**456**) in MeOH under reflux gave the homoleptic, dark blue, six-coordinate complex $[Tc(mtm)_3]$ (**455**) in 83% yield.[523] The X-ray crystal structure of this complex was determined and shows essentially perfect octahedral coordination. A number of other monothio-β-diketones have been prepared in the same manner (Scheme 61)[524].

5.2.2.5.4 Sulfur and mixed P,S and P,N and P,O ligands

Technetium(III) complexes containing sulfur donors exclusively in the coordination sphere are relatively rare. Most of the Tc^{III} complexes have various combinations of S and P, N, O, or even organometallic carbon ligands. A homoleptic complex of the type TcS_6 is represented by the tricationic thiourea complex $[Tc(tu)_6]^{3+}$ (**456**). This deep red complex is prepared from $[TcO_4]^-$ in 12M HCl and excess thiourea at room temperature. The thiourea ligands are coordinated through sulfur and are essentially planar, with Tc—S—C angles close to 120°. Although the complex is octahedral there are significant distortions, which are due to the Jahn–Teller effect and are also reflected in the corresponding Tc—S bond lengths. This complex has proved to be a versatile starting material. The reaction of (**456**) with dppe in 12M HCl gives $[TcCl_2(dppe)_2]^+$ (**400**) in moderate yield. The reaction with Bu^tCN in methanol yields the Tc^I complex $[Tc(CN^tBu)_6]^+$ (**457**).[525]

The interest in Tc^{III} complexes containing multidentate thioether ligands has also been motivated by the potential use of these compounds in radiopharmacy. The reaction of $[TcO_4]^-$ in acetone in the presence of Sn^{II}, with the tetradentate thioether ligands 3,6,9,12-tetrathiatetradecane (tttd, (**458**)) or 5,8,11,14-tetrathiaoctadecane (ttod, (**459**)) and a number of monodentate thiols (HSR) gave dark red to black complexes $[Tc(tttd)(SR)_2]^+$ (**460**) and $[Tc(ttod)(S\text{-}Ph)_2]^+$ (**461**), respectively. The X-ray structure of (**461**) was determined. Strong distortion of the octahedron leads to diamagnetism in these Tc^{III} complexes, in which the thiophemolato ligands are *cis*.[526] A more recent paper describes a novel class of sulfur-rich Tc^{III} complexes. The reaction of $[TcOCl_4]^-$ or $[TcNCl_4]^-$ with dithiobenzoic acid (piperidinium salt) in CH_2Cl_2 gives $[Tc(S_3CPh)_2(S_2CPh)]$ (**462**) in 67% yield as a dark red compound. X-ray structure analysis confirmed the presence of two perthiobenzoate ligands, forming two five-membered chelate rings around the Tc^{III} center. This type of coordination is unprecedented for Tc. A reversible, one-electron oxidation is observed by cyclic voltammetry at +0.894 V and a reversible reduction at −0.556 V.[527]

Complexes containing the methanethiolato ligand have been produced stepwise from $[TcO_4]^-$. An improved reaction with neat dmpe at room temperature gave the known Tc^V complex $[TcO(OH)(dmpe)_2]^{2+}$ (**204**) in 90% yield.[358] Further reaction with $Na[SCH_3]$ in degassed ethanol gave the blue Tc^{III} complex *trans*-$[Tc(SCH_3)_2(dmpe)_2]^+$ (**463**), which was structurally characterized.


[TcCl4(PPh3)2]
Hacac (362)
Cl
PPh3
(447)
Macac
[TcX6]2-
(362)
10h
PPh3
X
PPh3
(448)
(449)
H+/CH3CN
NCCH3
NCCH3
+
(451)
(452)
Ph
S
O
S
[Tc(tu)6]3+
(454)
(455)

Scheme 61

Analogous complexes with a number of other bidentate phosphine ligands were prepared similarly. Since the solution of this reaction is purple, it was suspected that another compound was also present. Indeed, reaction of (**463**) with Na[BH_4] or with Na[SCH_3] in EtOH gave a deep purple solution, attributed to the Tc^{II} complex [$Tc(SCH_3)_2(dmpe)_2$] (**464**). The equilibrium between the Tc^{III} and Tc^{II} is pH dependent, since addition of acid to (**464**) readily produces (**463**). The Tc^{III} compound undergoes a reversible reduction, slightly dependent on the diphosphine at about −0.55 V vs. Ag/AgCl and a second at −1.72 V. An irreversible oxidation is seen at +0.9 V. When (**204**) is reacted with H_2tdt, the orange Tc^{III} complex $[Tc(tdt)(dmpe)_2]^+$ (**465**) is formed, which was structurally characterized.[528] The geometry about Tc is intermediate between octahedral and trigonal prismatic, and represents a hybrid between octahedral $[Tc(dmpe)_3]^+$ and trigonal-prismatic geometry for $[Tc(bdt)_3]^-$.[128] The geometry is very similar to that of $[Tc(meph)(dmpe)_2]^+$ (**466**) (H_2meph = *o*-mercaptophenolate, (**467**)). This red compound is prepared by the direct reaction of (**467**) with the Tc^{III} precursor *trans*-$[TcCl_2(dmpe)_2]^+$ in 46% yield.[529] The complex $[Tc(tdt)(dmpe)_2]^+$ displays two reversible, one-electron reductions and one quasi-reversible oxidation, at potentials comparable to those for the complex $[Tc(SCH_3)_2(dmpe)_2]^+$.[530]

The ability of phosphine ligands to act as both reductant and ligand has been exploited in the synthesis of complexes of monosubstituted phosphines of the type $Ph_2P–RCO_2H$ (R = *o*-C_6H_4, C_2H_4, or CH_2). Pure complexes of the type [TcL_3] were readily obtained, giving an impetus for research with other functional groups.[531] Typically, direct reaction of $[TcO_4]^-$ with an excess of (*o*-aminophenyl)diphenyl-phosphine (Happ, (**188**)) in EtOH for several hours produces deep purple [$Tc(app)_3$] (**468**) in 85% yield (see also Section 5.2.2.3.2). The structure is octahedral with *trans*-N,N, *trans*-P,P and one *trans*-P,N coordination. In the presence of a strong acid such as CF_3COOH, the blue, monoprotonated complex $[Tc(adp)_2(Hadp)]^+$ (**469**) forms. Conductivity measurements are in agreement with a neutral and a monocationic species respectively. When no base was added to the original reaction mixture, the monoprotonated complex was present in significant amounts. A reversible acid/base equilibrium exists, with a pK_a value of about 9.1. The X-ray structure of the protonated form shows that the coordination geometry is distorted octahedral, with the phosphorus and the nitrogen atoms adopting a meridional arrangement. Two Tc—N bonds are short and the third, longer Tc—N distance is attributed to a protonated Tc—NH_2 bond.[345]

Similarly the reaction of a suspension of [NH_4][TcO_4] in EtOH with 2-diphenylphosphinophenol (POH, (**199**)) or –thiophenol (Hpbt, (**197**)) gave green [$Tc(PO)_3$] (**470**) or deep red [$Tc(pbt)_3$] (**471**), respectively. Both have been structurally characterized and show a strongly distorted octahedral structure. Both structures are almost perfectly superimposable and have magnetic moments of 3.0 B.M. and 2.7 B.M., respectively, which is in agreement with that expected for a Tc^{III} complex.[349,351] The complex (**470**) has been prepared with ^{99m}Tc and its biological properties investigated. In contrast to Tc complexes containing the same ligand but in different oxidation states, no accumulation in any particular organ was found.[532] In contrast, reaction of $[TcO_4]^-$ with an excess of the mixed bidentate thiol-phosphine ligands 2-diphenylphosphinoethanethiolate Hdpet, (**472**)) and -propanethiolate (Hdppt, (**473**)) gave neutral, five-coordinate complexes of the type [$Tc(PS)_2(SP{=}O)$] (**474**). The same complexes can also be prepared from $[TcOCl_4]^-$. The oxidized phosphine ligand originates from the reduction of $[TcO_4]^-$ and is coordinated by the thiolato group only. The structure is trigonal bipyramidal, and the three sulfur donors are located on one triangular face.[533] With these aliphatic backbone ligands, the corresponding tris-substituted, six-coordinate compound of the type [$Tc(PS)_3$] can be prepared applying the same conditions as described for the aromatic analogues above (see Section 5.2.2.3.2(viii)).[351]

Although Tc^{III} is electronically able to accommodate seven ligands, different coordination numbers are frequently found, especially with sterically crowded ligands or with those that impose a special geometry. A good example of this behavior is found with sterically hindered arene thiolates. The reaction of $[TcCl_6]^{2-}$ with 2,3,5,6-tetramethyl-benzenethiole (Htmbt, (**314**)) in MeOH/acetonitrile, and in the presence of a base and Zn dust as a reducing agent, gave after 30 min at room temperature dark blue [$Tc(tmbt)_3(NCCH_3)_2$] (**475**) in 70% yield. The same compound is also produced with other sterically hindered thiols, such as 2,4,6-tris-isopropylbenzenthiolate. The X-ray structure shows a trigonal-bipyramidal geometry, with the two $NCCH_3$ ligands *trans* and an N—Tc—N angle of 178.8°. The acetonitrile ligands are easily exchanged by other small π-acceptor molecules. This reaction with isopropyl-isocyanide gives within 1 min [$Tc(tmbt)_3(CN\text{-}^iPr)_2$] (**476**) as purple-pink crystals in quantitative yield. Bubbling CO through a solution of (**475**) overnight gave orange [$Tc(tmbt)_3(CO)_2$] (**477**). Exploiting the *trans* effect in the

last compound allows the replacement of one CO ligand by $NCCH_3$ or py to form the orange complexes $[Tc(tmbt)_3(CO)(NCCH_3)]$ (**478**) and $[Tc(tmbt)_3(CO)(py)]$ (**479**), respectively. In all the complexes, the *trans* arrangement of the small ligands is retained and the sterically demanding thiolato ligands occupy the trigonal plane. It was shown by NMR techniques that two conformers of (**478**) exist in solution and are rapidly interconverting into each other. In one the acetonitrile ligand is "up" and in the other one it is "down" with respect to the thiolate group. Prolonged heating under reflux in Pr^iNC leads ultimately to the formation of $[Tc(CN\text{-}^iPr)_6]^+$.[534]

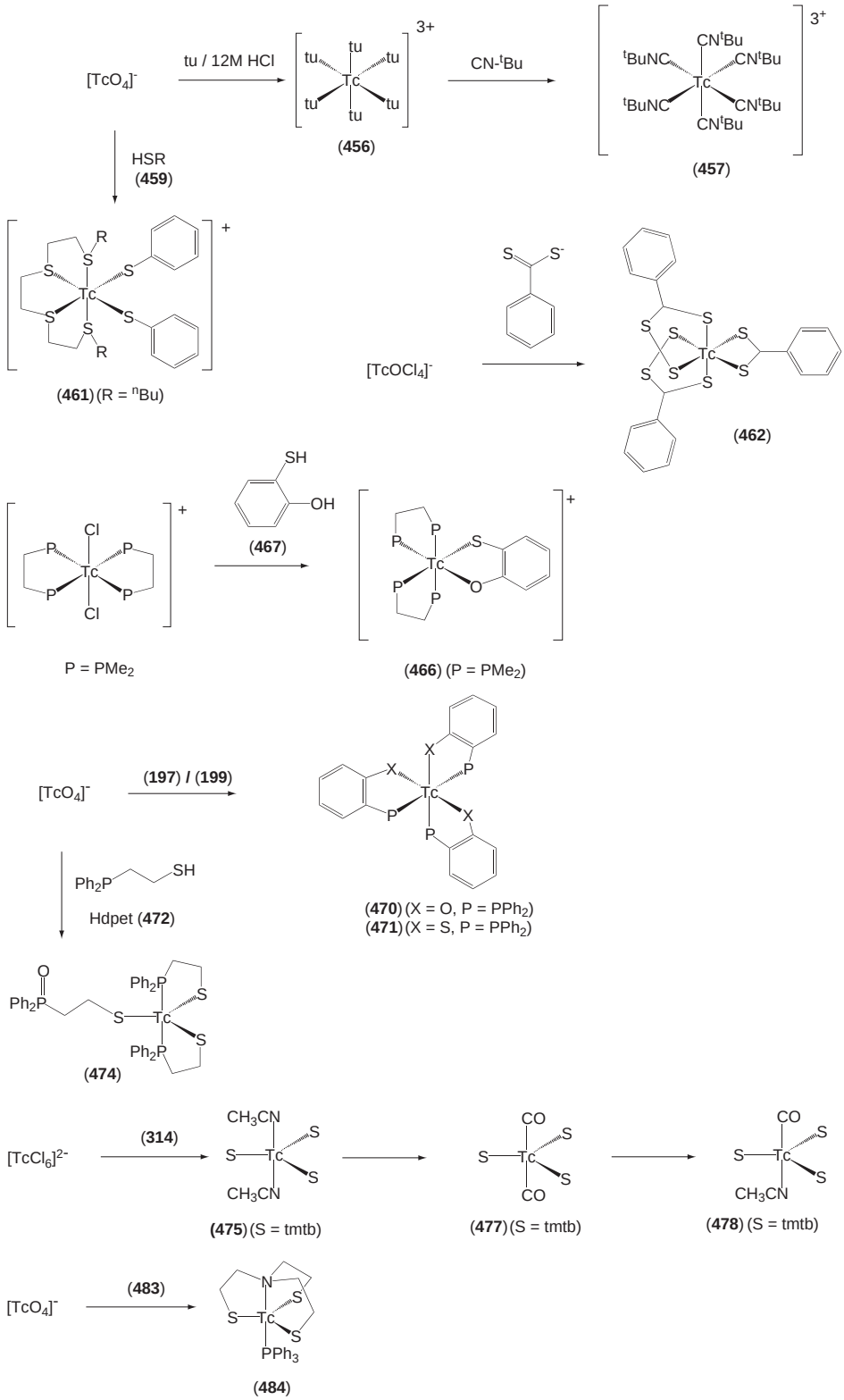
Various Tc^{III} complexes with several types of "umbrella" ligands have been prepared. The reaction of tris-(*o*-mercaptophenyl)-phosphane (H_3PS_3, (**315**)) with $[TcO_4]^-$ in acetonitrile/water, in the presence of $[S_2O_4]^{2-}$ and CH_3NC in chloroform, gave the five-coordinate, orange complex $[Tc(PS_3)(CNCH_3)]$ (**480**) in 82% yield. The same type of complex can also be prepared with PriNC instead of CH_3NC. When excess CH_3NC was reacted with $[Tc(PS_3)(CNCH_3)]$, the coordination of a second isocyanide ligand occurred to produce blue $[Tc(PS_3)(CNCH_3)_2]$ (**481**). With isocyanide ligands it is obviously possible to extend the coordination number from five to six. The addition of the second isocyanide is rapid, but reversible. *In vacuo* this second ligand is lost readily to regenerate the five-coordinate species.[535]

As described earlier, the reaction of $[TcO_4]^-$ in the presence of PPh_3 with 1-acetyl-2-phenylhydrazine yields the phenylimido complex $[TcBr_3(NPh)(PPh_3)_2]$ (see Section 5.2.2.3.4). This Tc^V complex reacts with an excess of PhSH or (**314**) to produce $[TcO(SPh)_4]^-$ and $[Tc(NPh)(tmbt)_4(PPh_3)]$, respectively. The reaction of $[TcBr_3(NPh)(PPh_3)_2]$ with the umbrella-type ligand (**315**) in MeOH and in the presence of "proton sponge" leads to reduction and the formation of red-brown $[Tc(PS_3)(PPh_3)]$ (**482**) in good yield. The loss of the phenylimido ligand is accompanied by reduction from Tc^V to Tc^{III}.[415]

Trigonal-bipyramidal complexes of Tc^{III} with umbrella-type ligands with H_3NS_3 donor sets have also been produced directly from $[TcO_4]^-$. The reaction of tris-(2-thioethyl)amine (H_3NS_3, (**483**)) with $[TcO_4]^-$ in the presence of PPh_3 in acidic $EtOH/H_2O$ gave the violet complex $[Tc(NS_3)(PPh_3)]$ (**484**) in 62% yield. A ligand-exchange reaction with $[TcCl_3(NCCH_3)(PPh_3)_2]$ gave the same complex, also in good yield. The X-ray crystal structure of the complex shows the expected trigonal-bipyramidal geometry. The PPh_3 ligand can be exchanged with isocyanides to give $[Tc(NS_3)(CNCH_2CO_2CH_3)]$ (**485**). A very low ν(CN) for (**485**) was observed in the IR. The long CN bond distance observed in the rhenium analogue supports the observation that strong donation by the sulfurs enhances the back-bonding ability of Tc.[536] This novel type of mixed-ligand complex enabled the preparation of a series of complexes with ^{99m}Tc, in which the biomolecule is attached to Tc via the ester group on the isocyanide ligand.[537] (Scheme 62)

A novel type of trigonal-bipyramidal Tc^{III} complex has been prepared by applying the methodology described earlier for a mixed-ligand complex with Tc^V. The five-coordinate complexes $[TcO(SES)(S\text{-}p\text{-}C_6H_4\text{-}OMe)]$, in which SES is a tridentate dithiolato fragment of the type $^-S(CH_2)_2E(CH_2)_2S^-$ (E = O,S), are converted via reduction/substitution in the presence of PMe_2Ph into the corresponding five-coordinate Tc^{III} complexes $[Tc(SES)(SC_6H_4OMe\text{-}4)(PMe_2Ph)]$ (**486**). In these complexes the electron density at the metal center has been increased by changes in the related geometry from square pyramidal to trigonal bipyramidal. They are characterized by the presence of strongly π-donating ligands at the trigonal base and π-acceptors at the *trans*-axial positions. The X-ray structures of several complexes have been determined. For $[Tc(SES)(SC_6H_4OMe\text{-}4)(PMe_2Ph)]$ (E is N, O, or S), the coordinating heteroatoms "E" is always found in the axial position *trans* to the phosphine ligand. These complexes can also be prepared at the n.c.a. level with ^{99m}Tc directly from $[^{99m}TcO_4]^-$ for possible radiopharmaceutical application. The synthesis and characterization of these so-called [3 + 1 + 1] mixed-ligand complexes opens new possibilities in the labeling of biomolecules.[538] This type of complex was also prepared by a different synthetic route. Reaction of $[TcCl_4(PPh_3)_2]$ with a substituted thiophenol and the tridentate ligand "SOS" gave, after 2 h reflux, the corresponding deep violet Tc^{III} complex $[Tc(SOS)(SPh)(PPh_3)]$ in moderate yield.[539] In contrast to many mixed-ligand complexes based on the [3 + 1] approach, the [3 + 1 + 1] complexes are more stable towards glutathione challenge.[540]

Neutral, seven-coordinate complexes with alkyl xanthates $[ROCS_2]^-$ (R = Et, Bu^n, etxan, (**487**)) can be produced from $[TcOCl_4]^-$ in EtOH in the presence of PPh_3. The brown-red, seven-coordinate complexes $[Tc(etxan)_3(PPh_3)]$ were produced in 60–70% yield. These complexes can also be prepared under similar conditions directly from $[TcO_4]^-$. The X-ray crystal structure of $[Tc(butxan)_3(PPh_3)]$ (**488**) shows a coordination number of seven, with geometry best described as capped octahedral. The Tc and the P are situated on a threefold axis.[541] ^{99}Tc NMR spectroscopy has been used to characterize these complexes, and the resonances were found at about 2,880 ppm relative to $[TcO_4]^-$. Complexes with ethylxanthate and dimethyldithiophosphate ($[dmtp]^-$ (**489**))


[TcO4]-
tu / 12M HCl
(456)
CN-tBu
(457)
HSR
(459)
(461) (R = nBu)
[TcOCl4]-
(462)
(467)
P = PMe2
(466) (P = PMe2)
(197) / (199)
Hdpet (472)
(470) (X = O, P = PPh2)
(471) (X = S, P = PPh2)
(474)
[TcCl6]2-
(314)
(475) (S = tmtb)
(477) (S = tmtb)
(478) (S = tmtb)
(483)
(484)

Scheme 62

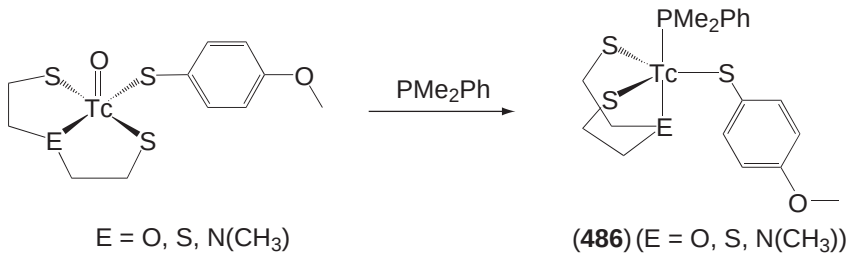
have also been prepared by direct substitution on $[TcCl_3(PMe_2Ph)_3]$ in THF, to give seven-coordinate complexes such as $[Tc(etxan)_3(PMe_2Ph)]$ (**490**). The reaction with (**489**) and $[TcCl_3(PMe_2Ph)_3]$ in acetone proceeded differently. One chloride and one phosphine ligand were replaced and the six-coordinate, orange-red complex $[TcCl_2(PMe_2Ph)_2(dmtp)]$ (**491**) formed in 66% yield. Both of the last complexes were structurally characterized.[542]

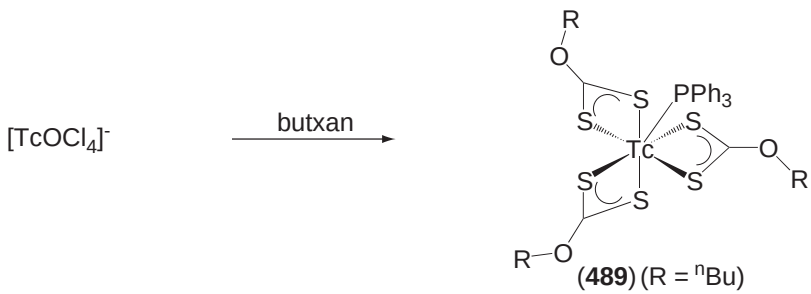
A unique example for the *in situ* formation of a carbonyl complex of Tc^{III} is the reaction of an aqueous solution of $[TcO_4]^-$ with formamidinesulphinic acid (Hfas, (**492**)) and Na[dtc]. A precipitate formed, which contained the orange-brown, seven-coordinate Tc^{III} complex $[Tc(dtc)_3(CO)]$ (**493**). The X-ray crystal structure confirmed the formula. The complex consists of a distorted pentagonal pyramid containing a terminal linear Tc—CO group. Two of the dtc ligands occupy equatorial positions, while the third spans an equatorial and the remaining axial site. The ν_{CO} appears at 1,895 cm^{-1}. The origin of the CO ligand is Hfas, since the use of other reducing agents did not result in the incorporation of CO. It is probable that the CO ligand is formed after coordination of $H_2N(NH)CSO_2H$ to Tc, since this reducing agent is known to ligate to Tc.[543] It is noteworthy that this seven-coordinate complex (**493**) adopts a pentagonal-bipyramidal geometry with one arm of a dtc ligand coordinated *trans* to CO, whereas $[Tc(S_2COR)_3(PPh_3)]$ (**488**) is capped octahedral.

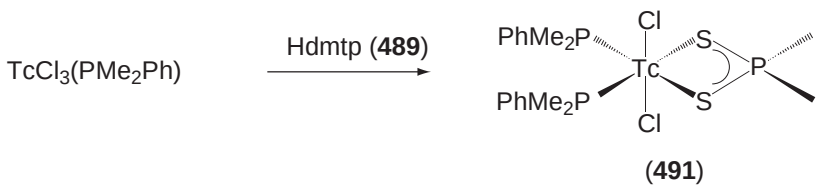
The reactivity of thioether ligands bound to Tc^{III} was demonstrated for complexes 1,4,7-trithiacyclononane (9-S-3, (**494**)). The reaction of $[TcO_4]^-$ in acetonitrile with (**494**) in the presence of HBF_4 gives, after addition of $SnCl_2$ as a reductant, the red-orange Tc^{II} complex $[Tc(9\text{-}S\text{-}3)_2][BF_4]_2$ (**495**) in 92% yield. In an attempt to prepare the corresponding Tc^{I} complex by reduction with ascorbic acid in water, one of the 9-S-3 rings loses ethene, with concomitant ring cleavage and the formation of the Tc^{III} complex $[Tc(9\text{-}S\text{-}3)(S(CH_2)_2S(CH_2)_2S)]^+$ (**496**). The same reaction occurs with both Re and with ^{99m}Tc. This type of reaction is known to occur for other transition-metal complexes. The cyclic voltammetry of the complex $[Tc(9\text{-}S\text{-}3)_2]^{2+}$ shows redox processes at +0.87 V and −0.4 V. However, the Tc^{I} species is short-lived and gas evolution takes place. The reaction mechanism clearly proceeds by the reduction of Tc^{II} to Tc^{I}, ethene formation, and oxidation of the metal to Tc^{III} (Scheme 63).[544,545]

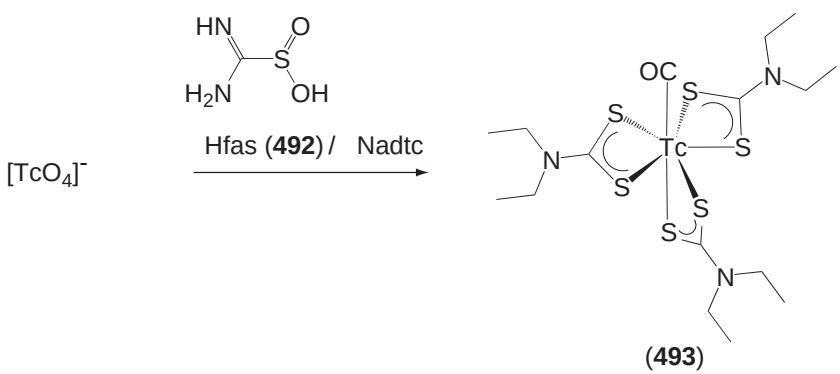
5.2.2.5.5 *Dinuclear Tc^{III} complexes containing multiple bonds*

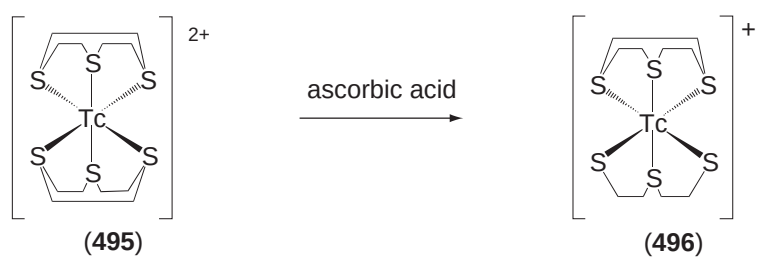
The identification of metal—metal multiple bonds belongs among the most important discoveries in coordination chemistry. Single and multiple bonds between metal centers have been rationalized and characterized for many elements. From the time when the true character of $[Re_2Cl_8]^{2-}$ was recognized, it seemed reasonable to anticipate the preparation of the Tc homologues. The existence of intermetallic bonds is not very extensive in Tc chemistry; however, some basic and important compounds have been prepared and fully characterized. Shortly before the establishment of Re—Re multiple bonds[546–548], the first such compound with a metal–metal multiple bond of Tc was prepared by the reduction of $[TcCl_6]^{2-}$ (**69**) with Zn° as a reducing agent in conc. HCl. Under these conditions, the mixed-valent complex $[Tc_2Cl_8]^{3-}$ (**497**) with NH_4^+ or Y^{3+} as a counterion was isolated as a black salt and characterized by elemental analysis. The oxidation state of +2.5 was confirmed by oxidative titration with Ce^{IV}. This compound, containing a Tc—Tc bond of order 3.5, is sensitive towards hydrolysis and oxidation.[549] The unambiguous proof of the existence of this compound was provided by structural characterization of $[NH_4]_3[Tc_2Cl_8]$ a few years later. The eclipsed conformation of the two $TcCl_4$ units and the very short Tc—Tc distance of 2.13(1) Å confirmed the presence of a Tc—Tc multiple bond. The presence of an unpaired electron in the multiple bond was confirmed by EPR measurements, which gave the magnetic moment of 1.78 B.M. The g values and hyperfine coupling constants, together with the susceptibility data, leave no doubt that the compound contains one unpaired electron delocalized over the two equivalent Tc atoms.[550,551] At about the same time, the X-ray crystal structures of the isomorphous complexes $K_3[Tc_2Cl_8]$ and $Y[Tc_2Cl_8]$ were solved. The Tc—Tc bond in the first complex is slightly longer than in the corresponding Y^{3+} salt at 2.117(2) vs. 2.105(1), respectively.[552,553] The Tc—Tc bond consists of one σ-, two π-, one δ-bond, and one electron residing in the antibonding δ^* orbital, giving rise to a bond order of 3.5. Spectroscopic studies reveal a band in the NIR between 6,000 cm^{-1} and 8,000 cm^{-1} showing vibronic structure. This band is attributed to the $\delta \rightarrow \delta^*$ transition.[554] This is the only band in the visible region of the spectrum.[555] From these data, the existence and characteristics of (**497**) became well established. Originally, the existence of the corresponding Tc^{III} complexes was


PMe2Ph
E = O, S, N(CH3)
(486) (E = O, S, N(CH3))


[TcOCl4]-
butxan
PPh3
(489) (R = nBu)


TcCl3(PMe2Ph)
Hdmtp (489)
PhMe2P
Cl
(491)


[TcO4]-
Hfas (492) / Nadtc
OC
(493)


2+
ascorbic acid
+
(495)
(496)

Scheme 63

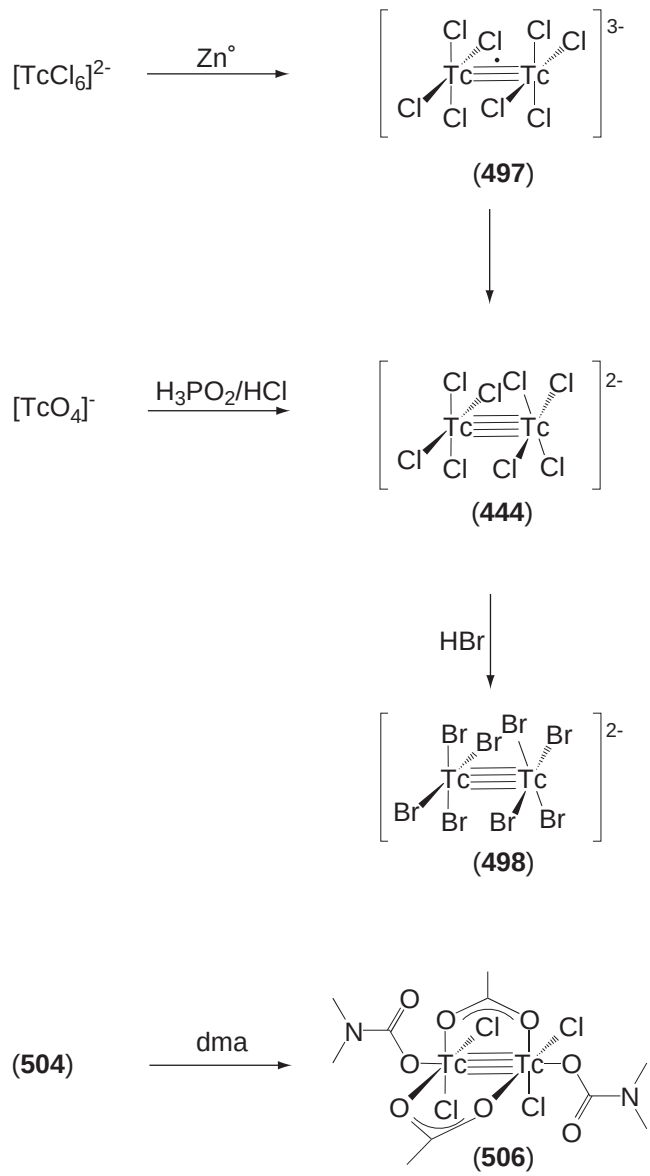
controversial. It had been reported that the reduction of (**69**) with Zn° led to the formation of $[Tc_2Cl_8]^{2-}$, besides $[Tc_2Cl_8]^{3-}$ [556,557] A quasireversible, one-electron oxidation at +0.14 V vs. SCE was found from cyclovoltammetric experiments. The lifetime of this species should be >5 min, which should allow its isolation. Interestingly the $[Re_2Cl_8]^{3-}$ is very short lived, while the corresponding $[Re_2Cl_8]^{2-}$ is indefinitely stable.[555] Soon after this conclusion, $[NBu_4]_2[Tc_2Cl_8]$ was synthesized directly from $[TcO_4]^-$ and conc. HCl, with H_3PO_2 as a reducing agent. A dark green solution was obtained, containing $[TcCl_6]^{2-}$ and (**444**). Repeated purification gave an olive-green product which was diamagnetic, and which is in agreement with an even number of electrons.[558] A strong absorption at 700 nm was attributed to a $\delta \rightarrow \delta^*$ transition. Although it was claimed that this synthesis is not reproducible,[188] $[Tc_2Cl_8]^{2-}$ was subsequently produced by Zn° reduction of (**69**) in conc. HCl. Both green (**444**) and blue greyish (**497**) could be isolated as the $[NBu_4]^+$ salts. Isolation was possible due to the different solubilities in acetone. $[Tc_2Cl_8]^{3-}$ is in fact sensitive as a solid and in solution towards aerobic oxidation, under which it forms the Tc^{III} compound $[Tc_2Cl_8]^{2-}$. Raman and IR spectroscopy confirmed the formulation. The Tc—Tc stretching vibration was found in the IR at 307 cm^{-1}. The reaction of $[Tc_2Cl_8]^{2-}$ in acetone and under argon in the presence of a few drops of bromine-free HBr gave for the first time the corresponding bromo complex $[Tc_2Br_8]^{2-}$ (**498**) as a deep red salt. The Tc—Tc stretching vibration was found in the IR at 323 cm^{-1}.[559] The structure of the complex was finally confirmed by X-ray structure analysis and is strictly isomorphous with the Re homologue. One of the most striking features in the structures is the Tc—Tc bond length. The removal of the δ^* electron is expected to shorten the M—M bond; however, the distance is 2.147(4) Å and is thus considerably longer than in $[Tc_2Cl_8]^{3-}$.[560]

These dinuclear complexes provide versatile starting materials for the preparation of complexes with other ligands. One of the first examples is the preparation of $[Tc_2Cl_2(piv)_4]$ (**500**) (piv = pivalato O_2CCMe_3, (**499**)). The reaction of $[NH_4]_3[Tc_2Cl_8]$ with pivalic acid at 150 °C for 36 hours produced the red complex. Obviously oxidation took place, and a quadruple bond is formed between the two Tc centers. The structure is paddle-wheel-like and consists of four bridging piv ligands and one chloride on each Tc along the central Tc—Tc axis. The quadruple bond is 2.192(1) Å, again considerably longer than in $[Tc_2Cl_8]^{3-}$.[561] In a similar procedure, $[NH_4]_3[Tc_2Cl_8]$ was reacted in molten 2-hydroxy-pyridine (Hopy, (**501**)) at 150 °C for 18 h with careful exclusion of air. This produced in almost quantitative yield the complex $[Tc_2Cl_2(opy)_4]^-$ (**502**), as a dark green solid in which the oxidation state of the precursor was maintained and the M—M bond is of order 3.5. The X-ray crystal structure shows infinite chains of paddle-wheel $[Tc_2(opy)_4]^+$ cations, bridged by linear chloride ligands. The coordination at one Tc center is alternating N,O from the opy ligands. The Tc—Tc distance is 2.095(1) Å and is one of the shortest known so far. The Tc bond order is 3.5 and the Tc—Tc stretching vibration is found in the IR at 383 cm^{-1}. The electronic absorption spectra have been examined in considerable detail and, for the rich vibrational structure of the $\delta \rightarrow \delta^*$ transitions, whose 0–0 band is at 12,194.4 cm^{-1}, a general assignment has been suggested.[562] The acetato analogue of $[Tc_2Cl_2(piv)_4]$, $[Tc_2Cl_2(ac)_4]$, was obtained from the reaction of $K[TcO_4]$ in HCl with acetic acid in different organic solvents, as cherry-red crystals.[563] Other synthetic routes from $[Tc_2Cl_8]^{3-}$ have also been described.[564,565] The reaction of $[Tc_2Br_8]^{2-}$ with acetic acid/acetic anhydride gave $[Tc(ac)_4Br_2]$ (**503**) as an orange-red powder in 80% yield. $[Tc(ac)_4Cl_2]$ has been prepared analogously. Thorough analysis of the IR and Raman bands allowed a full assignment and the calculation of force constants. The Tc—Tc stretching vibration is found in the IR at 319 cm^{-1} for the chloro and at 310 cm^{-1} for the bromo complex.[566]

The complex $[Tc_2(ac)_2Cl_4(OH_2)_2]$ (**504**) has been prepared by the direct reaction of acetic anhydride and HBF_4 with $[Tc_2Cl_8]^{2-}$. By treatment with donor bases such as dmf, dma, dmso, triphenylphosphinoxide, or py, the water ligands are substituted and complexes of general composition $[Tc_2(ac)_2Cl_4L_2]$ (**505**) are formed. The starting material (**504**) was also produced by a novel method. The reaction of $[TcOCl_4]^-$ in the presence of $[NBu_4][BH_4]$ in acetic anhydride at −30 °C with 50% HBF_4 gave, after a short time, deep green (**504**) in 89% yield. The complexes with the donor bases were achieved as green materials by mixing the starting material with a few drops of the appropriate compound. The X-ray crystal structure of $[Tc_2(ac)_2Cl_4(dma)_2]$ (**506**) shows a *cis* arrangement of the bridging acetate ligands and the terminal chlorides. The dma ligands are axial and coordinate via the amido oxygen. The Tc—Tc distance is 2.1835(7) Å, significantly longer than in (**444**). This elongation is due to the axial ligands, which clearly weaken the Tc—Tc bonds. Electronic spectra show only minor dependence on the base. The characteristic $\delta \rightarrow \delta^*$ transitions are found for all the adducts in the range 648–652 nm.[567] The correlation between the donor strength of the axial bases and the Tc—Tc vibrational bands has been investigated. A linear relationship between the Donor number D_N and the ν_{M-M} was found.

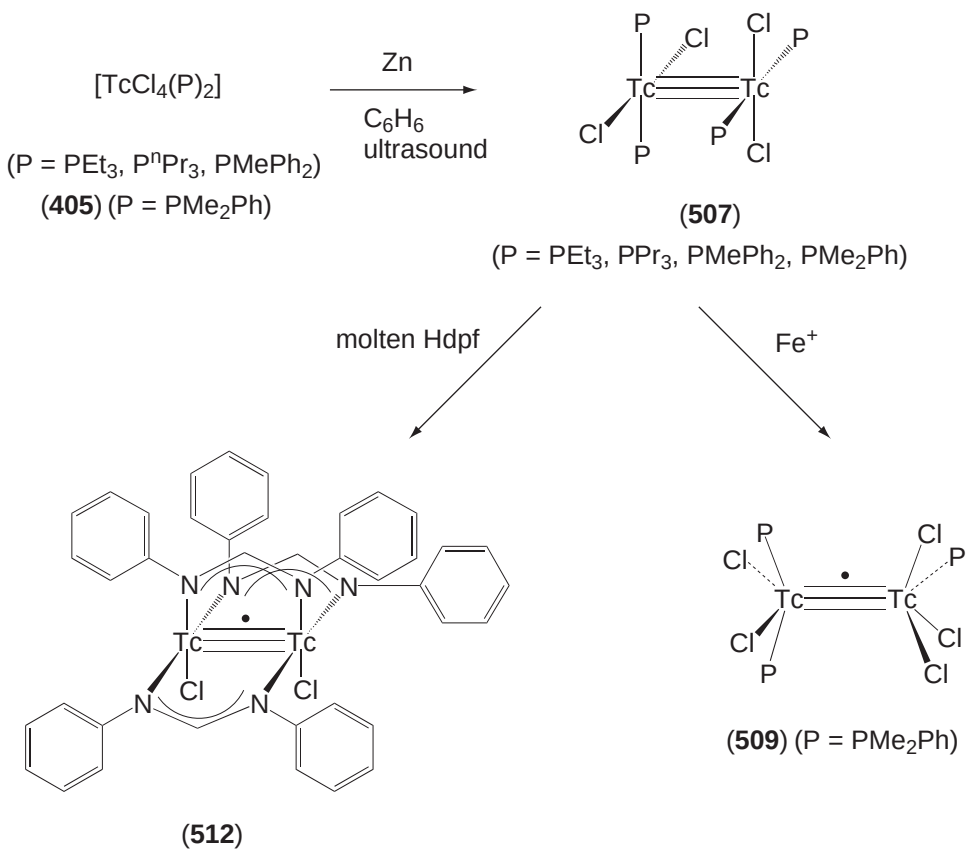
For the strongest donor py, the band is at 282 cm^{-1}; for the weakest donor, H_2O, at 311 cm^{-1}. The correlation for Re is less distinct.[568] (Scheme 64)

A series of triply metal—metal-bonded ditechnetium(II) phosphine complexes of the general formula $[Tc_2Cl_4(PR_3)_4]$ (**507**) have been prepared. Since they serve as synthons for a number of other ditechnetium complexes in higher oxidation states, these Tc^{II} complexes are also discussed here. These dinuclear complexes are prepared from the mononuclear precursor compounds $[TcCl_4(PR_3)_2]$. The starting materials with PEt_3, P^nPr_3 were prepared as blue solids from $[TcCl_4(PPh_3)_2]$ by phosphine exchange. The precursors $[TcCl_4(PMe_2Ph)_2]$ (**405**) and $[TcCl_4(PMePh_2)_2]$ were produced as green solids from $[NH_4][TcO_4]$ with a variation of the original method.[475] The dinuclear complexes were then prepared in benzene or THF in the presence of finely divided Zn and after sonification for 6 h, in almost quantitative yield for all the phosphines mentioned before. This rational synthetic design comprises a two-electron reduction of the Tc^{IV} center, precipitation of $ZnCl_2$ and the formation of the Tc≡Tc triple bond.[569] The complexes are diamagnetic and show a series of weak absorptions in the range 488–700 nm. The low molar aborptivities for these transitions are similar to the spin- and orbitally forbidden transitions found for other M—M-bonded complexes containing an electron-rich $\sigma^2\pi^4\delta^2\delta^{2*}$ triple



Scheme 64

bond. The structures of three complexes were elucidated. The structures are made up of two *trans*-$TcCl_2(PR_3)_2$ fragments that are rotated 90° with respect to each other, to give an eclipsed geometry with approximate D_{2d} symmetry. The Tc—Tc distance for the PEt_3 complex is 2.127(1) Å, the shortest for the three structures described. Two reversible oxidation couples were electrochemically measured. Depending on PR_3, the first oxidation wave is found between −0.48 V (PEt_3) and −0.26 V ($PMePh_2$), the second at +0.88 V and +0.92 V vs. Fc^+/Fc, respectively. The reversibility implies that synthesis of the mono- and dicationic species $[Tc_2Cl_4(PR_3)_4]^{2+/+}$ should be possible.[569] Indeed, mild chemical oxidation of $[Tc_2Cl_4(PMe_2Ph)_4]$ with $[Fc][PF_6]$ in acetonitrile produced green $[Tc_2Cl_4(PMe_2Ph)_4]^+$ (**508**) in 82% yield. In the presence of Cl^-, one of the phosphines is substituted to give neutral, orange $[Tc_2Cl_5(PMe_2Ph)_3]$ (**509**). The complexes are paramagnetic, which is consistent with a $\sigma^2\pi^4\delta^2\delta^*$ electronic configuration. The X-ray crystal structure of complex (**508**) shows that the dinuclear cation adopts an eclipsed structure, with an arrangement of ligands similar to that observed for the neutral counterpart. The Tc−Tc bond is shorter at 2.1074(9) Å, consistent with the bond order of 3.5 due to the depopulation of δ^*. $[Tc_2Cl_5(PMe_2Ph)_3]$ is structurally similar, in that it consists also of two eclipsed ML_4 fragments with a relatively short Tc—Tc separation of about 2.1092(4) Å.[570] Compounds of composition $[Tc_2Cl_4(PR_3)_4]$ reacted with molten formamidines such as diphenyl formamidine (Hdpf, (**510**)) to yield mixtures of tris- and tetrakis-bridged formamidinate complexes $[Tc_2(dpf)_4Cl]$ (**511**) and $[Tc_2(dpf)_3Cl_2]$ (**512**), in modest yield. The displacement of the chloride and the phosphine to form red (**511**) and purple (**512**) is accompanied by oxidation. The X-ray structures of the tolyl analogues have been determined. The structure of $[Tc_2(dtolf)_3Cl_2]$ can be described as a paddle wheel in which one of the bridging bidentate ligands has been replaced by two chlorides. The Tc—Tc bond lengths in both complexes are in the expected range, and the paramagnetism is consistent with a bond order of 3.5.[571] For better understanding of the bonding involved in these metal–metal-bonded systems, theoretical calculations have been performed. For both complexes the HOMO is the δ^*, and the ordering $\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$ was confirmed.[571] Other complexes containing a Tc—Tc multiple bond are also discussed in Section 5.2.2.6.3 (Scheme 65).



Scheme 65

5.2.2.6 Oxidation State (II)

Complexes containing technetium in the +II oxidation state are relatively few. In general, the complexes are prepared by reduction/oxidation reactions from other oxidation states rather than by direct ligand substitution on Tc^{II} precursors, since simple binary compounds are not known—with the exception of the serendipitously prepared $[TcBr_4]^{2-}$ mentioned in Section 5.2.2.3.3(ii).[157] The complexes usually have distorted octahedral geometries and are paramagnetic, as expected for the d^5 low-spin electronic state. EPR provides a useful tool for the detection of species in this oxidation state, and for reactivity studies in solution. The nuclear spin of ^{99}Tc is 9/2, which gives 10-line EPR spectra and, based on the following, the whole terminology can be treated as a d^1 configuration. The low oxidation state and the relatively high number of available electrons make Tc^{II} favor soft ligands such as phosphines, NO, or isocyanides, with considerable participation of backbonding. A number of these ligands are typically organometallic, and will not be treated here unless substantial "classical" coordination chemistry is involved. It is noteworthy that organometallic complexes of Tc^{II} are still rare, probably as a consequence of the odd number of electrons, which is not compatible with the 18-electron rule. For such paramagnetic complexes, ligands with an odd number of electrons such as NO are often involved in coordination. There is a considerable tendency to form metal—metal bonds, as exemplified by the Tc_2 compounds, but also by the considerable number of halide clusters in mixed oxidation states involving metal—metal bonds rather than bridging ligands.

5.2.2.6.1 Nitrosyl and thionitrosyl complexes

The preparation of the first nitrosyl complex goes back to the early days of Tc chemistry. The reaction of $[NH_4]_2[TcCl_6]$ with 2M hydroxylamine hydrochloride solution gave, after evaporation overnight and recrystallization from water/EtOH, a pink complex which was originally formulated as a hydroxylamine complex of Tc^{I}.[549] A later study showed that the precise composition of the pink complex is *trans*-$[Tc(NO)(NH_3)_4(H_2O)]^{2+}$ (**513**), the first Tc^{I} nitrosyl complex. The pK_a value of this complex is 7.3, as determined by potentiometric titrations. This strong acidity can be explained by the influence of the strong π-acid NO, which prefers a good σ- or π-base in the *trans* site for optimal thermodynamic stability. In that sense, $[OH]^-$ is the ideal ligand and, hence, the coordinated water in (**513**) is very acidic. The corresponding green Tc^{II} complex *trans*-$[Tc(NO)(NH_3)_4(H_2O)]^{3+}$ (**514**) was prepared in good yield by oxidation with Ce^{IV} in 2M $HClO_4$. The magnetic moment is 1.7 B.M and the complex is stable only in acidic solution.[572] A subsequent X-ray structure analysis confirmed the proposed formula, and the assigned oxidation number of I was evident from the diamagnetism in this compound. The NO ligand, which has to be considered as $[NO]^+$, is located *trans* to the water, whereas the four NH_3 ligands lie in the plane.[573]

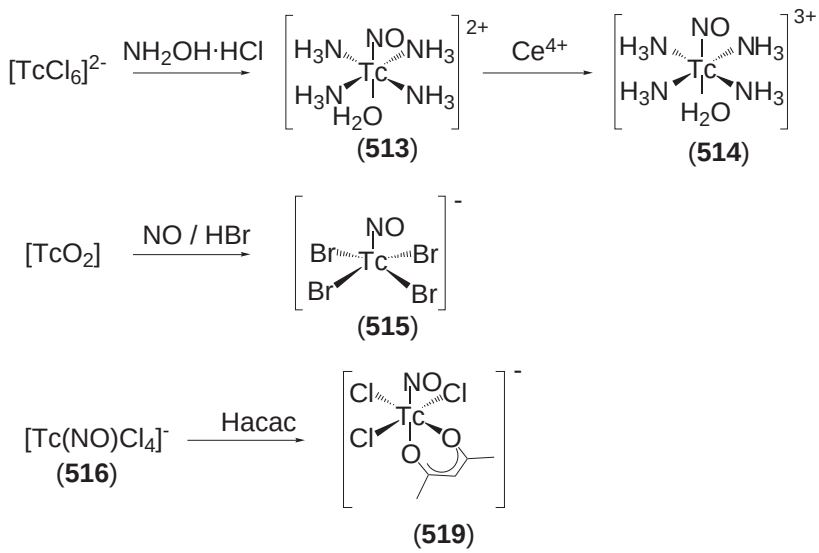
An interesting starting material for Tc^{II} nitrosyl chemistry is $[NBu_4][Tc(NO)Br_4]$ (**515**), which was first prepared in good yield by the direct interaction of NO gas with $TcO_2\ H_2O$ in 4M HBr. The blood-red crystals were precipitated from the solution by the addition of the bulky counterion. The complexes with Cl^- and I^- were prepared by anion exchange or by reaction with HI in acetone under reflux.[55,574] The green chloro complex $[NBu_4][Tc(NO)Cl_4]$ (**516**) can also be prepared by the direct reaction of $[NBu_4][TcOCl_4]$ or $[NBu_4]_2[TcCl_6]$ with hydroxylamine in MeOH. Recrystallization from $MeOH/Et_2O$ gave the six-coordinate, bright green complex $[NBu_4][Tc(NO)(HOCH_3)Cl_4]$, which was structurally characterized. The Tc—N—O angle is 175.5°, and thus in good agreement with the formulation as coordinated $[NO]^+$. The Tc—O bond is elongated to 2.126 Å as a consequence of the strong *trans* effect of the $[NO]^+$ ligand.[575]

The reaction of (**515**) with excess NCS^- allows the isolation of ink-blue $[Tc(NO)(NCS)_5]^{2-}$ (**517**), which can be reduced electrochemically to Tc^{I} at 0.14 V vs. SCE, or with hydrazine, to rust-colored crystals of $[NBu_4]_3[Tc(NO)(NCS)_5]$ (**518**). The ν_{NO} appear at 1,785 cm^{-1} for the Tc^{II} complex and at 1,685 cm^{-1} for Tc^{I}. Both are at lower frequencies than for the five-coordinate complex $[Tc(NO)Br_4]^-$, where ν_{NO} is at 1,795 cm^{-1}.[55,574]

The EPR spectra of various Tc^{II} complexes have been investigated in detail. The EPR of the six-coordinate, deep blue complex $[AsPh_4]_2[Tc(NO)(NCS)_5]$, prepared from $[NH_4][TcO_4]$ in dmf and in the presence of KNCS and $H_2NOH{\cdot}HCl$, has been studied in nonaqueous solution in the liquid and in frozen glass phases. With $g_\perp = (+)2.045$ and $g_{||} = (+)1.928$, and $A_{||} = 0.0236$ and $A_\perp = 0.0095\ cm^{-1}$, the spectrum is characteristic of a low-spin $4d^5$ system in an axial-symmetrical environment. The small quadrupole moment observed is solvent dependent.[576] When Hacac is

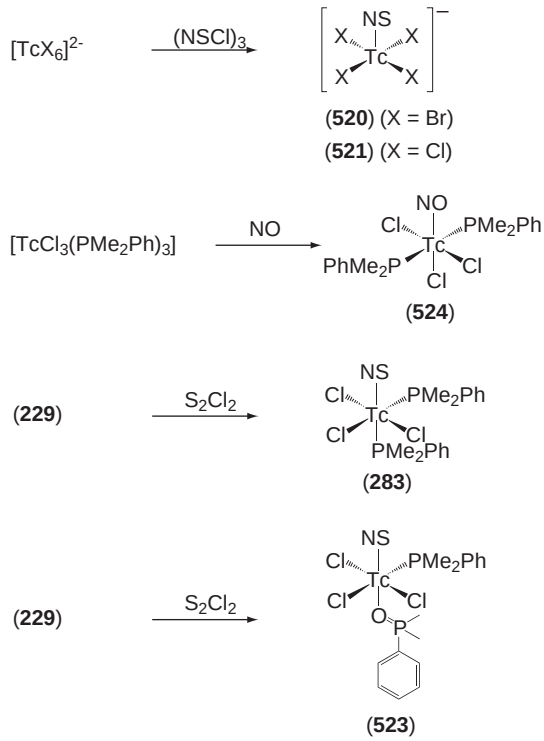
added to a solution containing freshly prepared $[Tc(NO)Cl_4]^-$ the red acac complex $[Tc(NO)(acac)Cl_3]^-$ (**519**) is produced, which can be extracted into organic solvent. The structure is distorted octahedral, with one of the acac oxygen donors *trans* to the nitrosyl ligand. The Tc—N—O bond angle is only 158.6°, which is considerably smaller than in the examples above. The ν_{NO} appears in the IR at 1,770 cm^{-1}. The EPR spectra at room temperature show the expected 10 lines, due to the splitting by Tc. At −196 °C the spectrum may be modeled with three g values: $g_x = 2.0107$, $g_y = 2.02225$, and $g_z = 1.94600$.[575,577] (Scheme 66)

A limited number of thionitrosyl complexes have been prepared. The reaction of $[TcX_6]^{2-}$ with trithiazyl chloride $(NSCl)_3$ in CH_2Cl_2 at room temperature overnight gave red-brown $[AsPh_4][Tc(NS)Br_4]$ (**520**) and yellow $[AsPh_4][Tc(NS)Cl_4]$ (**521**), together with considerable amounts of $[AsPh_4][TcNBr_4]$ and $[AsPh_4][TcNCl_4]$ (**34**). Both NS complexes react with NCS^- to yield deep purple $[AsPh_4][Tc(NS)(NCS)_4]$ (**522**). As is evident from EPR investigations, the reaction with trithiazyl chloride usually produces the thionitrosyl compound, which undergoes a slow desulfurization reaction over 24 h to give more than 80% of the nitrido complex. The reaction from (**520**) to $[TcNBr_4]^-$ with formation of S_8 is a formal four-electron oxidation, but similar desulfurization has also been observed for other thionitrosyl complexes such as $[Tc(NS)Cl_3(PMe_2Ph)(OPMe_2Ph)]^-$ (**523**). The ν_{NS} for (**521**) appear at 1,214 cm^{-1} and 1,219 cm^{-1}, respectively.[578] Nitrosyl complexes with mixed halide/phosphine coordination were obtained by direct nitrosylation of mer-$[TcCl_3(PMe_2Ph)_3]$ with NO in benzene. The blue-green complex $[Tc(NO)Cl_3(PMe_2Ph)_2]$ (**524**) was produced in 62% yield. ν_{NO} is at 1,805 cm^{-1}, and in the EPR spectra well-resolved ^{99}Tc hyperfine splitting is observed, indicating a ground state for the unpaired electron which is well separated from the other orbitals. At low temperature, analysis of the hyperfine splittings shows strong covalent interactions for the in-plane ligands.[579] The corresponding red thionitrosyl complex $[Tc(NS)Cl_3(PMe_2Ph)_2]$ (**283**) was prepared directly from $[TcNCl_2(PMe_2Ph)_3]$ (**229**), with S_2Cl_2 as the sulfurizing agent, from CH_2Cl_2 under reflux. For the nitrosyl and the corresponding thionitrosyl complexes, the chlorides can be exchanged for bromide by reaction with HBr in acetone 2/1 under reflux. The yield of green $[Tc(NO)Br_3(PMe_2Ph)_2]$ (**525**) is 95%, but for purple $[Tc(NS)Br_3(PMe_2Ph)_2]$ (**526**) it is only 29%. No evidence was found for the concomitant formation of $[Tc(NO)Br_4]^-$.[580] A more thorough study of formation of the thionitrosyl complexes of Tc^{II} by the S_2Cl_2 reaction revealed formation of the deep red, mixed phosphine/phosphineoxide complex $[Tc(NS)Br_3(PMe_2Ph)(O{=}PMe_2Ph)]$ (**523**) in 60% yield under reflux conditions.[581] The structure was elucidated, showing the NS and the phosphine-oxide in mutually *trans* orientations and the three chlorides and the remaining phosphine in a plane of the distorted octahedron. The structure of (**283**) remained unsolved for a long time. The reaction of $[TcNCl_2(PMe_2Ph)_3]$ with bis(diphenylthiophosphoryl)amide (**280**) gives the six-coordinate Tc^V complex $[TcNCl(PMe_2Ph)_2(dtp)]$ (**282**) and $[TcN(dtp)_2]$ (**281**) (see Section 5.2.2.3.3(ii)). The further reaction of (**282**) at room temperature in CH_2Cl_2 with S_2Cl_2 gave the thionitrosyl



Scheme 66

complex (**283**) in 27% yield, in which the bidentate ligand has been replaced. The structure reveals the two phosphine ligands are *trans*. It is noteworthy that the same reaction with rhenium produced the Re^{I} complex $[Re(NS)Cl_2(PMe_2Ph)_3]$ as *mer* and *trans* stereoisomers. The observed reduction to Re^{I} follows the general trend that the reaction of M^{V} nitrido precursors with S_2Cl_2 generates Re^{I} complexes, whereas Tc under the same conditions yields the complexes of Tc^{II} (Scheme 67)[403].



Scheme 67

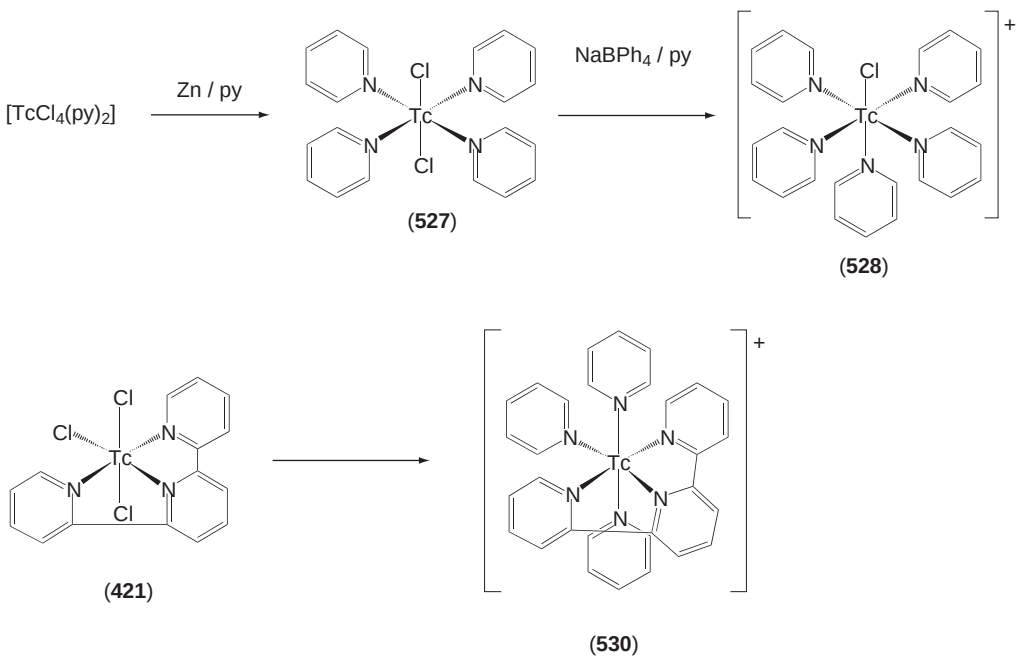
5.2.2.6.2 Heterocyclic amine ligands

As mentioned in Section 5.2.2.5.2, heterocyclic amines are versatile ligands which can stabilize low oxidation states of Tc. The Tc^{III} compound $[TcCl_3(PPh_3)_2(NCCH_3)]$ (**412**) has proven to be an extremely versatile starting material for complexes containing heterocyclic and nonaromatic mono- and bidentate amines, such as $[TcCl_2(Me_2bipy)_2]^+$ (**419**), $[TcCl_3(PPh_3)(tmeda)]$ (**420**), $[TcCl_3(terpy)]$ (**421**), $[TcCl_2(PPh_3)(py)_3]^+$ (**418**), and *trans*-$[TcCl_2(py)_4]^+$ (**422**). The interest in developing coordinatively unsaturated low-valent and electron-rich technetium centers led to the preparation of purple $[TcCl_2(py)_4]$ (**527**) and red-purple $[TcCl(py)_5]^+$ (**528**). The reaction of $[TcCl_4(py)_2]$ in pyridine with Zn dust as a reductant gave (**527**) in 67% yield. The X-ray crystal structure showed the chlorides to be *trans*. The reaction of $[TcCl_2(py)_4]$ in pyridine with $Na[BPh_4]$ gave the cationic complex (**528**). Reduction of the Tc^{III} complex (**421**) in pyridine with Zn° dust gave the Tc^{I} complexes $[TcCl(terpy)(py)_2]$ (**529**) and $[Tc(terpy)(py)_3]^+$ (**530**). The $Tc^{II/I}$ couple for complex (**528**) is observed at −1.33 V vs. NHE; however, attempts to reduce this complex to Tc^{I} with magnesium failed.[502] The comparison of structural data for these Tc^{III}, Tc^{II}, and Tc^{I} complexes provides evidence for the electron-rich character of these low-valent Tc complexes. For instance, a decrease of 0.04 Å and an increase of 0.07 Å are observed in the *trans*-Tc—N and *trans*-Tc—Cl bond distances, respectively, for the similar complexes (**527**) and (**415**).[501] Such structural differences are best explained by a dramatic increase in the π-basicity of Tc^{II} relative to Tc^{III}.

A further example of homoleptic Tc^{II} complexes with heterocyclic amines is provided by the dicationic complex $[Tc(bipy)_3]^{2+}$ (**531**). Starting from the Tc^{III} precursor $[TcCl_3(NCCH_3)\{(C_6H_4Me\text{-}3)_3\}_2]$, the reaction with phen, bipy, or terpy gave the dark blue (**531**) and $[Tc(phen)_3]^{2+}$ (**532**) or black $[Tc(terpy)_2]^{2+}$ (**533**), respectively, in good yields. The structure of (**531**) was determined. Both optical isomers were found to be present in the crystal.

Electrochemical analysis of (**531**) showed three reversible reductions at −0.34, −1.36, and −1.70 V vs. SCE, respectively.[499,582]

Another example of a Tc^{II} complex containing exclusively nitrogen donors is the potentially heptadentate ligand tren-py_3, produced from tren by condensation with three pyridine-aldehyde molecules bearing different substituents. The reaction of the Tc^{III} precursor (**412**) with a methanolic solution of tren and the corresponding pyridine-aldehyde gave, after 1 h of reflux, the complexes $[Tc(tren\text{-}py_3)]^{2+}$ (**534**) in moderate yield as purple compounds. The reaction with other Tc precursors in higher oxidation states gives the same dicationic complexes. The structure of one compound was determined, and showed hexadentate coordination. The mean imine nitrogen—Tc bond length is 2.071 Å. The bridging nitrogen in the tren framework is at a distance of 2.933 Å and the angles between the arms are almost 120°, demonstrating the strong repulsion between Tc and this nitrogen. The coordination geometry is best described as a trigonally distorted octahedron. As evident from electrochemical studies, at least two different stereoisomers exist in solution. Two compounds of the same composition could be isolated from the synthesis reaction, one product showing an irreversible oxidation at +1.02 V, the other major product at +0.17 V. The exact nature of the two isomers has not been elucidated.[583] (Scheme 68)



Scheme 68

5.2.2.6.3 Tertiary phosphine and arsine ligands in combination with other donors

Mixed halide-phosphine complexes of Tc^{II} date back to the early years of Tc chemistry. The first structurally characterized complex was $[TcCl_2(PPh(OEt)_2)_4]$ (**535**). This yellow complex was synthesized by the reaction of $[NH_4]_2[TcCl_6]$ with $PPh(OEt)_2$ and $Na[BH_4]$ as a reducing agent. The X-ray crystal structure shows the two chlorides *trans* and the four phosphines in a plane. Due to the packing requirements of the phosphine ligands, the octahedron is tetrahedrally distorted. When the reaction was performed in the absence of a reducing agent, the red cationic Tc^{III} complex $[TcCl_2(PPh(OEt)_2)_4]^+$ (**536**) formed in almost quantitative yield. Upon prolonged reaction with excess phosphonite ligand, the Tc^{III} complex reduced further to (**535**).[584,585] The corresponding diarsine complexes with *o*-phenylenebis(dimethylarsine) (opd, (**537**)) have been known for a long time. The complexes $[TcX_2(diars)_2]$ (**538**) are obtained by reduction of the Tc^{III} analogues with H_3PO_2.[183,586] Beside these "classical" diarsine-type complexes of Tc^{III} and Tc^{II}, the Tc^{V} precursor $[TcO(OH)(diars)_2]^+$ (**539**) has been shown to be a valuable precursor for

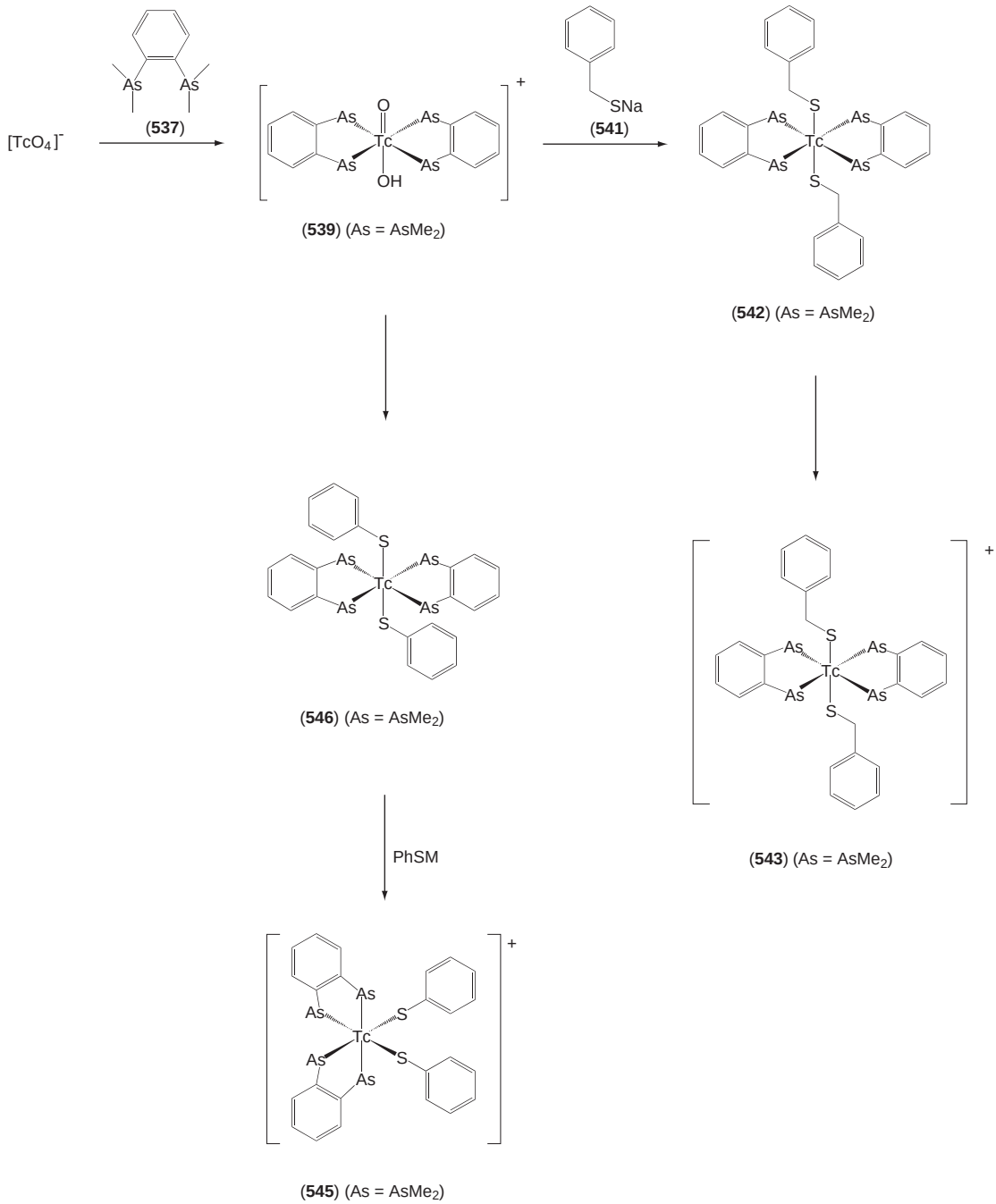
the preparation of mixed arsine-thiolato complexes. Dark yellow (**539**) is produced directly from $[TcO_4]^-$ with (**537**) in acidic MeOH and at elevated temperature, in 70% yield. When $NaSCH_3$ was added to this solution, the blue Tc^{III} complex *trans*-$[Tc(SCH_3)_2(opd)_2]^+$ (**540**) was produced in moderate yield. A similar reaction with $NaSCH_2Ph$ (Htbal, (**541**)) gave directly the corresponding blue-purple Tc^{II} complex $[Tc(SCH_2Ph)_2(opd)_2]$ (**542**) in 11% yield. This compound is not stable in solution, and decomposed over time to the blue Tc^{III} species *trans*-$[Tc(SCH_2Ph)_2(opd)_2]^+$ (**543**). The analogous blue-purple complex *trans*-$[Tc(SPh)_2(opd)_2]$ (**544**) was synthesized by the same route. By oxidation of the Tc^{II} complex with atmospheric oxygen, the isomer *cis*-$[Tc(SPh)_2(opd)_2]^+$ (**545**) was isolated in moderate yield. The isolation of the species *cis*-$[Tc(SPh)_2(diars)_2]$ was not possible. All the Tc^{III} complexes could be converted to the neutral Tc^{II} species by reduction with $[NBu_4][BH_4]$ in acetonitrile. The X-ray crystal structures of *trans*-$[Tc(SPh)_2(diars)_2]$ (**546**) and *trans*-$[Tc(SCH_3)_2(diars)_2]$ (**547**) were determined. Electrochemical investigations reveal that the complexes have reversible Tc^{III}/Tc^{II} and irreversible Tc^{III}/Tc^{IV} redox processes.[587] Similar reactions with corresponding bidentate phosphine ligands have been described in Section 5.2.2.5.4.[528,588,589] (Scheme 69)

The synthesis and properties of the Tc^{III} complexes $[TcX_2(dppe)_2]^+$ (**400**) with various bidentate phosphines have been described. These Tc^{III} compounds exhibit a rich electrochemistry, with reversible Tc^{III}/Tc^{II} redox couples.[258,487] It transpires that complexes of Tc^{II} such as $[Tc(NCS)_2(dppe)_2]$ with $[NCS]^-$ (**548**) are stable, in contrast to their analogues with halides. The redox couples for Tc^{III}/Tc^{II} and Tc^{II}/Tc^{I} are found at +0.39 V and −0.60 V vs. Ag/AgCl, respectively, clearly indicating the stability of the Tc^{II} compound. In contrast the first redox couple for the chloride complex is at −0.001 V. This dramatic stabilization presumably reflects the more effective π-accepting ability of $[NCS]^-$. The X-ray structure analysis of (**548**) confirms that the thiocyanates are nitrogen bound and are *trans*.[590] More recently, in an attempt to prepare cationic Tc complexes with monodentate phosphines, several phosphine $[NCS]^-$ complexes of Tc^{IV} and Tc^{II} have been prepared. The reaction of $[TcO_2(PR_3)_4]^+$ with excess NaNCS in CH_2Cl_2 gave the Tc^{IV} complex $[Tc(NCS)_4(PR_3)_2]$, (**377**). The reaction with $P(OMe)Ph_2$ or PMe_2Ph and $[TcO_4]^-$ in MeOH and in the presence of NaNCS gave the Tc^{II} complex *trans*-$[Tc(NCS)_2(PR_3)_4]$ (**549**) in moderate yield. The structures of both complexes were established showing that in complex (**549**) the $[NCS]^-$ ligands are *trans*.[469]

Complexes of the general formula *cis*(X),*trans*(P)-$[TcX_2(PR_2R')_2(L)]$ (R is Me or Et and R′ is Ph, L is bipy or phen) have been prepared by the replacement of one halide and one phosphine ligand in mer-$[TcX_3(PR_2R')_3]$ (**407**), followed by reduction to Tc^{II}. The green complex *cis*(X),*trans*(P)-$[TcX_2(PMe_2Ph)_2(bipy)]$ (**550**) has been prepared in this manner, as has the related, green terpy complex *trans*-$[TcBr(PMe_2Ph)_2(terpy)]^+$. For the latter complex, evidence suggests a two-step procedure, in which the terpy ligand first displaces one halide and one phosphine and displacement of a further halide is accompanied by reduction to Tc^{II}. Reduction is induced by addition of hydroxide, but does not take place in acetonitrile: only in EtOH. It is assumed that the reductant is in fact the ethoxide ion, which is oxidized to aldehyde, a well-known process for transition-metal ions.[591,592]

A similar approach for the preparation of the complexes with heterocyclic amines discussed above started from $[TcCl_3(PPh_3)_2(NCCH_3)]$ (**412**). Reaction with bipy, phen, or bpm gave directly the corresponding Tc^{III} complexes *fac*-$[TcCl_3(PPh_3)(NN)]$ (**428**), where NN is the heterocyclic amine. The same reaction starting from *mer*-$[TcCl_3(PMe_2Ph)_3]$ gave the corresponding complexes $[TcCl_2(PMe_2Ph)_2(NN)]^+$ (**427**) or $[TcCl_3(PMe_2Ph)(NN)]$ (**429**). The corresponding Tc^{II} complexes were formed as by-products (see Section 5.2.2.5.2). Upon the addition of KOH solution to complex (**427**), reduction to the corresponding green Tc^{II} complex (**550**) occurred. Heating (**427**) in MeOH under reflux and in the presence of excess PMe_2Ph gave the dark brown, cationic Tc^{II} complex $[TcCl(PMe_2Ph)_3(NN)]^+$ (**551**) in good yield.[593]

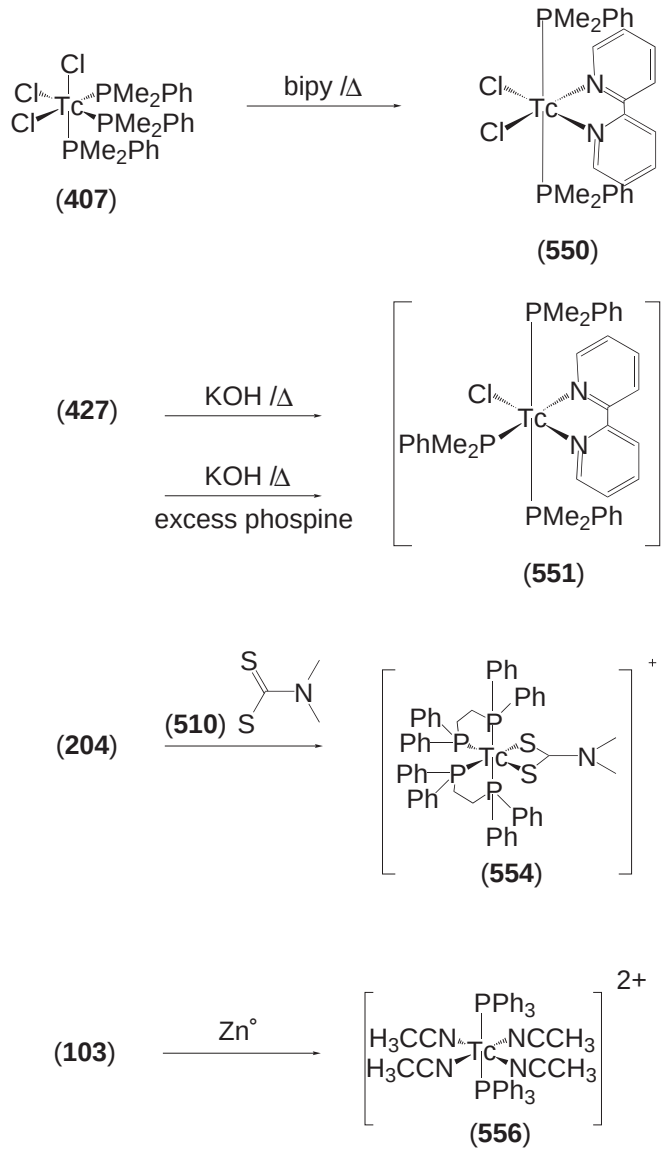
The direct reaction of $[TcO_4]^-$ in ethanolic solution with dppe and oxalic acid produces the red Tc^{II} complex $[Tc(ox)(dppe)_2]$ (**552**). Attempts to prepare similar complexes with succinic acid, phthalic acid, or salicylic acid failed, or the complexes were stable in solution only.[594] Similarly, cationic complexes of Tc^{II} are produced by reaction of the versatile precursor $[TcO(OH)(dppe)_2]^+$ (**204**) with various dithiocarbamates, which produces several complexes of general formula $[Tc(dtc)(dppe)_2]^+$ (**553**). For this reaction the reductant formamidine sulphinic acid (**510**) was required in an alkaline solution. The X-ray crystal structure of $[Tc(S_2CNMe_2)(dppe)_2]^+$ (**554**) shows a distorted octahedral geometry. Cyclic voltammetry reveals a reversible reduction wave Tc^{II}/Tc^{I} couple at −0.53 V, and a reversible oxidation at +0.3 V for the Tc^{III}/Tc^{II} couple.[595] The same compound (**554**) was also prepared from the thiourea precursor $[TcO(tmtu)_4]^{3+}$ (**91**).The reaction of this precursor in dmf in the presence of dppe produced a mixture of brown $[TcO(dtc)(tmtu)_2]^{2+}$ and the Tc^{II} complex (**553**). The first compound is probably an intermediate



Scheme 69

in the reaction. The coordinated dimethyl dithiocarbamate dtc is produced by rearrangement of the original thiourea ligands. The X-ray crystal structures of both complexes were determined.[221] The yellow, phosphine-containing Tc^{II} complex $[TcCl_2(PMe_2Ph)(dmpe)]$ (**555**) was prepared by concomitant substitution/reduction of the Tc^{III} precursor $[TcCl_3(PMe_2Ph)_3]$ with excess dmpe in ethanol. The structure shows a distorted octahedral geometry around the Tc.[596]

A novel and potentially very useful Tc^{II} complex with PPh_3 has been prepared. The reaction of $[TcCl_4(PPh_3)_2]$ (**103**) with Zn° in CH_3CN gave the Tc^{II} complex *trans*-$[Tc(NCCH_3)_4(PPh_3)_2]^{2+}$ (**556**), which was structurally characterized. This complex can be reduced with cobaltocene to the corresponding Tc^{I} complex $[Tc(NCCH_3)_4(PPh_3)_2]^{+}$ (**557**). This chemistry is mirrored by the reversible redox couple at −0.55 V vs. ferrocene for Tc^{II} / Tc^{I} (Scheme 70)[597].



Scheme 70

Macrocyclic thioether complexes of technetium are relatively rare. The first example of a sandwich-like complex has been described with Tc^{II}. The synthesis of $[Tc(9\text{-}S\text{-}3)_2]^{2+}$ (**495**) (see Section 5.2.2.5.4) was achieved by reaction of $[NBu_4][TcO_4]$ with 9-S-3 in refluxing acetonitrile, with $SnCl_2$ as reducing agent and $HBF_4{\cdot}Et_2O$ 85% yield. The magnetic moment is 1.8 μ_B at 310 K, which is consistent with that expected for a low-spin d^5 system with minimal orbital contribution. Cyclic voltammetry reveals quasi-reversible processes at +0.05 V and +1.4 V vs. SCE, corresponding to the Tc^{II}/Tc^{I} and Tc^{II}/Tc^{III} couples, respectively. Controlled potential electrolysis gave the corresponding pale yellow Tc^{III} and cherry-red Tc^{I} complexes. The X-ray crystal structure of (**495**) reveals an average Tc—S bond length of 2.38 Å.[598] As described in Section 2.5.4, what was believed to be the Tc^{I} complex $[Tc(9\text{-}S\text{-}3)_2]^{+}$ turned out to be a Tc^{III} complex in which one ring spontaneously expelled ethene, with C—S bond cleavage and formation of coordinated 1,5-dithiol-3-thiapentane.[544,545] This unusual behavior was investigated by ESI-MS, and theoretically by extended Hückel-theory MO calculations. The complexes $[Tc(9\text{-}S\text{-}3)_2]^{+/2+}$ were investigated in comparison to other isoelectronic 9-S-3 complexes such as Ru, Rh, or Pd. It was concluded from the theoretical calculations, that the C—S bond is indeed weakest in the Tc^{I} and Re^{I} complexes, followed by Tc^{II} and Re^{II}, while the C—S bonds in later transition metals

with d^5 and d^6 configuration are weakened much less significantly. The theoretical predictions are supported by the experimental results, in particular from ESI-MS.[599]

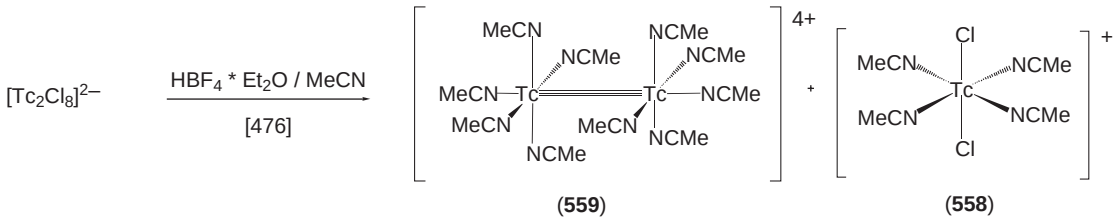
5.2.2.6.4 *Complexes of Tc^{II} with Tc—Tc multiple bonds*

As mentioned earlier in Section 5.2.2.5.2, the reaction of $[Tc_2Cl_8]^{2-}$ (**444**) in acetonitrile and with $HBF_4 \cdot Et_2O$ gave the Tc^{III} complex $[TcCl_2(NCCH_3)_4]^+$ (**558**) in 30% yield as a side product. The major product in this reaction was the unique and fully solvated blue ditechnetium cation $[Tc_2(NCCH_3)_{10}]^{4+}$ (**559**). This Tc^{II} complex has been prepared in several ways. These include the reaction of $HBF_4 \cdot Et_2O$ with $[Tc_2Cl_4(PEt_3)_4]$ in acetonitrile (81%), or reduction of $[TcCl_6]^{2-}$ in toluene with $^nBu_3SnH$ and subsequent acidification with $HBF_4 \cdot Et_2O$ (54%). Alternatively, starting from $[NBu_4]_2[Tc_2Cl_8]$ in acetonitrile, as described above, produced (**559**) in 14% yield beside the side product (**558**). The reaction of $[Tc_2(NCCH_3)_{10}][BF_4]_4$ with eight equivalents of $Tl(O_3SCF_3)$ gave the structurally characterized complex $[Tc_2(NCCH_3)_8(O_3SCF_3)_2][BF_4]_2$ (**560**) as a blue solid. It consists of two $[Tc(NCCH_3)_4]$ fragments which are linked by a short Tc—Tc triple bond of 2.122(1) Å. The pseudoplanar $[Tc(NCCH_3)_4]$ units are staggered with respect to each other, resulting in a torsion angle of 43.5°. The two triflate ligands are axial; ignoring triflates, the molecular cation has D_{4d} symmetry. A ground-state configuration of $\sigma^2\pi^4\delta^2\delta^{*2}$ is expected. The absence of δ-bonding between the technetium atoms means there is no rotation barrier between the two fragments, and the molecule adopts the sterically favored, staggered geometry. Complex (**559**) was characterized by spectroscopic methods. The ^1H NMR spectrum in CD_3NO_2 gave two separate signals from coordinated acetonitrile in a ratio of 4:1. As evident from the ^1H NMR in CD_3CN, the two axial ligands are readily displaced by solvent molecules.[516] Acetonitrile solutions of $[Tc_2(NCCH_3)_{10}][BF_4]_4$ gradually lose their color when exposed to light, and the process is accelerated by irradiating a sample with a tungsten lamp for 12–24 h. The mononuclear, fully solvated Tc^{II} complex $[Tc(NCCH_3)_6][BF_4]_2$ (**561**) could be precipitated from the solution and its structure was determined. The Tc center is coordinated to six acetonitrile ligands, with almost perfect octahedral geometry. The magnetic moment is 2.1 μ_B, as determined by the Evans method. A plausible mechanism for the formation of (**561**) could be that photoexcitation gives a mixed-valent, charge-separated Tc^I—Tc^{III} species that undergoes bond cleavage and subsequent comproportionation to the observed Tc^{II} species.[600] The lability of the coordinated ligand suggests that this compound could be a very versatile synthon for further Tc^{II} chemistry. A reversible reduction at −0.81 V vs. Fc^+/Fc and a quasi-reversible oxidation at +0.72 V were found. The analogous Re—Re bond cannot be broken under photolytic conditions.

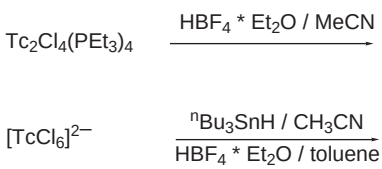
Reduction of $[Tc_2(NCCH_3)_{10}][BF_4]_4$ (**559**) in acetonitrile with cobaltocene leads to a mixed-valence Tc^I/Tc^{II} complex $[Tc_2(NCCH_3)_{10}][BF_4]_3$ (**562**), in which one acetonitrile adopts a very unusual μ,η^1,η^2 coordination mode. The reaction is performed at r.t. and the color gradually changes from blue to brown to give (**562**) in 70% yield. The X-ray crystal structure confirms the unusual coordination mode of one acetonitrile ligand which is bridging via its nitrogen atom, and binds furthermore via the nitrile carbon to one of the Tc centers. Based on the reduction potential of −0.82 V, it is believed that the complex is first reduced and then undergoes a rearrangement to the product complex. The question of which of the two nonequivalent Tc centers is in oxidation state +II cannot be answered conclusively. Electrochemical studies show that the mixed-valence complex can be further reduced at −1.12 V, probably to a bridged Tc^I Tc^I complex. The observed oxidation at +0.25 V would correspond to a bridged Tc^{II} Tc^{II} complex. Although these compounds have not so far been isolated, the observed redox chemistry is unparalleled among homoleptic acetonitrile complexes.[601] (Scheme 71)

5.2.2.7 Oxidation State (I)

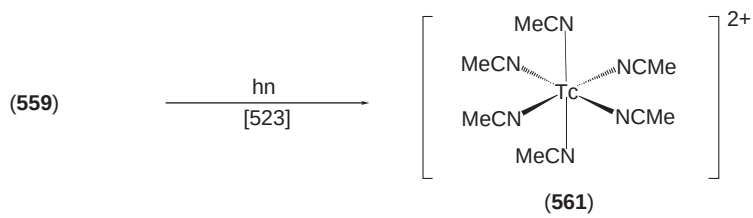
The chemistry of Tc^I is dominated by organometallic complexes. The relatively high electron density of the d^6 system demands stabilization by substantial participation of π-accepting ligands in the coordination sphere. Carbonyl, isocyanide, or phosphine ligands are thus, frequently encountered. Complexes containing cyclopentadienyl ligands are also quite numerous, but these classical organometallic complexes will not in general be treated here. The low-spin d^6 electronic configuration of the Tc^I center in an octahedral environment leads to 18-electron complexes, which explains both the thermodynamic and kinetic stability of many complexes. Tc^I chemistry



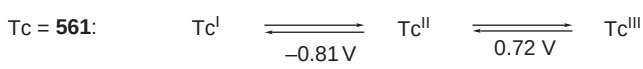
(**559**) (**558**)

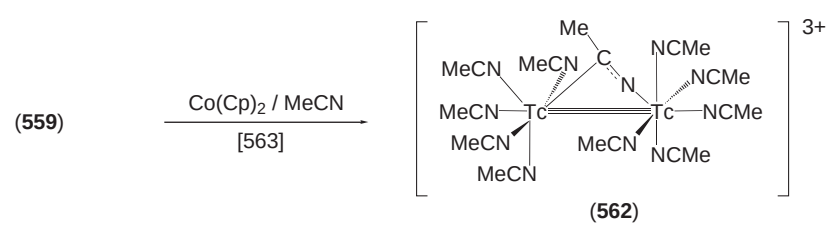


(**559**)

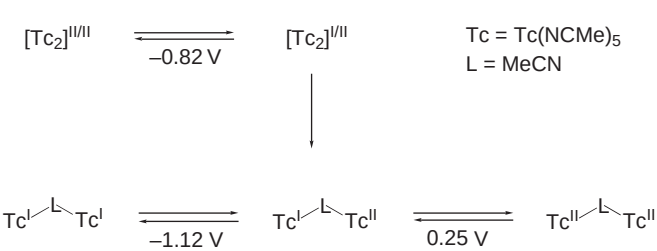


(**561**)





(**562**)



Scheme 71

became important in particular, since the preparation of cationic homoleptic isocyanide complexes allowed the preparation of useful myocardial imaging agents.

5.2.2.7.1 Complexes containing C and P ligands

The importance of cyanide in the development of the coordination chemistry of virtually all transition-metal elements is illustrated for technetium, where homoleptic cyano complexes are

among the first that appeared in the literature. The bright olive-green Tc^{I} complex $K_5[Tc(CN)_6]$ (**563**) was prepared directly from $[TcO_4]^-$ or from $[TcO(OH)(CN)_4]^{2-}$ (**219**) (see Section 5.2.2.3.2(ix)) by reduction with potassium amalgam in the presence of KCN.[602,603] The complex is isomorphous with the corresponding Mn and Re complexes. ν_{CN} is found in the IR at 1,950 cm^{-1}, slightly higher than for Re at 1,940 cm^{-1}. The compound is stable in dry air, but is readily oxidized to higher oxidation states when wet. Probably due to the stability of the cyanide ligands and the insolubility in common organic solvents, no attempts to substitute one or more cyanides have been undertaken. Nevertheless, (**563**) could represent an attractive starting material for the preparation of new, mixed-ligand compounds of Tc^{I} or other oxidation states.

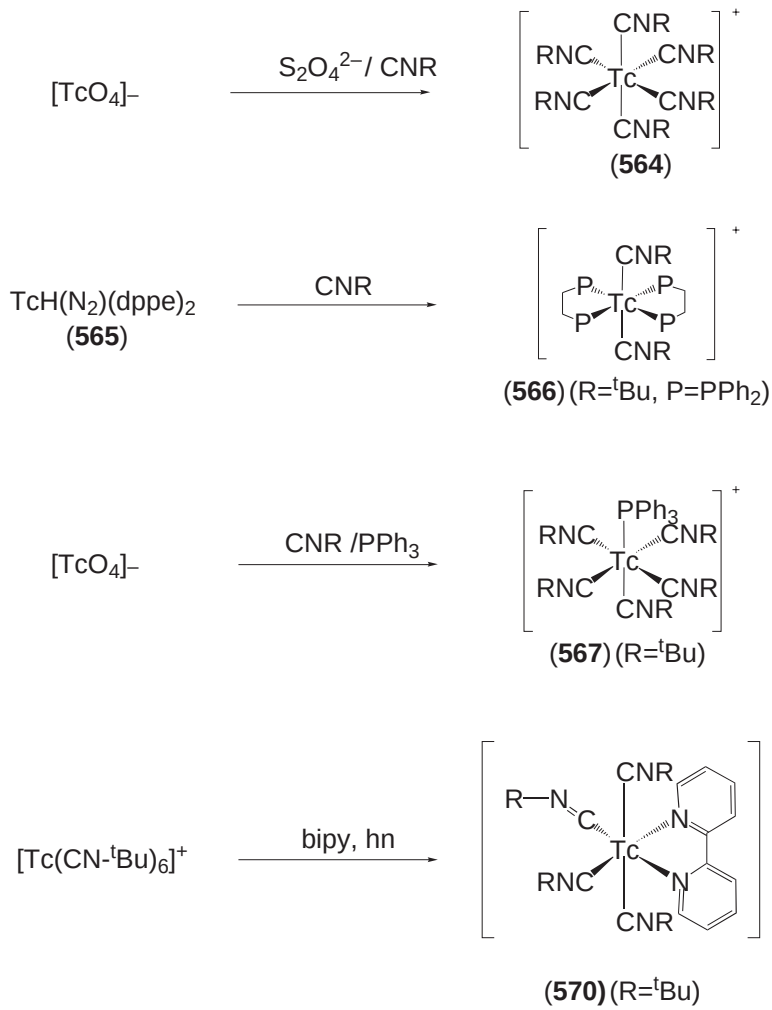
Although technically organometallic, the homoleptic isocyanide complexes of Tc^{I} $[Tc(CNR)_6]^+$ (**564**) have to be mentioned here since they represent a fundamental class of complexes, not only in terms of their chemistry but also because of their radiopharmaceutical application (see Section 5.2.3.1.1). In spite of their stability, they are important starting materials for further complexes. The reaction of $[NH_4][TcO_4]$ in alkaline water/EtOH under reflux for 30 min with various isocyanides and $[S_2O_4]^{2-}$ as reductant gave pale yellow (**564**) in moderate to very good yields. These isocyanide complexes display a reversible, one-electron oxidation in the range of +0.8 V to +1.2 V, depending on the organic substituent. The same reaction with $[ReO_4]^-$ was not successful, since $[S_2O_4]^{2-}$ is not a sufficiently strong reductant. With the alternative starting material $[ReOCl_3(PPh_3)_2]$, the Re^{I} compounds were produced in moderate yield.[485] The X-ray crystal structure of complex (**564**) showed a highly symmetric octahedral geometry. The Tc—C bond distances are 2.029(5) Å and the angles are almost rectangular.[604]

Mixed isocyanide/phosphine complexes can be obtained via several routes. The reaction of the suitable Tc^{I} starting material $[TcH(N_2)(dppe)_2]$ (**565**)[605] with excess $CNBu^t$ in MeOH under reflux gave colorless *trans*-$[Tc(CNBu^t)_2(dppe)_2]^+$ (**566**) in good yield. The ν_{CN} IR bands appear at 2,049 cm^{-1} and 2,079 cm^{-1} for $CNBu^t$, and at 2,058 cm^{-1} and 2,115 cm^{-1} for the corresponding cyclohexylisocyanide. The frequencies suggest a strong back-donation from Tc to isocyanide.[606] Since (**565**) is not a widely available starting material, an alternative route to mixed isocyanide/phosphine complexes was sought. The reaction of the Tc^{III} precursor $[Tc(tu)_6]^{3+}$ (**456**)[525] with dppe and $CNBu^t$ in EtOH under reflux gave the colorless compound (**566**) after 10 h, but only in low yield. The X-ray crystal structure confirmed the expected *trans* configuration and a Tc—C bond distance of 2.034(4) Å. The compound undergoes a reversible single electrochemical oxidation at +0.91 V vs. SCE, which is about +0.11 V higher than for the Re analogue.[607] The preparation of mixed isocyanide Tc^{I} complexes of the type $[Tc(CNR)_x(CNR')_{(6-x)}]^+$ from (**456**) has been explored. Heating (**456**) under reflux in MeOH with a mixture of CNR and CNR′ in various ratios and in an overall hundredfold excess gave mixtures of all possible complexes. Since they all exhibit different chemical shifts in ^{99}Tc NMR spectroscopy, the relative amounts of each present could be estimated directly from integration of the NMR spectra. Their chemical shifts range from −1,800 ppm to −1,840 ppm. The preparation of mixed-ligand complexes by conproportionation of pure compounds $[Tc(CNR)_6]^+$ and $[Tc(CNR')_6]^+$ under reflux for hours failed. No ligand exchange occurred at all, reflecting the very high kinetic stability of binary Tc^{I} isocyanide complexes. Treatment of, e.g., $[Tc(CN\text{-}R)_6]^+$ with a large excess of CN–R′ under forcing conditions was equally unsuccessful. This behavior clearly implies that the mixed isocyanide complexes must be formed prior to reduction to Tc^{I}, or no exchange would occur.[608]

Direct reaction of $[NH_4][TcO_4]$ with $CNBu^t$ in the presence of PPh_3 under reflux in EtOH gave, after 1 h, the white cationic complex $[Tc(CNBu^t)_5(PPh_3)]^+$ (**567**) in poor yield. The five isonitrile ligands give rise to three IR bands, at 2,170, 2,094, and 2,059 cm^{-1}. Similar conditions with less $CNBu^t$ gave the complex $[Tc(CN\text{-}^tBu)_4(PPh_3)_2]^+$, again in poor yield. The ν_{CN} IR bands for the complexes appear at 2,154, 2,090, and 2,059 cm^{-1}. The ^1H NMR implies that the two phosphines are *trans*. Interestingly, for these syntheses the phosphines adopt the function of reducing agents.[609] This synthetic approach was optimized using the Tc^{III} complex *mer*-$[TcCl_3(PMe_2Ph)_3]$ (**407**) as a starting material. When this complex was heated in EtOH under reflux in the presence of 10 equivalents of $CNBu^t$, the mixed-ligand complex $[Tc(CNBu^t)_4(PMe_2Ph)_2]^+$ (**568**) was produced in 50% yield, and a higher excess of the isocyanide produced $[Tc(CNBu^t)_5(PMe_2Ph)]^+$ (**569**) in 35% yield. The X-ray crystal structures of both complexes were elucidated. It is again interesting that the complex (**568**) could not be converted into (**569**) even under forcing conditions.[610]

Due to their high kinetic stability, the homoleptic isocyanide complexes of Tc^{I} undergo only a limited number of subsequent reactions. When (**564**) (R = ^{t}Bu) is irradiated with a UV lamp for four days in acetonitrile with bipy, the color of the solution becomes deep red and the red-orange compound $[Tc(CN^tBu)_4(bipy)]^+$ (**570**) can be isolated in 6% yield. The same reaction with a number of bipy derivatives such as Me_2bipy, Me_4phen, or NO_2phen gave analogous compounds

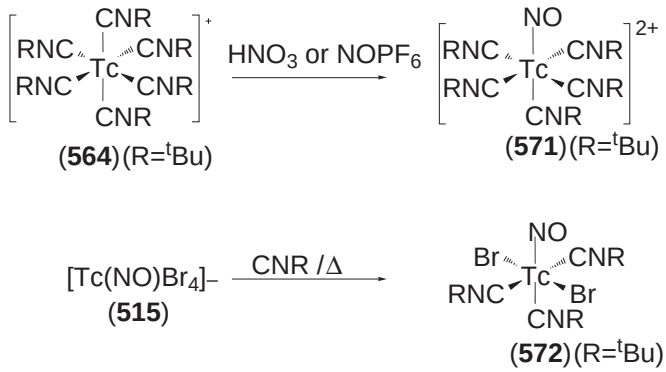
in comparably low yields. The direct reduction of $[TcO_4]^-$ in alkaline water with $[S_2O_4]^{2-}$ in the presence of different bipy derivatives and $CNBu^t$ gave the complexes (**570**), $[Tc(CNBu^t)_4(Me_4phen)]^+$, $[Tc(CNBu^t)_4(Me_2bipy)]^+$, and $[Tc(CNBu^t)_4(NO_2phen)]^+$, in variable yields. The structure of (**570**) was determined. The most remarkable feature is the bent C—N—C angle at one of the isocyanide ligands *trans* to bipy (148°). The Tc—C bond distance of 1.90(2) Å is significantly shorter than for normal isocyanides. It appears that the σ-donating properties of the bipy ligand allow the Tc center to back-donate electrons into the Tc—C bond, to the point where the bent nitrogen rehybridizes. The oxidation state of Tc is now formally +III as a consequence of the intramolecular oxidation of Tc^I, which is supported by ^{99}Tc NMR data in which the chemical shift is in a range typical for Tc^{III} complexes at around −860 ppm. The isocyanide nitrogen can be protonated with strong acids, which is typical behavior for electron-rich metal sites.[611] (Scheme 72)



Scheme 72

The oxidation potential of the homoleptic isocyanide complexes (**564**) suggests that they could be oxidized to the corresponding Tc^{II} complexes $[Tc(CNR)_6]^{2+}$ with moderate oxidizing agents such as NO^+. This reaction is well established for the Mn analogues. However, the reaction of $[Tc(CNBu^t)_6]^+$ with various oxidizing agents, such as $NOPF_6$ or nitric acid in glacial acetic acid, led to the formation of the yellow nitrosyl Tc^I complex $[Tc(NO)(CNBu^t)_5]^{2+}$ (**571**) in good yields, which has ν_{CN} in the IR spectrum at 2,220 cm^{-1} and 2,240 cm^{-1} and ν_{NO} at 1,865 cm^{-1}. There was no detectable reaction with NO gas. The reaction of the Tc^{II} starting material $[Tc(NO)Br_4]^-$ (**515**) with $CNBu^t$ in MeOH under reflux gave the purple Tc^I complex $[Tc(NO)Br_2(CNBu^t)_3]$ (**572**), with ν_{CN} at 2,230 cm^{-1} and 2,160 cm^{-1} and ν_{NO} at 1,755 cm^{-1}. Both complexes are formally 18-electron

species. The relatively high frequencies of all these IR bands reflect the 2+ charge, and indicate that π-backbonding does not play an important role. The X-ray structure of the complex (**572**) was determined. One $CNBu^t$ is *trans* to the NO ligand, the two Br^- are *trans*, and the CN^tBu ligands are therefore meridional. Due to the strong *trans* effect of the NO ligand, the Tc—C distance *trans* to it is significantly elongated. In contrast, attempts to prepare the analogous Mn nitrosyl compound failed, and only the homoleptic Mn^{II} complexes $[Mn(CNBu^t)_6]^{2+}$ were isolated (Scheme 73)[612].



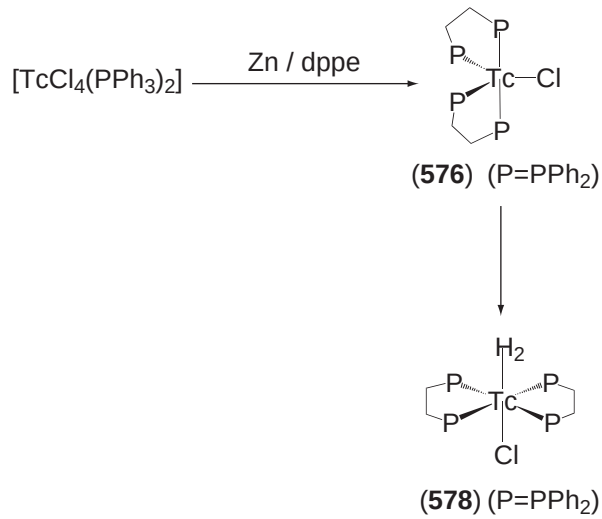
Scheme 73

5.2.2.7.2 Tertiary phosphines and dihydrogen complexes

A homoleptic Tc^I complex with phosphine ligands was first produced by the direct reaction of $[TcO_4]^-$ with dmpe in strongly alkaline water/EtOH mixture at 132 °C for 1 h. Precipitation with bulky anions gave the Tc^I complex $[Tc(dmpe)_3][PF_6]$ (**206**) as colorless crystals in moderate yield. The complex can also be prepared from $[TcO_2(dmpe)_2]^+$ (**203**) or *trans*-$[TcCl_2(dmpe)_2]^+$ (**205**).[358] Electrochemical studies revealed that the Tc^I compounds $[Tc(dmpe)_3]^+$ and $[Tc(depe)_3]^+$ undergo reversible oxidation to the corresponding Tc^{II} complex at a moderate potential. For the dmpe ligand, the oxidation potential in DMF for Tc^{II}/Tc^I is at +0.422 V (vs. SCE) and for depe at +0.276 V.[488] The purple Tc^{II} complexes $[Tc(dmpe)_3]^{2+}$ (**573**) and $[Tc(depe)_3]^{2+}$ (**574**) could be prepared in acetonitrile by oxidation of (**206**) with H_2O_2 and precipitation with saturated $[NH_4][PF_6]$ solution. The synthesis of the Tc^I complex with the monodentate phosphite ligand $[Tc(P(OCH_3)_3)_6]^+$ (**575**) is accomplished in a similar manner, by reaction of the phosphite with $[TcO_4]^-$ in a sealed pressure bottle at 100 °C in MeOH for 0.5 h. The ease with which reduction from Tc^{VII} to Tc^I takes place with $P(OCH_3)_3$ is remarkable and confirms the reductive capabilities of this phosphite ligand. The ^{99}Tc NMR spectrum of (**575**) exhibits the expected septet centered at −422 ppm vs. $[TcO_4]^-$, with a Tc–P coupling constant of 909 Hz.[613]

The first η^2-H_2 complex of Tc has been prepared by the treatment of $[TcCl_4(PPh_3)_2]$ (**103**) with Zn powder and dppe to give as a first step the deep green, 16-electron species $[TcCl(dppe)_2]$ (**576**), which is extremely reactive towards oxygen. This strong Lewis acid is stable under an inert gas atmosphere, but readily forms the yellow N_2 complex $[TcCl(N_2)(dppe)_2]$ (**577**), reversibly, when exposed to nitrogen. In solution, the structure of complex (**576**) is dynamic, whereas in the solid it adopts trigonal-bipyramidal geometry with the chloride in the basal plane. Surprisingly, the complex does not appear to undergo any *o*-metalation reactions with the phosphine phenyl groups. Reaction with H_2 leads to an instantaneous color change to yellow, and the formation of $[TcCl(H_2)(dppe)_2]$ (**578**). The H_2 resonance in ^1H NMR appears at −13.3 ppm. An X-ray crystal structure analysis confirmed the octahedral geometry but, because of disorder, the H_2 could not be located. However, the visualized pentagonal pyramid formed by the other ligands indicates the presence of the η^2-H_2 ligand. Furthermore, the T_1 criterion as a discrimination between classical and nonclassical "H_2" coordination showed between 200 K and 300 K a sharp V-shaped plot, as predicted by theory, and a minimum T_1 value at 20+/−2 ms at 245 K, supporting the σ-coordination of H_2. The isolation of $[TcCl(dppe)_2]$ is vital in the synthesis of Tc dihydrogen complexes.[614] $[TcCl(dppe)_2]$ has also been utilized for the synthesis of carbene and carbyne complexes of Tc^I.[615]

The interesting mixed aqua-phosphine compound $[Tc(OH_2)_2(dppe)_2]^+$ (**579**) has been produced as a by-product in the preparation of $[TcNCl_2(PPh_3)_2]$ (**227**). This is one of the rare cases of low-valent Tc complexes containing water as a ligand. The X-ray crystal structure confirmed that the H_2O ligands are *trans*, with elongated Tc—O distances of 2.252 Å and 2.307 Å. Although no further chemistry has been reported, this interesting compound merits further study.[616] (Scheme 74)



Scheme 74

5.2.2.7.3 Dinitrogen complexes and nitrogen ligands

The N_2 complex $[TcCl(N_2)(dppe)_2]$ (**577**) was described in the previous section. The related hydrido dinitrogen complex can be prepared by the reduction of (**103**) in benzene with sodium amalgam under an N_2 atmosphere, in the presence of dppe. The yellow and air-stable complex $[TcH(N_2)(dppe)_2]$ (**565**) was isolated[605] and structurally characterized.[617] The hydrido ligand is *trans* to N_2 and the Tc—N distance is 2.05(1) Å. In the ^1H NMR the hydride resonance is found at −10.1 ppm. As already demonstrated (see previous section), (**565**) is a versatile starting material for Tc^I, as both the dinitrogen ligand and the hydride can be replaced by appropriate ligands. When (**565**) is dissolved in benzene under an atmosphere of CO, the complex $[TcH(CO)(dppe)_2]$ (**580**) is formed in good yield, and has ν_{CO} at 1,859 cm^{-1}. If complex (**580**) is heated under reflux in acetonitrile, the hydride ligand is replaced and the cationic complex *trans*-$[Tc(CO)(NCCH_3)(dppe)_2]^+$ (**581**) is formed in 57% yield, with the ν_{CO} at 1,882 cm^{-1}. The reaction of (**565**) with various isocyanides or $P(OCH_3)_3$ replaces the N_2 ligand cleanly, with formation of $[TcH(CNR)(dppe)_2]$ (**582**) or $[TcH(P(OCH_3)_3)(dppe)_2]$ (**583**). Similarly, $[TcH(CN\text{-}R)(dppe)_2]$ in acetonitrile gives $[Tc(CNBu^t)(NCCH_3)(dppe)_2]^+$ (**584**), in 59% yield. The *trans* disposition of the $CNBu^t$ and CH_3CN ligands is confirmed by ^{99}Tc NMR, where the Tc resonance is split into a quintet disposition due to coupling to the four equal phosphorus donors.[618]

A complex with a bridging N_2 ligand has been prepared from $[Tc\{HB(pz)_3\}(CO)_3]$ (**585**) by UV irradiation. One CO ligand is cleaved in a coordinating solvent, and the intermediate $[Tc\{HB(pz)_3\}(CO)_2(sol)]$ reacts with N_2 to give the dinuclear, μ-N_2-bridged, brown complex $[Tc\{HB(pz)_3\}(CO)_2]_2(\mu\text{-}N_2)$ (**586**) in 15% yield. The X-ray crystal structure reveals that the Tc—N bond distances are 2.19 Å and 2.21 Å, and that the N–N distance of 1.160(3) Å is slightly longer than in elemental N_2.[619] When $[Tc(NCCH_3)_3(CO)_3]^+$ (**587**), which is prepared from $[TcBr(CO)_5]$, is reacted with tri- and bidentate ligands such as 9-N-3, 9-S-3, or bipy, the complexes $[Tc(9\text{-}N\text{-}3)(CO)_3]^+$ (**588**), $[Tc(9\text{-}S\text{-}3)(CO)_3]^+$ (**589**), and $[Tc(NCCH_3)(bipy)(CO)_3]^+$ (**590**) are formed in very good yield. The reaction of (**590**) with two equivalents of tertiary phosphines gave complexes of the type $[Tc(PR_3)_2(bipy)(CO)_2]^+$ (**591**).[620]

As mentioned in Section 5.2.2.6, the reaction of $[TcCl_3(PPh_3)_2(NCCH_3)]$ (**412**) with Zn dust with heterocyclic amines produces complexes of Tc in oxidation states +III, +II, and +I. When $[TcCl_3(terpy)]$ (**421**) prepared in this manner is reacted with Zn dust in pyridine, the two Tc^I complexes $[Tc(terpy)(py)_3]^+$ (**530**) and *trans*-$[TcCl(terpy)(py)_2]$ (**529**) are formed. The X-ray structures of both compounds were elucidated. Electrochemical data for the complex (**529**) shows a

reversible Tc^{III}/Tc^{II} couple at 0.41 V and a Tc^{II}/Tc^{I} couple at −0.82 V vs. NHE, whereas the cationic complex (**528**) had corresponding redox processes at +0.7 V and −0.43 V vs. NHE.[502]

A further example of a complex containing no Tc—C bonds with a formal Tc^{I} oxidation state is provided by chelating diazene ligands. When $[NBu_4][TcO_4]$ is reacted with the organohydrazine hydrazaline $C_8H_5N_2NH\text{-}NH_2$ (hypyz, (**338**); see also Section 5.2.2.3.5) in MeOH under reflux, the green-blue tris-diazene complex $[Tc(hypyz)_3]^+$ (**592**) is formed in 55% yield. The reaction involves a six-electron reduction of Tc^{VII}, which is accomplished by oxidizing each of the three organohydrazines by two electrons, which then coordinate as neutral diazenes. The compound was characterized by FAB-MS, IR and ^{99}Tc NMR spectroscopy. It has been proposed that the NH ligands adopt a facial arrangement. For further discussion of the ^{99}Tc NMR spectrum, see Section 5.2.2.8.1.[426]

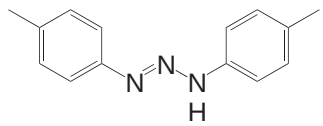
The reactivity of the versatile Tc^{I} starting materials $[TcCl(PMe_2Ph)_3(CO)_2]$ (**410**)[496] and *mer*-$[TcCl(PPh_3)_2(CO)_3]$ (**593**) towards pseudoallyl ligands such as triazenido, formamidinato, and acetamidinato has been investigated. Deprotonation of ArNHXNAr (X = N, Htaz, (**594**), X = CH, Hfaz, (**595**), X=CCH_3, Haaz, (**596**)) with BuLi in benzene and addition of the complex (**410**) gives, after 3 h under reflux, the general complexes $[Tc(PR_3)(CO)_2(ArNXNAr)]$ (X = N, $C(CH_3)$ and CH, (**597**)). The color of the compounds ranges from orange to pale yellow and the yields are in general very good. For all of the complexes the phosphine ligands are *trans*, and ν_{CO} appears as two strong bands at 1,920 cm^{-1} and 1,840 cm^{-1} in the IR, suggesting *cis* CO arrangement. The slight increase in CO stretching in comparison to (**410**) is reasonable based on the π-acceptor order CO > pseudoallyl > phosphine. The triazenido complex shows an IR band at 1,260 cm^{-1}, which is characteristic for the chelating ligand.[621] The reaction of (**593**) with the lithium salt of *N*-2-hydroxy-benzylidene-2-thiazolylimine (Hohbt, (**598**)) leads to replacement of one halide and one CO and formation of the red-violet, structurally characterized species $[Tc(ohbt)(PPh_3)_2(CO)_2]$ (**599**). The ohbt ligand is bound via the imine N and the deprotonated hydroxy group, and the ν_{CO} is at 1,940 cm^{-1} and 1,855 cm^{-1}.[622] The tridentate amine ligands $[HB(pz)_3]^-$ and 9-N-3 react with (**593**) to substitute the halide, one CO, and one phosphine to yield the cationic complexes [Tc(9-N-3)$(CO)_2(PPh_3)]^+$ (**600**) and $[Tc\{HB(pz)_3\}(CO)_2(PPh_3)]$ (**601**) in good yields. These complexes have been structurally characterized and no isomers were detected. The ν_{CO} values are at 1,936 cm^{-1} and 1,849 cm^{-1} for (**601**) and at 1,937 cm^{-1} and 1,856 cm^{-1} for (**600**).[623]

Another example of a facially coordinating tridentate nitrogen ligand was described quite early in the context of porphyrin chemistry. When $[Tc_2(CO)_{10}]$ (**602**) is reacted in boiling decaline with mesoporphyrin IX dimethyl ester (H_2MP), the Tc^{I} complex $[Tc(CO)_3]_2(\mu\text{-MP})$ (**603**) is produced, in which the X-ray structure confirmed that the two Tc centers occupy the two different faces of the porphyrin plane.[624] The X-ray structure confirmed this quite uncommon configuration. Each Tc is coordinated to three adjacent pyrrole nitrogen atoms; two of the nitrogens coordinate to both Tc, whereas the other two are bound to one Tc only. The mechanism of formation is remarkable. When the ratio H_2MP/Tc is about 1, the mononuclear complex (**604**) is observed and can be isolated. However, when the same reaction is carried out for longer periods of time, only the dinuclear complex (**603**) and free H_2MP are present. Similarly, the isolated mononuclear complex (**604**) disproportionates thermally into the dinuclear complex and free H_2MP, implying that the mononuclear complex is a kinetic intermediate. The ν_{CO} resonances in the IR appear at 2,025 cm^{-1} and 1,925 cm^{-1} for the mononuclear species, and at 2,036 cm^{-1} and 1,925 cm^{-1} for the dinuclear complex (Scheme 75).[625]

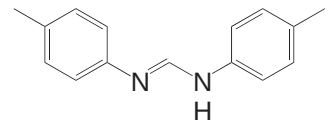
5.2.2.7.4 Nitrosyl and thionitrosyl ligands

In addition to the nitrosyl complexes mentioned above in the context of isocyanides in Section 5.2.2.7.1, there are limited numbers of other NO and NS species formally containing Tc^{I}. The direct reaction of $[TcNCl_4]^-$ (**34**) with heterocyclic amines as solvent and $[S_2O_4]^{2-}$ as reducing agent produces green *mer*-$[TcCl_2(NS)(py)_3]$ (**605**) and *mer*-$[TcCl_2(NS)(pic)_3]$ (**606**), respectively, in good yields. Both have ν_{NS} at 1,173 cm^{-1}. The X-ray crystal structure of the picoline complex confirmed the formula. The Tc—NS bond is 1.73 Å and is therefore significantly shorter than a normal Tc—N bond, implying substantial π-bonding. Other thionitrosyl complexes have been made with S_2Cl_2 as the sulfur donating agent; it appears that dithionite can serve the same purpose with the advantage of also being a powerful reducing agent. It is known that $[S_2O_4]^{2-}$ is in equilibrium with $[SO_2]^-$, which is a good one-electron reductant.[626]

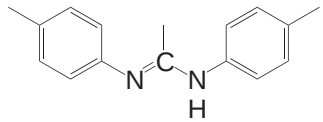
The reaction of $[Tc(NO)Cl_4]^-$ (**516**) with PPh_3 in acetonitrile gave, after 6 h under reflux, the orange-yellow Tc^{I} complex $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ (**607**), in 71% yield[627] (ν_{NO} 1,721 cm^{-1}).



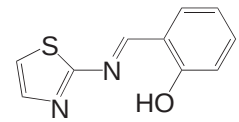
(**594**)



(**595**)

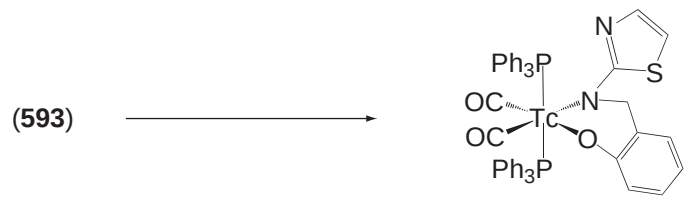


(**596**)

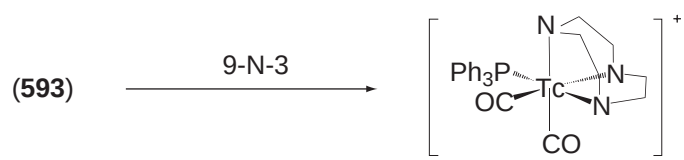


(**598**)

(**410**) (**597**)



(**593**) (**599**)



(**593**) 9-N-3 (**600**)

Scheme 75

This complex is a versatile starting material for the preparation of further Tc^{I} nitrosyl compounds. It has a similar reactivity to $[TcCl_3(PPh_3)_2(NCCH_3)]$ (**412**), in that the acetonitrile and one halide are easily replaced by incoming ligands.[628] Thus reaction with one equivalent of a xanthate or mercaptopyridine gave complexes of the types $[Tc(NO)Cl(PPh_3)_2(S_2COR)]$ (**608**) and $[Tc(NO)Cl(PPh_3)_2(S\text{-py})]$ (**609**) in good to very good yield. The complexes are bright yellow, with ν_{NO} around 1,700 cm^{-1}. With an excess of xanthate, further substitution of a chloride and one PPh_3 was achieved, and the bright red compounds $[Tc(NO)(PPh_3)(S_2COR)_2]$ (**610**) were formed. The product is determined by reaction stoichiometry and similar selectivity can be achieved with (**412**) and xanthates. IR characterization of these xanthate derivatives suggests that the linear NO^{+} binding mode has not been changed by the ligand exchange, as ν_{NO} remains around 1,700 cm^{-1}. Spectroscopic analysis of the bis-xanthate complexes by ^{1}H NMR is straightforward, with no fluxional behavior evident, and is consistent with one xanthate in a *cis*,*cis* position relative to the nitrosyl group and the other one *cis*,*trans*.[629] When $[Tc(NO)Cl_4]^{-}$ [55,574] is reacted

with PPh_3 in MeOH, the orange-pink solvent complex $[Tc(NO)Cl_2(PPh_3)_2(HOCH_3)]$ (**611**) is formed in 56% yield. If $[Tc(NO)Cl_2(PPh_3)_2(NCCH_3)]$ (**607**) is heated under reflux in pyridine for 24 h, the two phosphines and the $NCCH_3$ ligand are replaced by py and the structurally characterized red complex $[Tc(NO)Cl_2(py)_3]$ (**612**) is formed. The same reaction in neat pyridine at room temperature gave deep orange $[Tc(NO)Cl_2(PPh_3)(py)_2]$ (**613**), and with pyridine in MeOH under ambient conditions the monosubstituted, bright orange complex $[Tc(NO)Cl_2(PPh_3)_2(py)]$ (**614**) was produced. The reaction of (**611**) with terpy under reflux gave dark green $[Tc(NO)Cl_2$ (terpy)] (**615**), whereas with phen the dark purple $[Tc(NO)Cl_2(PPh_3)(phen)]$ (**616**) is formed.[630]

The reaction of (**412**) with the organohydrazine 2-hydrazinopyridine (hypy, (**337**)) in MeOH under reflux replaces the $NCCH_3$ ligand, one phosphine, and the dark purple organodiazene complex $[Tc(NO)Cl_2(PPh_3)(HN{=}NC_5H_4N)]$ (**617**) is formed in 85% yield. The X-ray crystal structure shows a chelating diazene ligand, with the pyridine nitrogen *trans* to NO. When 2-hydrazino-4-trifluoromethyl)pyrimidine is reacted the same way in CH_2Cl_2, the diazenido complex $[Tc(NO)Cl(PPh_3)_2(N{=}NC_5H_2N_2CF_3)]$ (**618**) is formed. Here the product contains a diazenide derived from the organohydrazide ligand, and a chloride is consequently lost instead of a PPh_3.[631] (Scheme 76)

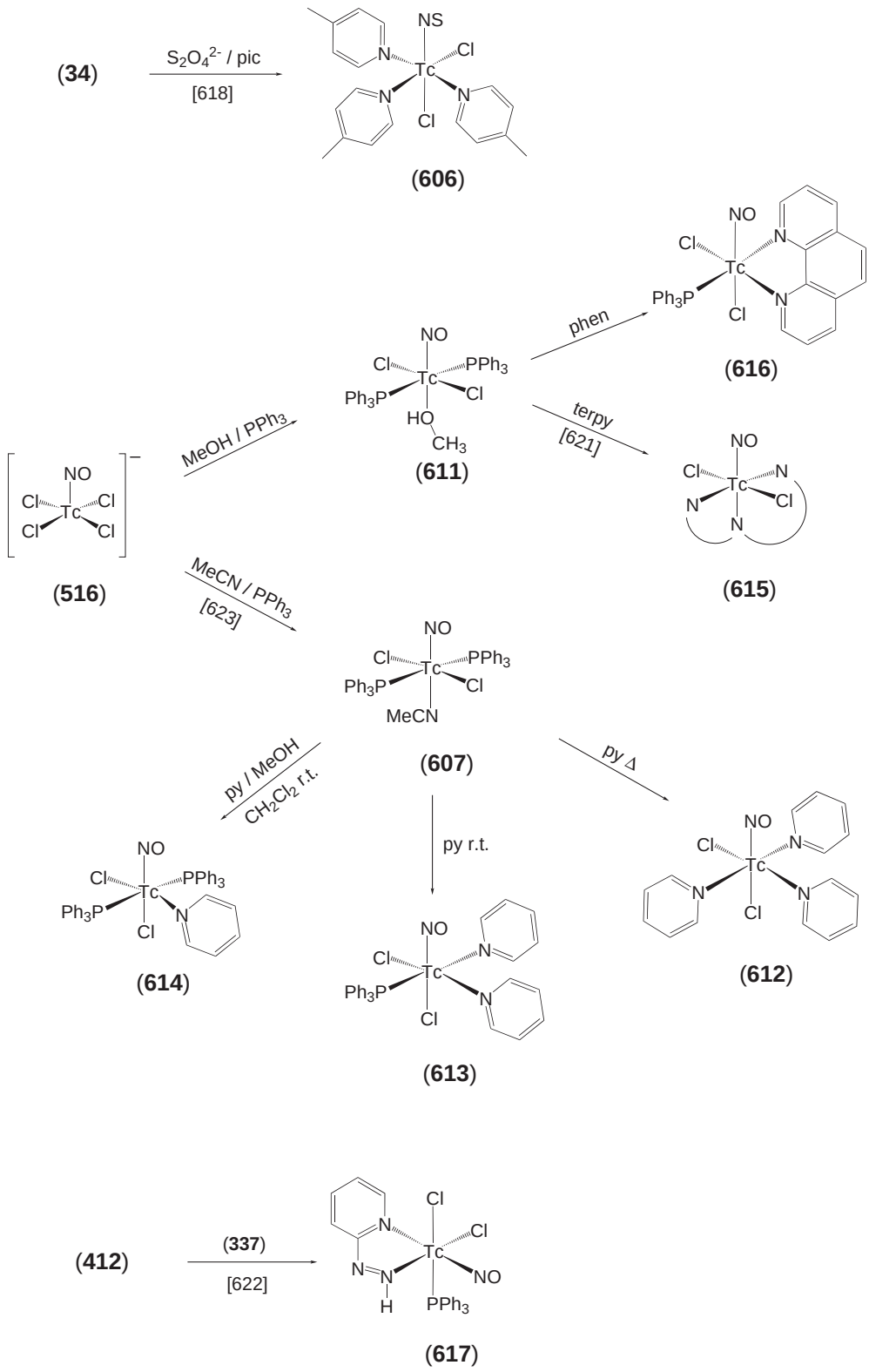
5.2.2.7.5 CO complexes

Organometallic complexes in general are not regarded as being compatible with the aqueous aerobic conditions normally encountered in radiopharmaceutical chemistry, although hexakis (isocyanide) complexes of Tc^I suggest the contrary. Complexes incorporating the *fac*-$[Tc(CO)_3]^+$ core have been shown to be versatile starting materials for the preparation of classical coordination compounds in water. When $[TcO_4]^-$ or $[TcOCl_4]^-$ react with $BH_3{\cdot}THF$ under 1 atm of CO, the water-soluble, colorless, dianionic complex $[TcCl_3(CO)_3]^{2-}$ (**620**) is formed in good to very good yield.[632] The unusual, hydride-bridged, trinuclear complex $[Tc_3(\mu\text{-}H)_3(CO)_{12}]$ (**621**) was isolated as an intermediate and structurally characterized.[633] Upon dissolution in water or organic coordinating solvents, complexes of general formula $[Tc(sol)_3(CO)_3]^+$ are readily formed, of which the organometallic aqua-ion $[Tc(OH_2)_3(CO)_3]^+$ (**622**) is of particular importance in the context of radiopharmacy. This precursor reacts with many mono-, bi-, or tridentate ligands in water and in organic solvents, and this chemistry has been reviewed.[63] The reaction with $CNBu^t$ readily gives the complexes $[TcCl(CNBu^t)_2(CO)_3]$ (**623**) and cationic $[Tc(CNBu^t)_3(CO)_3]^+$ (**624**), which have been structurally characterized. The reaction with S-donors such as 2-mercaptoethanol (HSetoh) leads to the triply-bridged complex $[Tc_2(\mu\text{-}SEtoh)_3(CO)_6]^-$ (**625**), which also has structurally been characterized.[632] In alkaline water, $[Tc(OH_2)_3(CO)_3]^+$ is hydrolyzed reversibly to dinuclear $[Tc_2(\mu\text{-}OH)_3(CO)_6]^-$ (**626**), trinuclear $[Tc_3(\mu\text{-}OH)_3(\mu^3\text{-}OH)(CO)_9]^-$ (**627**), and tetranuclear $[Tc_4(\mu^3\text{-}OH)_4(CO)_{12}]$ (**628**).[634,635] Reaction of (**620**) in MeOH with tridentate and hexadentate thiacrowns produced $[Tc(9\text{-}S\text{-}3)(CO)_3]^+$ *(**629**), $[Tc_2(18\text{-}S\text{-}6)(CO)_6]^{2+}$ (**630**), and $[Tc_2(20\text{-}S\text{-}6)(CO)_6]^{2+}$ (**631**), all in good yield, and these were structurally characterized.[636] The halide-free tri-aquo species (**622**) can be prepared as for (**620**) directly from water and $[^{99m}TcO_4]^-$ in quantitative yield for ^{99m}Tc, using $Na[BH_4]$ as reductant under 1 atm of CO, or more directly and elegantly using the compound boranocarbonate $[H_3BCO_2H]^-$, which acts both as reductant and source of CO (see Section 5.2.3.1.2).[637,638] (Scheme 77)

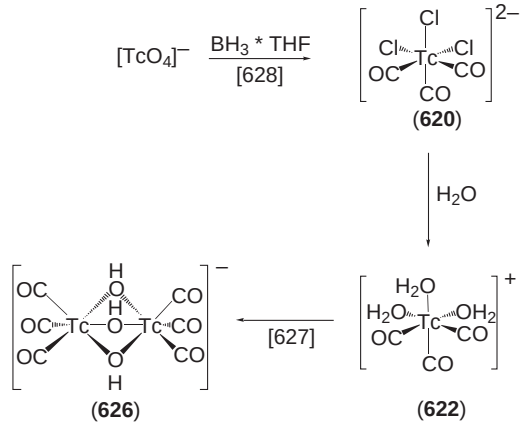
5.2.2.8 Selected Topics in Technetium Chemistry

5.2.2.8.1 ^{99}Tc NMR spectroscopy

Of the many spectroscopic tools that have been employed to investigate Tc complexes, ^{99}Tc NMR is the least known. However, a number of thorough studies discussed later in this section show that ^{99}Tc NMR spectroscopy is a very versatile and convenient method to follow reactions in solution, and to gather some mechanistic insights. Moreover, the chemical shifts give information about the electronic state of the Tc. One of the key advantages of the ^{99}Tc nucleus is its very high receptivity. It is the fourth most sensitive nucleus for NMR detection, 2,134 times more receptive than ^{13}C and 0.275 times than ^1H. Since only one isotope is available, no "isotope dilution" takes place. The gyromagnetic ratio is 6.0211 and the quadrupole moment is 0.3×10^{-25} cm^2.[639] Usually a solution of $[NH_4][TcO_4]$ in D_2O is used as the relative reference for quoting the chemical shifts of new compounds. The exact resonance of this sample was determined to be at


(34)
$S_2O_4^{2-}$ / pic
[618]
NS
Cl
Tc
N
Cl
(606)
NO
Cl
Tc
N
Ph3P
Cl
N
(616)
phen
NO
Cl
PPh3
Tc
Ph3P
Cl
HO
CH3
(611)
terpy
[621]
NO
Cl
Tc
N
N
Cl
N
(615)
MeOH / PPh3
MeCN / PPh3
[623]
[
NO
Cl
Cl
Tc
Cl
Cl
]−
(516)
NO
Cl
PPh3
Tc
Ph3P
Cl
MeCN
(607)
py / MeOH
CH2Cl2 r.t.
py r.t.
py Δ
NO
Cl
PPh3
Tc
Ph3P
N
Cl
(614)
NO
Cl
N
Tc
Ph3P
N
Cl
(613)
NO
Cl
N
Tc
N
Cl
(612)
(412)
(337)
[622]
Cl
N
Cl
Tc
N
N
NO
H
PPh3
(617)

Scheme 76



Scheme 77

22.508311 MHz relative to the protons in Me_4Si at exactly 100 MHz. The effect of quadrupole line broadening is attenuated to some extent by the magnitude of I ($I = 9/2$), and the line widths are among the narrowest of all quadrupolar nuclei studied to date. One would expect efficient relaxation via the quadrupole moment, giving very short T_2 times and consequently broad NMR signals. Also if the electronic distribution around the nucleus is symmetrical, sharp resonances can be obtained.

No recent, systematic studies of ^{99}Tc chemical shifts are available in the established literature. The range of chemical shifts as a function of oxidation state has been from an earlier systematic compilation of data. Although the chemical shifts of a number of complexes fall outside the range defined for particular oxidation states, they rationalize the realtionship between δ and other physico-chemical data such as, for instance, spectroscopic properties. It can be stated in general that the resonances decrease monotonically by reducing the oxidation state. Technetium(V) compounds typically appear between 5,500 ppm and 0 ppm, Tc^{III} compounds between 0 and −1,400 ppm, and Tc^{I} complexes from −1,400 ppm up to −4,000 ppm. This shift to higher field is related to an increased shielding when going from high valencies to low valencies. According to molecular orbital theory, the paramagnetic shielding term is proportional to r^{-3} and inversely proportional to ΔE as a number directly related to the HOMO-LUMO gap. Thus, a lower oxidation state goes along with larger, more diffuse orbitals and is directly related to ligand effects such as their position in the spectrochemical series. In a particular oxidation state, the resonances of complexes with strong field ligands will lead to lower shielding and, hence, the resonances appear at higher field; whereas weak field ligands display this effect less markedly and the chemical shifts will be found in the low field region, attributed to the low deshielding effects of such ligands. This is demonstrated with the two Tc^{V} complexes (**218**) and $[TcO_2(py)_4]^+$ (**110**). The chemical shift of the former is found at 882 ppm, the resonance of the latter at 2,881 ppm. Weak field ligands decrease shielding; strong field ligands increase shielding. This is confirmed by another Tc^{V} complex, $[TcOCl_4]^-$, which has a resonance at ≈5,000 ppm in accordance with the even weaker field ligand Cl^-. Even the electronic properties of substituents in ligands can significantly influence the chemical shift of ^{99}Tc, demonstrating its high sensitivity towards electronic ligand properties. In agreement with the influence of the parameters mentioned above is the observation that the ^{99}Tc nucleus in complexes of formula $[Tc(CN\text{-}R)_6]^+$ is appreciably deshielded relative to alkyl substituents, when R is an aromatic system.[640]

The high receptivity of the ^{99}Tc nucleus is expected to allow the detection of very low concentrations in solution. Obviously, the sensitivity and the limit of detection does not only depend on the receptivity, but also on the NMR spectrometer used. A study with a 250 MHz NMR spectrometer investigated the possible detection limits under optimized conditions with $[TcO_4]^-$. Since $[TcO_4]^-$ has a rather sharp line, good signal/noise ratios could be achieved even for very dilute solutions. A sample with a concentration of about 40 μg L^{-1} (0.4 μM) gave, after 2 h time and 3,200 transients, an SN of 2; for a solution of 12 μg L^{-1} (0.12 μM) the same ratio was found after 12 h or 20,000 scans. More concentrated solutions gave the corresponding spectra after reduced scanning time. It is an important result of this study that the SN ratio does not decrease linearly with concentration, but decreases approximately proportionally to the square

root of the concentration.[641] It has to be emphasized that the most dilute solution used in these determinations approaches the concentrations that are available from the radiopharmaceutically relevant $^{99}Mo/^{99m}Tc$ generators. The high receptivity of ^{99}Tc was applied in a biochemical study which extended the use of ^{99}Tc NMR for analysis of the chemical state of Tc compounds within subcellular compartments of living cells. As mentioned earlier, the complexes $[Tc(CN—R)_6]^+$ have a narrow single line in the range of −1,900 ppm, an important base for direct measurement of this complex in living systems. Heart cells that were equilibrated with $[Tc(CN—R)_6]^+$ ($R{=}C(CH_3)_2(OCH_3)$) showed a narrow single peak, with the expected chemical shift and without evidence for significant line broadening or chemical shift displacement compared to an external aqueous chemical standard. This directly implies that the complex exists unbound to proteins within the cell and within the mitochondrial matrix. Separation of mitochondria from the cells showed that 87% of the complex was related to mitochondria and, thus, demonstrates the localization of this lipophilic organometallic complex *in situ* even at high dilution. Since it is of the utmost importance to know the nature and the metabolism of radiopharmaceuticals, ^{99}Tc NMR might serve as an extremely versatile tool for such a purpose, however limited to relatively symmetrical species.[642]

The ^{99}Tc NMR spectrum of an aqueous $[NH_4][TcO_4]$ solution was determined very early,[643] but was then all but ignored until the 1980s when the first detailed report about NMR characterization of $[TcO_4]^-$ appeared. A relatively diluted sample of $[NH_4][TcO_4]$ gave a sharp signal after only one transient. The relaxation parameters T_1 and T_2 were measured by inverse recovery and CPMG methods, respectively, and yielded $T_1 = 0.13$ s and $T_2 = 0.10$ s. The similarity in these values is expected for quadrupolar relaxation of ^{99}Tc and they are in excellent agreement with the value for T_2 estimated from half-height peak width, $\Delta\nu_{1/2}$. Normal ^{17}O abundance of water was sufficient to observe the decet in ^{17}O NMR due to the coupling to ^{99}Tc; however, 750,000 transients and a measurement time of 34 h were required.[644] In another initial study, $[TcO_4]^-$ was stirred in ^{17}O-enriched water over one week in order to get ^{17}O-enriched $[TcO_4]^-$. The ^{17}O spectrum recorded consists of an equal intensity decet at 748.6 ppm, with $\Delta\nu = 23$ Hz arising from spin coupling to $I = 9/2$ of ^{99}Tc. The ^{99}Tc spectrum yielded, in addition to a strong central line and couplings caused by $Tc^{17}OO_3$, and $Tc^{17}O_2O_2$, a set of smaller splittings that appear on each of the main lines. These splittings were attributed to primary isotopic shielding effects arising from a statistical distribution of $^{16}O/^{17}O/^{18}O$ isotopomers. The isotopic shift per oxygen mass unit was 0.22 ppm and the $\Delta\nu_{1/2}$ of the main signal is 2.7 Hz.[545] In this early study, a number of other Tc^{VII} complexes were also studied. The resonance for $[TcO_3F]$ (**5**)[100] in HF(l) was found at 43.7 ppm, with $\Delta\nu_{1/2} = 23$ Hz. The ^{99}Tc–^{17}O coupling is 139.8 Hz, comparable to 131.4 H_2 found in $[TcO_4]^-$, suggesting that there is little distortion from the tetrahedral O—Tc—O angle. Since fluoride can be abstracted from (**5**), addition of AsF_5 to this solution gave new resonances at higher frequencies. A signal at 160.7 ppm ($\Delta\nu_{1/2} = 670$ Hz) was shown to be due to the $[TcO_3]^+$ cation with corresponding ^{17}O resonance at 1,214 ppm. Two other resonances at 245.9 ($\Delta\nu_{1/2} = 135$) and 396.3 ($\Delta\nu_{1/2} = 375$) ppm were attributed to the complexes $[Tc_2O_5F_4]$ and $[TcO_2F_3]$ (**6**), respectively, (see later in this section). Furthermore, the compound $[TcO_2(CN)_4]^{3-}$ (**218**) was investigated, showing a resonance at 806.0 (642) ppm. The deshielding for Tc^V with respect to Tc^{VII} is contrary to the trend anticipated on the basis of formal oxidation state alone. The binary hydride complex $[TcH_9]^{2-}$ has been found to resonate at −3,672 (22) ppm. The ^1H resonance appears at −7.22 ppm and the ^1H–^{99}Tc coupling is 24Hz.[645] The coupling constants ^1H, ^{17}O to ^{19}F are generally quite small and do not suggest a strong interaction between ^{99}Tc and these isotopes. The ^{99}Tc resonance in the homoleptic Tc^I complex $[Tc\{P(OCH_3)_3\}_6]^+$ (**575**) is the expected septet centered at −422 ppm (see later in this section), with a Tc–P coupling constant of 909 Hz. This coupling constant is much larger than those with H, O, and F and implies a strong ^{99}Tc—^{31}P interaction. The chemical shift of ^{31}P is at −158.8 ppm and is in the range observed for other phosphite complexes. The signal is the expected decet, with an Overhauser enhancement of the two outermost peaks.[613] This ^{99}Tc NMR study was extended to comparable complexes containing dimethylmethylphosphonite (dmmp) or the bidentate phosphine ligand reported as dmpe. The ^{99}Tc resonance for $[Tc(dmmp)_6]^+$ is found as a septet at −248 ppm, with a Tc—P coupling constant of 778 Hz. The resonance for $[Tc(dmpe)_3]^+$ (**206**) is a septet at −13 ppm, with a coupling constant of 574 Hz.[358] Both the ^{99}Tc chemical shifts are linearly related to the number of oxygens bound to phosphorus, since shielding is related to the π-donor and the π-acceptor ability of the ligand. The coupling constants for the dmmp ligand indicates that through π-backbonding it is dominated by orbital and dipolar terms.[646]

While the three chemical shifts above for the "$[Tc(P)_6]^+$" complexes have the expected relative values, they appear wrong relative to $[TcO_4]^-$. The very broad spectral window (10,000 ppm) over

which ^{99}Tc resonances are found brings the danger that folded spectra, rather than the true resonances, are measured: thus, careful investigations are required to determine the real signal. This is obviously the case in these compounds; it was shown later that these signals at anomalously low field were wrong, and the real resonances were found at −1,854 ppm for $[Tc(dmpe)_3]^+$ and at −1,658 ppm for $[Tc(tmp)_6]^+$, with the same coupling constant of 574 Hz.[647]

^{99}Tc NMR spectroscopy was subsequently applied to investigations of high-valent, mixed oxo-fluoro complexes of Tc^{VII}. As mentioned earlier, the resonance of $[TcO_3F]$[100] in HF(l) was found at 43.7 ppm, with $\Delta\nu = 23$ Hz. When $[Tc_2O_7]$ is reacted with XeF_6, the Tc^{VII} complex $[TcO_2F_3]$ (**6**) is produced. This compound behaves as a Lewis acid and adds one more fluoride, with formation of the anion $[TcO_2F_4]^-$ (**7**) or neutral $[TcO_2F_3(NCCH_3)]$. The ^{99}Tc NMR spectra of (**7**) dissolved in CH_3CN displays a broadened 1:2:1 triplet at 343.2 ppm, with a coupling constant of 235 Hz to ^{19}F. In HF(l), however, a well-resolved triplet at 247.4 ppm was found, with a coupling constant of 260 Hz. The resonance of (**6**) in CH_3CN is broad, excluding the measurement of ^{99}Tc—^{19}F coupling constants, and δ is about 265 ppm.[102] The ^{99}Tc NMR spectrum of (**6**) was measured at −120 °C in SO_2ClF in order to quadrupole collapse the ^{99}Tc—^{19}F couplings. The spectrum now shows two signals in a relative ratio of 2:1 at 76.2 ppm and at −148.6 ppm, which is consistent with a cyclic, fluoride-bridged, trinuclear complex (see Section 5.2.2.1.1). When the temperature was raised to 30 °C, one single resonance at 211 ppm was found, with partially resolved couplings to the terminal fluoride ligands.[103] The ^{99}Tc NMR spectra of $[TcOF_5]$ (**8**) recorded at 35 °C and at 30 °C in HF showed broad resonances at 394.5 ppm and at 433.8 ppm, respectively.[104] At −110 °C in SO_2ClF the ^{19}F NMR resonances appears as a doublet at 364.1 ppm and a quintet at 62 ppm, with a ratio of 4:1 as expected for the known mononuclear structure of $[TcOF_5]$.[105]

The first ^{99}Tc NMR spectra of carbonyl complexes were reported in 1987. The Tc^0 complex $[Tc_2(CO)_{10}]$ (**602**) gives one single resonance at −2,477 ppm, showing the magnetic equivalence of the two Tc centers. Relaxation time measurements gave $T_1 = 0.42$ and $T_2 = 0.38$ sec, respectively, with $\Delta\nu_{1/2} = 1.4$ Hz. When this compound is brominated to yield $[TcBr(CO)_5]$ the symmetry is lowered, and the corresponding single-line signal was found at −1,630 ppm with $\Delta\nu_{1/2} = 186$ Hz. The relaxation times are also much shorter, with $T_1 = 2.8$ ms and $T_2 = 1.7$ ms.[648] Shortly afterwards, systematic studies were undertaken with complexes containing the *fac*- and *mer*-$[Tc(CO)_3]^+$ moiety.[649] Starting from $[TcBr(CO)_5]$, compounds containing the "*fac*-$[Tc(CO)_3]$" core with C, N, and P ligands were synthesized and the ^{99}Tc NMR systematically investigated. Compounds of the general type $[TcBr(CO)_3(P)_2]$ give resonances in the range −1,450 ppm and −1,650 ppm; complexes of the type $[TcBr(CO)_3(N)_2]$, where N is an aromatic amine or a monodentate ketonoxime, gave between −1,000 ppm and −1,100 ppm; and $[TcBr(CO)_3(C)_2]$, where C is an isocyanide, gave between −1,750 ppm and −2,100 ppm. Different stereoisomers of *mer*- and *fac*-geometry can be distinguished clearly, not only via their chemical shifts but also by line width. Line broadening is not only a consequence of the symmetry of the complex, but is also influenced by the electronic properties of the participating ligands. For instance, the *trans*-$[TcCl(CO)_3(PPh_3)_2]$ has $\Delta\nu_{1/2} = 2{,}800$ Hz, while the corresponding *fac* isomer has $\Delta\nu_{1/2} = 500$ Hz, despite the lower symmetry of the latter one (C_s vs. C_{2v}).[650] Reaction of $[TcBr(CO)_5]$ with phenyl-4,6-0-(R)-benzylidene-2,3,0-bis(diphenylphosphino-β-D-glucopyranoside (Ph-β-glup) gave exclusively the *fac* isomer of $[TcBr(CO)_3(Ph\text{-}\beta\text{-glup})]$, whose ^{99}Tc resonance was found at −1,655 ppm with $\Delta\nu_{1/2} = 3{,}800$ Hz. The resonance lies well within the range found for complexes of the type $[TcBr(CO)_3P_2]$.[651] Complexes with dithiolate ligands and various $Tc(CO)_x$ groups were also investigated, and these ^{99}Tc resonances are at lower field relative to the $Tc(CO)_3$ complexes. The complex $[Tc(CO)_4(dtc)]$ has a peak at −1,072 ppm, with $\Delta\nu_{1/2} = 760$ Hz.[652] $[TcH(N_2)(dppe)_2]$ (**565**) is the starting point for a number of other complexes (see Section 5.2.2.7.1). The resonance of complex (**565**) is found at −1,676 ppm, with $\Delta\nu_{1/2} = 5{,}130$ Hz. When the N_2 was replaced by a number of other π-acceptors, the resonance shifted to −1,321 (L = CO), to −1,310 (L = $C_6H_{11}NC$), and to −1,080 ppm (L = CNBut). A similar trend is observed when CO is replaced by dppe: the resonance for $[Tc(CO)(NCCH_3)(dppe)_2]^+$ is at −1,436 ppm, but for $[Tc(CO)_3(NCCH_3)(dppe)]^+$ it is at −3,517 ppm.[618]

As mentioned earlier, the position of the ^{99}Tc NMR signals gives some information about the electronic state and the formal oxidation number. This is illustrated by the substitution of isocyanide ligands in homoleptic Tc^I isocyanide complexes. The ^{99}Tc resonances are typically in the region of −1,900 ppm, depending on the substituent on the isocyanide. Substitution of two isocyanide ligands in $[Tc(CNBu^t)_6]^+$ (**564**) by phen, bipy, and others to give $[Tc(CNBu^t)_4(NN)]^+$ (**570**) shifts the resonances downfield to about −850 ppm, which is within the range for Tc^{III} complexes. This assignment of an oxidation state of three is in agreement with the X-ray structural data, which shows that the isocyanide ligand *trans* to bipy is significantly bent at the

nitrogen, having a C—N—C angle of 148°. The Tc–C distance is significantly shorter as well, and displays clear double bond character. A further interesting feature of these complexes is the linear relationship between the ^{99}Tc chemical shifts and λ_{max} values of their UV spectra. The values of the observed chemical shifts in the complexes of type (**570**) are accounted for by the paramagnetic shielding term σ_p, which is inversely proportional to the HOMO-LUMO gap ΔE. As ΔE decreases and σ_p becomes more negative, the chemical shift becomes more positive. This gives a linear relationship within this class of compounds between λ_{max} values and δ which is nicely verified.[611] Coligands such as PPh_3 do not show this effect to a similar degree, due to decreased donating ability. When one or two isocyanide ligands are displaced in $[Tc(CNBu^t)_6]^+$ to give $[Tc(CNBu^t)_5(PPh_3)]^+$ or $[Tc(CNBu^t)_4(PPh_3)_2]^+$, the ^{99}Tc resonances appear at −1,827 (3,000 Hz) and −1,760 (6,000 Hz) ppm, respectively.[609]

Resonances located outside the typical Tc^I region are also found for some compounds of formula $[Tc(sol)_3(CO)_3]^+$ (sol = H_2O, MeOH). When $[TcCl_3(CO)_3]^{2-}$ (**620**) is dissolved in water the organometallic aquo-ion $[Tc(OH_2)_3(CO)_3]^+$ (**622**) is formed, which has a ^{99}Tc resonance at −876 ppm, with $\Delta\nu_{1/2}$ of 67 Hz. The enhanced π-backbonding to CO results in a depletion of electron density at Tc^I. When good anionic donors such as Cp or Cp* (Cp = C_5H_5, Cp* = C_5Me_5) are introduced into these compounds to give the pianostool structure complexes $[CpTc(CO)_3]$ or $[Cp^*Tc(CO)_3]$, the chemical shifts appear again within the expected limits for Tc^I at −1,716 ppm and −1,874 ppm, respectively.[634] In less coordinating solvents, such as MeOH, the resonance of $[Tc(HOCH_3)_3(CO)_3]^+$ is shifted downfield from the Tc^I region to −744 ppm. Replacing the solvent molecules by macrocyclic thioethers shifts the resonances back to higher field and into the typical Tc^I region. The chemical shift for $[Tc(9\text{-}S\text{-}3)(CO)_3]^+$ is at −1,656 ppm, and for the dinuclear compound $[Tc_2(20\text{-}S\text{-}6)(CO)_6]^{2+}$, in which three thioether groups coordinate to the Tc center, is at −1,468 ppm with $\Delta\nu_{1/2}$ of 360 Hz. Interestingly, in the dinuclear complex the smaller thiacrown 18-S-6 coordinates only through two sulfurs, and the remaining coordination site is occupied by one tosylate on each Tc. The chemical shift of $[Tc_2(tosylate)_2(18\text{-}S\text{-}6)(CO)_6]$ is at −1,488 ppm, comparable to the dicationic complex.[636] The stepwise substitution of the solvent in complexes such as $[Tc(sol)_3(CO)_3]^+$ by isocyanide ligands illustrates the trends which occur on replacing the solvent by π-acceptors. In D_2O/THF (**622**) shows a resonance at −896 ppm. When one equivalent of $CNBu^t$ is added a strong signal appeared at −2,372 ppm, which persisted after addition of one further equivalent, implying that the −2,372 ppm resonance is due to $[Tc(sol)(CNBu^t)_2(CO)_3]^+$. After the addition of one further equivalent of $CNBu^t$, there was one sharp resonance at −2,106 ppm, which was assigned to $[Tc(CNBu^t)_3(CO)_3]^+$.[632] The triply thiolate-bridged anionic complex (**625**) displays a resonance at −1,354 ppm. Two other complexes illustrate the relationship between the electronic properties of ligands and ^{99}Tc NMR chemical shifts. The Tc^I complexes $[Tc\{HB(pz)_3\}(CO)_2(PPh_3)]$ and $[Tc(9\text{-}N\text{-}3)(CO)_2(PPh_3)]^+$ were prepared from *mer*-$[TcCl(PPh_3)_2(CO)_3]$. The resonances for these complexes are found at −1,198 ppm and −934 ppm, respectively. This demonstrates again that account must be taken of the electronic effects of ligands before relating chemical shift to formal oxidation state.[623] A ^{99}Tc NMR study of the exchange of ^{13}CO in (**622**) under moderate pressure demonstrated the kinetics involved in this reaction. A further interesting result of this study arose on extended storage of this sample under CO pressure, which generated a new septet centered at −961 ppm with a ^{99}Tc–^{13}C coupling constant of 261 Hz. This signal must be due to the homoleptic carbonyl complex $[Tc(CO)_6]^+$, which is surprisingly formed in the aqueous medium.[653]

The capped octahedral complexes $[Tc(S_2COR)_3(PPh_3)]$ have chemical shifts that are slightly dependent on the substituent R in the xanthate ligands, and are found around 2,860 ppm. This is the typical range for the Tc^V complexes (800–5,500 ppm). This strong downfield shift of the resonances can again be attributed to the paramagnetic shielding effect. The weak field (small ΔE) sulfur donors in this ligand will result in a strong deshielding of the Tc nucleus, since the paramagnetic deshielding term is small.[531]

5.2.3 RADIOPHARMACEUTICAL TECHNETIUM-CHEMISTRY

The major driving force for the development of technetium coordination chemistry has undoubtedly been the potential applications in diagnostic nuclear medicine. The primary requirements for a radionuclide to be used in imaging are that the radiation emitted must be of appropriate energy, the decay half-life must lie in a suitable time window, it must be relatively cheap and readily available in the radiopharmacy, and finally it must have highly flexible co-ordination chemistry.

^{99m}Tc meets all these requirements. A widely available generator system is the source of ^{99m}Tc for nuclear medicine and consists of an alumina column loaded with ^{99}Mo in the form of $[^{99}MoO_4]^{2-}$. ^{99}Mo decays by β-emission over 67 h to give $[^{99m}TcO_4]^-$, which can be eluted as a solution of 0.9% saline and at an approximate concentration between 10^{-6} M and 10^{-8} M. With suitable generator design and careful use, there is no ^{99}Mo co-eluted with the ^{99m}Tc.

The ^{99}Mo does not decay directly to ^{99}Tc but via the metastable ^{99m}Tc. The conversion of ^{99m}Tc to ^{99}Tc is spin forbidden and therefore slow, with a half-life of 6 h, and is accompanied by the emission of pure γ-radiation with an energy of about 140 keV, which is ideal for imaging target sites within the body.

The preparation of the pharmaceutical is achieved simply by injection of generator eluate into a vial containing ligand and reductant. Heating may be necessary, to ensure complete reaction. A portion of the vial contents is then injected into the patient for imaging.

^{99m}Tc imaging started in 1961 with the use of $[^{99m}TcO_4]^-$ to image the thyroid, prompted by the presumed similarity between $[TcO_4]^-$ and thyroid-essential I^-. This was the first so-called technetium essential agent, in which the biodistribution was based on the physical properties of the complex (charge, size, lipophilicity, etc.). Subsequently ^{99m}Tc complexes were successfully developed for the imaging of organs such as heart, liver, kidney, brain, and also bone. Examples of each of these are considered in more detail below.

There was, however, an increasing demand for more sophisticated diagnosis tools which would image specific receptor sites in the body. This led to the development of the so-called second-generation ^{99m}Tc agents which comprise a stable ^{99m}Tc complex linked to a targeting biomolecule such as a monoclonal antibody, a peptide, or other biologically active molecules. This is achieved by using a bifunctional chelating agent which binds strongly to ^{99m}Tc and also has a site to covalently attach the targeting molecule. This is very much a nontrivial task, as the metal chelate fragment of the conjugate must not interfere with the receptor-binding ability of the targeting entity. Careful manipulation of charge, size, and lipophilicity of the metal chelate component is needed to optimize receptor binding.

It would be ideal if the receptor-binding capability could be directly incorporated into the peripheral structure of the ligand. Preliminary steps have been taken with the synthesis of complexes in which the exterior surfaces of the complex resemble a steroidal hormone (see Section 5.2.3.1.2), but much remains to be done to optimize receptor binding.

There are formidable obstacles for technetium coordination chemists to overcome in the synthesis of suitable complexes. The starting point must be $[^{99m}TcO_4]^-$ and syntheses must proceed in high yields (>95%) in aqueous solution, in air at high dilution and in the presence of a very large excess of chloride. Once prepared the chelate must be kinetically inert, of appropriate charge, size, and lipophilicity characteristics, and resistant to oxidation or reduction at biologically accessible potentials. Despite all these challenges, a significant numbers of 99m-technetium complexes are in routine use in hospitals for diagnostic imaging. Reviews which link coordination chemistry with chemical applications are comparatively rare, but several have appeared and give good summaries of the current state of technetium-based radiopharmaceutical development.[76–78] The sections below summarize the chemistry underlying the major imaging agents in actual clinical use or with promising biological characteristics.

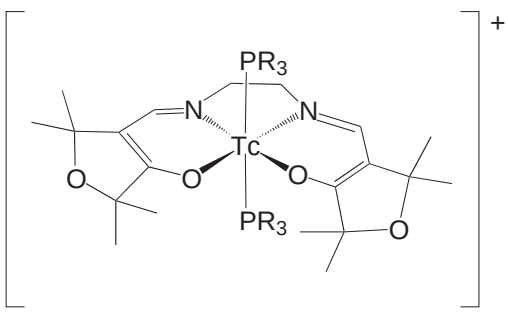
5.2.3.1 Co-ordination Complexes for Radiopharmaceutical Applications

5.2.3.1.1 Heart imaging agents

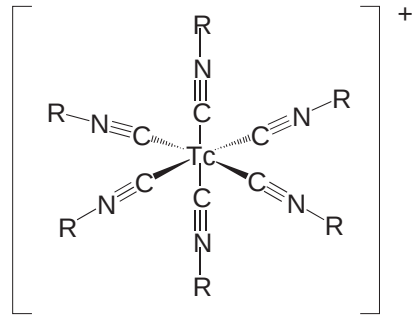
In the past ^{201}Tl has been the agent of choice for myocardial imaging, as it is taken up by myocytes via the Na^+/K^+ ATPase pump.[654] However the unfavorable physico-chemical properties of ^{201}Tl have led to strenuous efforts to replace this isotope by ^{99m}Tc. Early structure–activity relationship studies suggested that effective myocardial agents must be monocationic. This was supported by studies that showed that $[^{99m}TcCl_2(dmpe)_2]^+$ (**205**) and $[^{99m}TcCl_2(diars)_2]^+$ demonstrated good heart uptake in dogs.[258,487,655,656] The preparation of $[^{99m}TcCl_2(dmpe)]^+$ (**205**) was conveniently performed directly from $[^{99m}TcO_4]^-$. However, the heart images in humans were poor and the complexes were not pursued.[657] The lack of heart retention of $[^{99m}TcCl_2(dmpe)_2]^+$ is ascribed to its reduction to the neutral Tc^{II} species $[^{99m}TcCl_2(dmpe)_2]$, which is eliminated via the liver. Several strategies were adopted to overcome this problem, involving the introduction of stronger electron-donating ligands. Attempts to reduce the oxidizing potential by introducing

donating groups such as $[CH_3S]^-$ were chemically successful, but did not lead to the development of a useful myocardial imaging agent based on the respective framework.

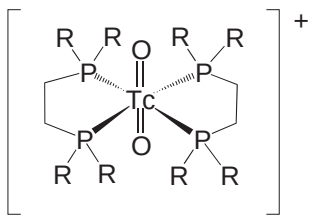
Schiff bases fall into this category and the complex (**433**), as shown in Scheme 78, was successfully prepared and has been described in Section 5.2.2.5.2. An extensive series of complexes of this type ("Q" compounds)[506,510] were subject to exhaustive biological testing. The furanone group improves clearance from the blood and enhances the blood/heart ratio. The best *in vivo* performance was achieved with tris(1-methoxypropyl)phosphine as the axial ligands.[74] The preparation of the ^{99}Tc complex started from $[TcOCl_4]^-$. Initial reaction with the Schiff-base ligand at r.t. is followed by the action of the phosphine at elevated temperature, which leads to reduction/substitution to the final Tc^{III} compound. The synthesis of the radiopharmaceutical is a two-step procedure as well: $[^{99m}TcO_4]^-$ is first reacted with the Schiff-base ligand in the presence of $SnCl_2$ and then the phosphine is added as the Cu^I complex. An alternative procedure does not require Sn^{II} as an additional reducing agent. $[^{99m}TcO_4]^-$ is directly reacted for 10 min at 100 °C in the presence of the corresponding ligand and then phosphine in the form of the complex $[Cu(tmpp)_4]^+$ to afford the single, mixed-ligand product in over 95% yield, despite the fact that two ligands are present in large excess. This procedure is ideal for a radiopharmaceutical preparation and demonstrates the ultimate synthetic stage that has to be achieved. Q compounds have also found applications in the context of multiple-drug resistance (MDR), as discussed below.



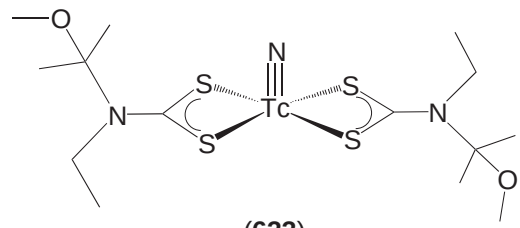
(**433**) (R=$(CH_2)_3OCH_3$)



(**564**)



(**632**) (R=CH_2CH_2OEt)



(**633**)

Scheme 78

A number of other attempts to prepare cationic complexes which retain physiological stability were undertaken. The major obstacle to the use of cationic complexes with a predominance of phosphine ligands is their facile reduction. However, Tc^V complexes of the type $[TcO_2(P–P)_2]^+$ (P–P = bidentate phosphine) are resistant to reduction, and this has been exploited in the development of the successful heart-imaging agent Myoview® by Amersham International. This complex, abbreviated as $[^{99m}TcO_2(P53)_2]^+$ (**632**) (P53 = bis(2-ethoxyethyl)phosphinoethane) has a single positive charge, and the ethoxyethyl groups confer the appropriate lipophilicity to optimize the biodistribution in terms of heart uptake and clearance from blood and liver. It has a first-pass heart uptake of about 1–2% of injected dose[56] and is believed to be taken up into myocardial cells with a similar mechanism to the hexakis(isocyanide) complexes (see below).

One of the first and most successful heart agents to be developed was based on the cationic, homoleptic, Tc^{I} isocyanide complexes described in Section 5.2.2.7.1. Complexes of the type $[^{99}Tc(CN\text{-}R)_6]^+$ (**564**) were synthesized for the first time in the early 1980s by direct reduction of $[^{99m}TcO_4]^-$ with $[S_2O_4]^{2-}$ in the presence of the corresponding isocyanides.[485,658] These complexes are extremely stable, due to the d^6 electronic configuration, thus avoiding dissociative ligand loss or associative substituion of competing ligands in biological systems. The complexes are excreted essentially unchanged. The use of methoxyisobutylisocyanide (mibi) optimises heart retention versus organ and blood clearance, and permits excellent heart images to be obtained.[659] The compound is conveniently synthesized from saline, with $SnCl_2$ as a reducing agent and mibi present in the form of the Cu^{I} complex $[Cu(mibi)_4]^+$. ^{99m}Tc-sestambi (Cardiolite®) and Myoview® have now largely replaced ^{201}Tl for myocardial imaging and are in worldwide use. Although monocationic, it has been shown that uptake does not occur via the Na^+/K^+ channels, but rather by a metabolism process involving electrochemically driven diffusion of the cations across the membranes The uptake is dependent on lipophilicity and is mainly a metabolism-dependent process.[660–662] The mitochondrial localization of the ^{99m}Tc cations appears to be related to the high negative charge (−165mV) across the membrane. The rate of loss of $[Tc(mibi)_6]^+$ from myocardial cells has been measured and shown to be much slower than uptake, explaining the minimal redistribution of such agents.[662–664] Thus, uptake mechanism of this cationic complex differs completely from $^{201}Tl^+$ in that they do not act as potassium analogues, but do require metabolic integrity for uptake by the myocytes.

Many studies have been performed in order to compare the mode of action, and retention kinetics in the myocardium, and the way of excretion of these different cationic species for both cell cultures, as well as in whole heart preparations. Even ^{99}Tc NMR spectroscopy has been used to characterize *in vivo* the nature of the compounds for sestamibi (see Section 5.2.2.10.1). A recent comparative kinetic study between the different cations can be taken as a base for the clinical interpretation of the different perfusion imaging findings.[665]

$[^{99m}Tc(CN—R)_6]^+$ and other cationic complexes have also been found to be taken up by various tumors by mechanism and kinetic rate laws comparable to those found in myocardial uptake. Therefore, these compounds are investigated for tumor imaging, and are studied in particular for breast-tumor imaging.[664,666–668]

Two neutral complexes also show promising behavior as heart-imaging agents. ^{99m}Tc teboroxime (Cardiotec®) is a member of the so-called BATO class of complexes, and has been discussed in Section 5.2.2.5.2. It is neutral and seven-coordinate, and is formed in a Tc-templated reaction from $[TcO_4]^-$ under reducing conditions.[511] The compound is marketed as a myocardial imaging agent that is useful in differentiating normal from ischaemic and infarcted myocardium, using rest-and-stress techniques for the evaluation of coronary artery disease.[669] It has a very high first-pass uptake, which is achieved within a few minutes after injection, but the mechanism by which it enters and leaves cells is unknown. The rate of myocardial washout is biphasic, with both rapid and relatively slow components.[670] Under physiological conditions, the chloride ligand is quite labile and exchanges for hydroxide with a half-life time of 13 min, which seems not to affect the potential of this agent.[671] However, images have to be taken within a few minutes after administration, which presents difficulties in clinical studies.

The second neutral myocardial imaging agent is the complex $[TcN(NOEt)_2]$ (**633**) (*CIS*Bio) (where $NOEt = S_2CNEt(CH_2OMe)$). Dithiocarbamato Tc^{V} nitrides have been discussed in Section 5.2.2.3.3(ii). The convenient synthesis from $[^{99m}TcO_4]^-$ using *S*-methyl-*N*-methyldithiocarbamate gives the product in high yield, and has been crucial for the viability of $[^{99m}TcN(NOEt)_2]$ as a radiopharmaceutical.[672] Although complex (**633**) has a very favorable initial heart uptake of 5% of injected dose, clearance from the blood is comparable to the cationic agents.

The search for other myocardial imaging agents goes on, and it remains a challenge for coordination chemists to synthesize new complexes based on the known mechanisms of heart uptake and heart retention. As is obvious from the described compounds, a cationic charge is not a necessity, but the mechanism related to the retention of such compounds has been the most thoroughly studied and rationalized (Scheme 78).

5.2.3.1.2 Brain-imaging agents

Brain imaging has become a major goal of ^{99m}Tc coordination chemistry, both for perfusion imaging and, more recently, for the labeling of so called central nervous system (CNS) receptor

ligands. These biological ligands target receptors in the brain and are important because of their implication in a wide range of mental disorders, such as Parkinson's and Alzheimer's disease or schizophrenia. This latter type is discussed later in this section. ^{99m}Tc-based perfusion agents still play an important role in the assessment of regional cerebral blood flow, although other diagnostic techniques such as MRI and ultrasound are now strongly competitive. However, the ability of radioactive tracers to detect small structural changes or brain-function disturbances remains an advantage. Such agents must have specific chemical and biological characteristics in order to traverse the intact blood brain barrier (BBB). The extraction of the complex must be high and proportional to the blood flow, and it must cross the BBB by passive diffusion. The complexes are invariably small, lipophilic, and neutral. A further desirable characteristic is the availability of a functional group that is metabolized in the brain, leading to a charged compound that is subsequently trapped in the brain. Otherwise washout is rapid and imaging difficult. Apart from such a specific partial degradation reaction such as ester hydrolysis, the radiopharmaceutical should be metabolically stable.[673]

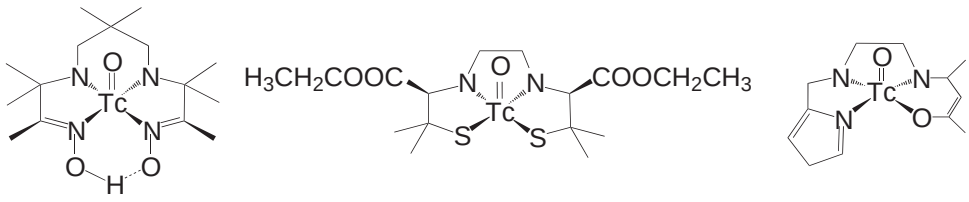
The genuinely promising first complexes were Tc^{V} compounds containing the $[Tc{=}O]^{3+}$ core and derivatized propyleneaminoxime ligands. The ligand is triply deprotonated, which leads to neutral complexes of general formula [TcO(PnAO)] (**119**) in which the two amineoxime units are bridged by a propylene backbone. The synthesis and the structure of this type of compound, as well as some SARs, in terms of coordination chemistry have already been discussed in Section 5.2.2.3.2(iv). In 1983 it was found that this type of complex with the ligand (3,3,9,9)-tetramethyl-4,8-diazaundecane-2,10-dione dioxime) was lipophilic and able to cross the blood brain barrier quite efficiently, but was not trapped. This and analogous complexes are synthesized by reduction of $[^{99m}TcO_4]^-$ in the presence of the ligand and $SnCl_2$ as a reducing agent.[263,674] The required trapping was achieved by varying the position of the substituents on the basic amine-oxime framework, as in (RR,SS)-4,8-diaza-3,6,6,9-tetramethyl-undecane-2,10-dione dioxime. The abbreviation for this compound is ^{99m}Tc-*d,l*-HMPAO and it is available commercially under the name Ceretec® from Amersham International. It is noteworthy that ^{99m}Tc-*d,l*-HM-PAO was the first radiopharmaceutical fully characterized at the molecular level prior to FDA approval. In contrast to pnao, this complex shows brain uptake which is blood-flow dependent in man[675,676] and in animals.[264,677] Interestingly, [^{99m}Tc-HMPAO] is retained in the brain, although the exact mechanism is still not known. It is assumed that the complex is enzymatically converted (rather than decomposed) into a more hydrophilic compound which cannot traverse the BBB again. Such a mechanism is well known for the ecd complex (**157**) discussed later in this section. The ligand has chiral centers, leading to the possibility of stereoisomers, and the complex has also been synthesized with *meso*-HMPAO in the same way. However, although brain uptake is comparable to the *d,l*-form, supporting the passive diffusion mechanism, retention is much less than for its optically active congener. *In vitro* studies showed that the complex with *meso*-HMPAO is much more resistant to conversion to the more hydrophilic species and back-diffusion is therefore much more rapid: so the complex ^{99m}Tc-*meso*-HMPAO is not a useful brain-imaging agent.[678] This clearly illustrates the difficulties encountered in the development of novel radiopharmaceuticals when there are chiral centers present in the bifunctional chelators or in ligands for the production of new perfusion agents. Although the mode of retention is not clear, the behavior of the two stereoisomers supports the assumption that retention is due to biochemical transformation.

A ligand which has all the physical and structural features required for an effective brain-imaging agent is ethylenecysteine dimer (ecd). In this tetradentate ligand, two cysteine units have an ethylene bridge between the two amine nitrogens of cysteine. This ligand belongs to the class of diamino-dithiols (DADT), the coordination of which has been discussed in Section 5.2.2.3.2(vi). A radiopharmaceutical is commercially available from DuPont under the name Neurolite. The two cysteine carboxylic acids are present as the ethyl esters. The two chiral centers give rise to three possible isomers, *d,d*-, *l,l*-, and *d,l*-[^{99m}TcO(ecd)] (**157**). The ligand is triply deprotonated on coordination at the two thiol groups and at one of the secondary amines, producing a neutral and highly lipophilic complex. There are two ester side chains in the ligand which can be hydrolyzed to carboxylic acid groups. This yields a charged complex, which is then trapped in the brain. The hydrolytic reaction is remarkably stereospecific. The *d,d*-form hydrolyzes very slowly and diffuses back through the BBB, but hydrolysis of the *l,l*-form is quite rapid and this compound is trapped specifically.[679] A second effect supports the quality of this complex for *in vivo* application. This (probably enzymatic) conversion takes place not only in the brain, but also in the bloodstream for the fraction of complex not taken up by the brain. The resulting mono- and di-anionic hydrolytic products are rapidly cleared from the rest of the body via the kidneys, and 5 min after injection only about 10% of activity is left outside the brain.[680] The

overall biodistribution characteristics of *l,l*-Tc(ecd) are very favorable. Brain uptake is 5–6% within a few minutes, and decreases to a stable level of 4% after about one hour.[681,682] Interestingly, the behavior of *l,l*-^{99m}Tc(ecd) is the inverse of species such as $[TcCl_2(dmpe)_2]^+$. As mentioned earlier, this cation showed excellent myocardial uptake in rats, but no uptake in man. The compound *l,l*-^{99m}Tc(ecd) is the reverse and no retention could be detected in most animal models; only in humans was favorable trapping observed.[679,683] This demonstrates the necessity of testing a new agent in both animal models and in man. The complex *l,l*-^{99m}Tc(ecd) provides good images of cerebral blood flow and allows delineation of the cortical gray matter, the basal ganglia, the thalamus, and cerebellum hemispheres. White matter displays substantially less uptake than gray matter. The agent is particularly important in the evaluation of patients with stroke.

A number of other Tc complexes were or are under investigation as potential brain-imaging agents. An interesting example is drawn from the BATO class of complexes discussed above[512,513] and in Section 5.2.2.5.2. The ligand is a boronic acid adduct of dimethylglyoxime, and the complex is sufficiently lipophilic to cross the blood brain barrier. The dione backbone was the subject of many variations to achieve reasonable brain uptake, which was about 2.8% for [^{99m}TcCl(DMG)$_3$(B-R)] 5 min post injection. Since the compound is very lipophilic, with log $P = 3.8$, the activity very slowly clears from the body and the brain. The washout is still significant and it appears that there is little or no significant trapping.[670] Based on the known coordination chemistry, a reasonable trapping mechanism could be the exchange of the chloride for water to produce a cation. However, this reaction takes place very slowly, as shown by a study with ^{99g}Tc.[671] In view of the disappointing studies, further development has been terminated.[683,684]

The ligand *N*-{2(1-H-pyrolylmethyl)}*N*′-(4-pentene-3-one-2)ethane-1,2-diamine (MRP20) forms the promising neutral and highly lipophilic complex [TcO(MRP20)] (**634**), which shows very high and rapid brain uptake. At 1 min post injection, up to 6% of the compound had crossed the BBB and the uptake remains constant at about 4.5% over 24 h. MRP20 and related derivatives are under active clinical investigation. Excellent SPECT pictures can be obtained even 7 h post injection, and these allow clear differentiation between gray and white matter. It seems that the retention pattern is closely related to the regional cerebral blood flow. The trapping mechanism is different from the one discussed above for ^{99m}Tc(ecd). *In vitro* experiments showed that the complex tends to hydrolyze and to form a monocationic species.[685–687] (Scheme 79)



(**119**) (**157**) (**634**)

Scheme 79

5.2.3.1.3 Kidney- and bone-imaging agents

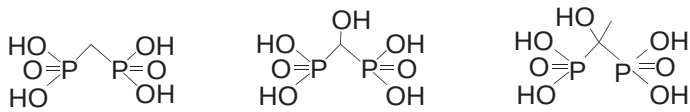
Radiopharmaceuticals are the preferred agents for the assessment of function, as opposed to structure. Renal imaging agents are classic examples in that sense, since they allow the monitoring of the imaging of glomerular filtration and tubular secretion functions of the kidneys. Currently there are two agents available; one is ^{99m}Tc-DTPA of unknown structure, and the other one is the fully characterized [^{99m}TcO(MAG$_3$)]$^-$ (**170**). The trade name of the DTPA complex is ^{99m}Tc-Penetate® and it is available from several sources. The synthesis is perfomed in a vial using μmol amounts of DTPA, with $SnCl_2$ as the reductant. The chemical composition has been the subject of many investigations and much speculation. On the macroscopic level, the principal products formed from this reaction are dimers, with Tc in the oxidation states +III, +IV, or +V.[688,689] However, the concentration of generator-eluted ^{99m}Tc is too low for dimers to form in high concentration, and it appears likely that the active species is monomeric. The overall charge would be −1 or −2, depending on whether Tc^{III} or Tc^{IV} is present. Despite the uncertainity of the structure, ^{99m}Tc Penetate® is in regular radiodiagnostic use for renal-function imaging.

Five-coordinate $[^{99m}TcO(MAG_3)]^-$ (**170**) was introduced comparatively early in the development of radiopharmaceuticals.[690] It is commercially available under the trade name Technescan® (Mallinckrodt Med.). The ligand is present in the Kit in the S-protected form and requires heating in a boiling water-bath for a short time, when coordination and deprotection take place. Oxidation of excess $SnCl_2$ is sometimes required and also converts by-products into the desired complex. This compound shows good *in vivo* renal-clearance characteristics. Since the ligand does not have any chiral centers, one single species is formed in which the three amides and the thiolato group are deprotonated, yielding a mono-anionic species. The terminal carboxylato group does not participate in co-ordination. Related compounds comprising diamido-dithiol ligands (dads) give rise to mono-anionic species and show very good renal-clearance properties, but have the disadvantage that they contain two chiral centers and isomer problems were encountered.[303,690,691]

Complexes with 2,3-dimercaptosuccinic acid (H_3dmsa, (**95**)): see also Section 5.2.2.3.2(ii) and glucoheptonate are of minor importance for imaging the morphology of the kidneys. The composition and the structure of the dmsa complex with ^{99m}Tc used for renal imaging is not known for certain, although the X-ray crystal structure of the Re analogue has been determined.[692] [^{99m}Tc-dmsa] is prepared by the reaction of H_3dmsa with $[^{99m}TcO_4]^-$ in water at a pH around 3, in the presence of $SnCl_2$. The complex with ^{99g}Tc is believed to be in the oxidation state +III.[693–695] When $[^{99m}TcO_4]^-$ is reduced under alkaline conditions with $[S_2O_4]^{2-}$a Tc^V complex is formed with H_3dmsa, which has found use as a tumor-imaging agent. Analytical data clearly indicate that the complex obtained under these conditions is $[TcO(dmsa)_2]^-$.[223] *Meso*-dmsa is expected to give three different isomers with syn-endo, syn-exo, and anti orientation of the –COOH groups with respect to the Tc=O group. HPLC confirmed the occurrence of all three isomers in solution from the reaction with *meso*-dmsa, and these are shown to be in rapid equilibrium as by ^{1}H NMR.[654,655] Although no structure of any of the isomers of $[TcO(dmsa)_2]^-$ (**640**) is available, the structure of syn-endo-$[ReO(dmsa)_2]^-$ has been described and shows the expected square-pyramidal geometry. For renal imaging, a significant amount of the injected compound accumulates in the cortical tubules within 1 h, and remains in the renal cortex for up to 24 h. Remarkably, the complex is excreted unchanged.[696] $[^{99m}TcO(glucoheptonate)_2]^-$ is prepared by the reaction of calcium glucoheptonate with $SnCl_2$ and $[^{99m}TcO_4]^-$. The structure of the complex is square pyramidal, with an apical oxo group, and has two five-membered rings derived from the carboxylate group and the deprotonated alcohol function in glucoheptonate. The other hydroxyl functions do not participate in co-ordination and are the reason for the high hydrophilicity of the complex. The complex has also been used for brain imaging when the BBB is damaged, and the compound can diffuse into the brain. The compound is very stable in water (up to 200 days with ^{99g}Tc), but is nevertheless used extensively as a precursor for further substitution reactions in which the glucoheptonate ligands are replaced by more potent chelators. When used as a renal-imaging agent, the complex is excreted by glomerular filtration, and half-life in plasma is only a few minutes.[697] Both complexes are not now used extensively in clinics, as other diagnostic methods such as MRI or ultrasound give clearer images of renal morphology.

Complexes of ^{99m}Tc with phosphonate ligands are widely used as diagnostic agents for the detection and monitoring of metastatic disease in bone and bone infarction infections. The ligands are in general diphosphonates, with various types of substituent on the backbone. Major ligand types in that respect are methylene-diphosphonate (mdp, (**635**)), hydroxymethylene-diphosphonate (hmdp, (**636**)), 1-hydroxyethylidenediphosphonate (hedp, (**637**)), and 1-hydroxy-4-aminobutylidene-1,1-diphosphonate (abp). The preparation of the complexes is standard for radiopharmaceutical use and is performed by reduction of $[^{99m}TcO_4]^-$ with $SnCl_2$ or $[BH_4]^-$ in the presence of the ligand. The reaction yields product mixtures, and the exact compositions or structures have yet to be determined. Nevertheless they are very effective bone-imaging agents. The presence of uncoordinated phosphate oxygen provides a mechanism for absorption of the complexes on the surface of newly formed hydroxy-apatite. In this respect they can be considered to act as ligands for exposed Ca^{2+} on the newly formed crystals of hydroxy-apatite. Many efforts have been made to characterize the complexes formed by the reaction of various ^{99}Tc starting materials with phosphonates such as (**635**) or (**636**). Size-exclusion chromatography or mass spectrometry suggests the complexes are polymeric.[698,699] Unfortunately, but typically for polymers, the composition of the product depends strongly on the reaction conditions and is significantly different when pH or concentration are altered.[700] From spectrophotometric measurements it was concluded that the oxidation state of Tc in [Tc-(hedp)] is +IV; however, polarographic studies suggested mixed oxidation states, involving Tc^{III}, Tc^{IV}, and Tc^V.[701] The structure of one mdp complex has been elucidated. The reaction between $[TcBr_6]^{2-}$ and excess

(**635**) gave brown crystals, and the X-ray crystal structure showed a polymeric chain structure of stoichiometric composition $[Tc(OH)(mdp]_{\infty}$. Each ligand (**635**) bridges two symmetry-related technetiums, and each Tc atom is bound to two mdp ligands. The polymeric repeat is completed by an oxygen atom, probably a hydroxo group which bridges two Tc atoms. The geometry is approximately octahedral, but the oxidation state cannot be unambiguously assigned since it is not clear whether a hydroxy or an oxo group bridges the two technetium atoms.[702] The structure shows that diphosphonates can act as bidentate ligands and can bridge metal centers, as is the case for their binding to Ca^{2+} in bone. Raman spectroscopy suggested that for the hedp complex both $[Tc{=}O]^{3+}$ and $[O{=}Tc{=}O]^{+}$ may be present, with bands observed at 970 cm^{-1} and 878 cm^{-1}.[703] The amount of skeletal uptake of the species obtained from the phosphonate ligands lies in the sequence [^{99m}Tc-hmdp] > [^{99m}Tc-mdp] > [^{99m}Tc-hedp]. This reflects the general observation that the biodistributions of ^{99m}Tc-based radiopharmaceuticals are significantly altered by even small changes in the ligand structure.[704] Scheme (80)



Scheme 80

5.2.3.1.4 Multidrug resistance

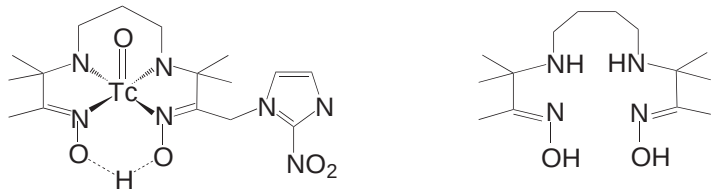
Tumors that are initially sensitive to cytotoxic agents often become refractory to multiple chemotherapeutic drugs. Cells grown in the presence of a specific cytotoxic drug can develop cross-resistance to this and other drugs in the same class and to other classes of drugs entirely. This phenomenon is related to the overexpression of the multidrug resistant (MDR1) transmembrane P-glycoprotein (Pgp). It is an objective of pharmaceutical research to develop molecules called modulators, which are able to block the action of Pgp in order to re-establish chemotherapy. A noninvasive method to detect MDR in tumors would be an important diagnostic assay for management and prognostic stratification of cancer patients, and a number of ^{99m}Tc co-ordination compounds have been tested for their ability to indicate the Pgp level in tumor cells. These are cationic and/or highly lipophilic complexes such as ^{99m}Tc-sestamibi[705], ^{99m}Tc-tetrofosmin,[706] and ^{99m}Tc-furifosmin (Q-compounds).[707,708] The structures of these compounds have been discussed under the section on myocardial imaging agents, since they fall within this class of radiopharmaceutical. These compounds have been tested as transport substrates for Pgp for a variety of multidrug-resistant cells in humans.[709,710] It was shown that the net cellular accumulation is inversely proportional to the amount of Pgp expressed, and was significantly enhanced after the administration of modulators. Clearly, the diagnosis of MDR is a field in which ^{99m}Tc may play an important role, since it would allow the determination of chemotherapeutic regimes before and during treatment.

5.2.3.1.5 Hypoxia-imaging agents

The development of ^{99m}Tc-based compounds capable of imaging hypoxic regions is one of the dominant themes in current radiopharmaceutical research. Complexes containing nitroimidazole attached to the backbone of a chelator are among the most promising in this direction. The rationale behind this approach emerges from the normally higher resistance of hypoxic tissue for chemotherapy or radiotherapy.[711,712] It is of the utmost importance to be able to detect hypoxic tissue in order to plan and execute a successful therapeutic procedure. Hypoxic tissue has an oxidation potential lower than that of normal, oxygenated cells, and the strategy for a useful hypoxia marker involves the use of a redoxactive side chain or metal center. So far, the strategy has mainly focused on the approach using a technetium complex with a redox-active side chain, in general nitro-imidazole or dihydropyridine, both of which are reduced to ionic species in hypoxic cells. The complex has to be capable of diffusion into the cell and then reduction, which must lead to trapping by virtue of formation of more hydrophilic species. In normal, oxygenated tissue the

complex is excreted in a reasonable period of time. The position emitting ^{18}F-labeled misonidazole is taken as the standard to which all ^{99m}Tc compounds are compared. The compounds tested so far for hypoxia are classical co-ordination compounds with the $[Tc{=}O]^{3+}$ core. The challenge of producing a technetium complex that has appropriate redox properties has not yet been met, although certain copper bis(thiosemicarbazones) are hypoxic selective through metal-based reduction. Currently there are two basic types of complex under investigation. The first are nitroimidazole-coupled derivatives of amineoxime such as [TcO(PnAO)-2-(2-nitroimidazole)], designated as BMS181321 (**638**).[713,714] The second is a nitroimidazole derivative of the amine phenol-type ligand, bis-(amine-phenol)-nitroimidazole.[715,716]

A further class of compounds does not contain a nitroimidazole, but is also based on the amine-oxime framework as a tetradentate ligand. The complex is [TcO(BnAO)] (**639**), which has a $(CH_2)_4$ backbone, but the structure of which with ^{99m}Tc is not absolutely certain. As mentioned in Section 5.2.2.3.2(iv), an ethylene and a propylene bridge between the two amine nitrogens will lead to a mono-oxo core, whereas pentylene leads to a complex with the $[O{=}Tc{=}O]^{+}$ moiety.[269] Possibly in the butylene case the complex may have an oxo and an aquo ligand in *trans* locations. The mechanism of hypoxic selectivity is also unknown, but does not appear to involve metal-based redox processes. Recently, the [3+1] concept was used for a further strategy to hypoxic-imaging agents. Dihydronicotinamide or methylpyridinium were attached through a linker to a thiol group making up the derivatized monodentate component. The tridentate ligand was a dithiol-thioether (SSS) chelate. The compound showed promising results in imaging hypoxic tissues.[717] (Scheme 81)



(**638**) (**639**)

Scheme 81

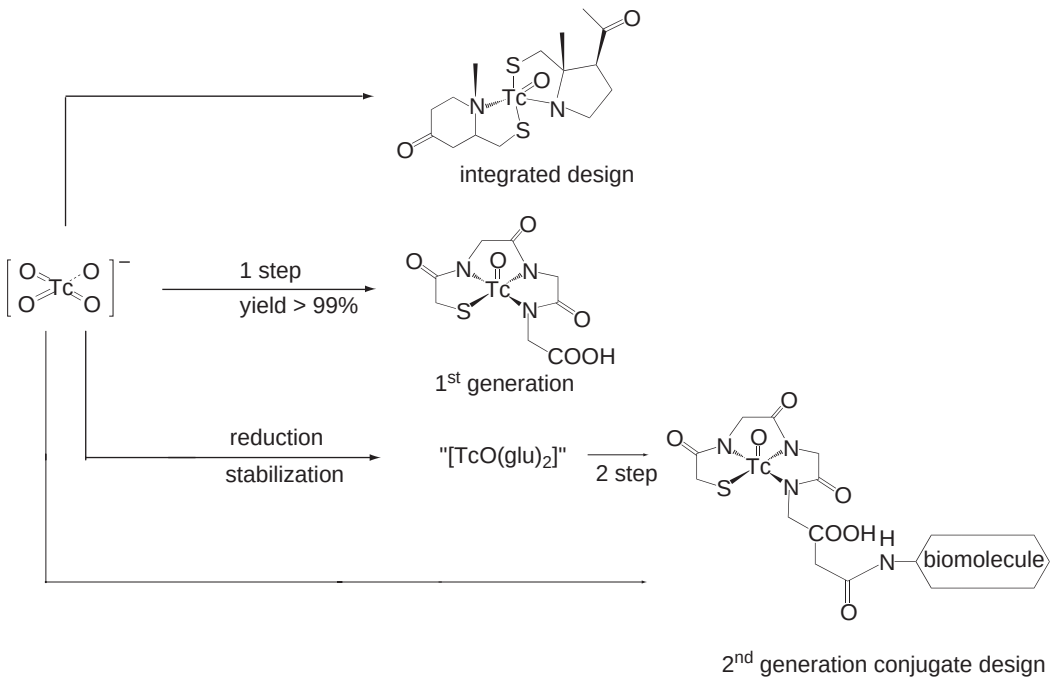
5.2.3.2 Second-generation Technetium-based Radiopharmaceuticals

A brief account of first- and second-generation radiopharmaceuticals has been given at the beginning of this section (Scheme 82).

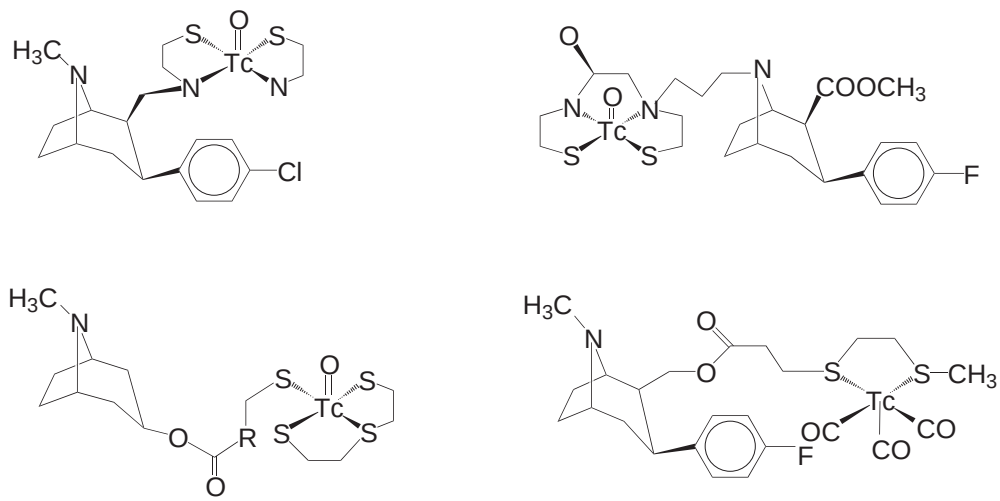
In general, strong chelators are chosen to coordinate to the Tc to ensure that the conjugate does not decompose under physiological conditions and, of these, tetradentate ligands with N,S,O donors which stabilize the $[Tc{=}O]^{3+}$ core are the most common.[268,299,302,307,315,322,329,332] The so-called [3+1] approach[718] is currently decreasing in importance, since it has been shown that the complexes have limited stability in human serum.[342] A number of other approaches have appeared recently, which include the labelling of peptides via the so called HYNIC approach (see later in this section), the use of the $[Tc{\equiv}N]^{2+}$ core in combination with tridentate PXP ligands,[410,411] and the $[Tc(CO)_3]^{+}$ fragment.[633,638] All of these new methods provide high flexibility in terms of ligand choice, and although they are not yet in very widespread use they will undoubtedly play a significant role in the development of novel, second-generation radiopharmaceuticals (Scheme 83).

The labelling of steroid hormone-receptor ligands is important, since it would probably allow early detection and treatment of breast and prostate cancer. Attempts to apply the second-generation approach in which a chelator is conjugated to the steroid have been made, but with little success so far. Both the [3 + 1] approach and derivatization of the $[Tc(CO)_3]^{+}$ core have been used to target the estrogen or androgen receptor.[719,720] In a more recent approach, a [4 + 1] approach was used to label 17α-substituted estradiol. In this approach a pendant isonitrile group binds the steroid hormone to the Tc^{III}/Re^{III} center, which is coordinated to a tetradentate, umbrella-type NS_3 ligand. Although promising binding constants were found for a number of these complexes, *in vivo* data for ^{99m}Tc are not yet available.[720]

A comparable challenge is presented by the labeling of CNS receptor ligands, and an excellent review has summarized current development.[721] The potential for the development of ^{99m}Tc-based



Scheme 82



Scheme 83

radioligands for the study of receptor functions is well recognized, although there are many difficulties to overcome. Such a radiopharmaceutical has to cross the BBB and be taken up into the brain in significant amounts, must stay in the brain for a sufficient time to reach and bind to the appropriate receptor, and must have a substantial affinity for the receptor. The review summarizes what has been achieved with a focus on *in vitro* binding and *in vivo* distribution data.[721] With the exception of a tropane derivative labeled with ^{99m}Tc, the success in this field has been modest, due to difficulties in establishing the detailed requirements for a useful CNS-receptor ligand. The coordination chemistry is usually based on tetradentate, N_2S_2-type ligands, since they provide high stability and high lipophilicity. The ^{99m}Tc-labeled compound ^{99m}TcTRO-DAT1 involves a DADS-type ligand conjugated to a tropane, and has been successfully employed for the imaging of dopamine transporter for the *in vivo* assessment of loss of dopamine neurones

in Parkinson's and other neurodegenerative diseases.[722,723,724] Various CNS-receptor ligands have been labeled via the pendant approach using DADT ligands, including the 5-HT_{1A} receptor ligand WAY 100635 (which has been labeled with ^{99m}Tc[725]), the tropane derivative,[726] and active fragments of the 5-HT2A antagonist ketanserin. Other approaches based on these CNS-receptor ligands employed the [3+1] approach. The biomolecule was usually derivatized with a thiol group, and the tridentate dithiol-thioethers were used as coligands.[244,726]

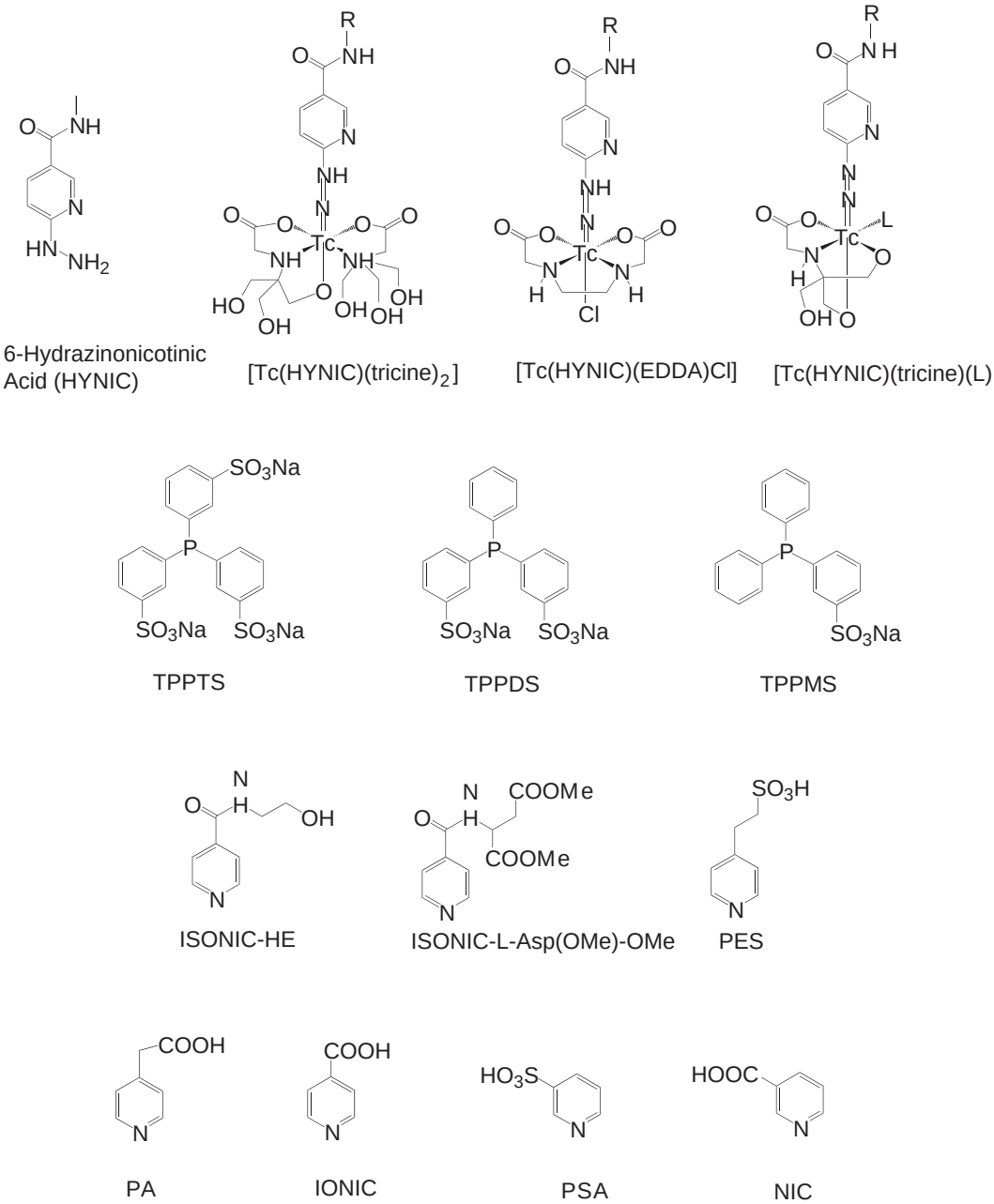
A very different approach towards coupling a technetium complex to biomolecules, and in particular to peptides, is represented by the so-called "HYNIC" agent,[78] first used for the labeling of polyclonal IgG with ^{99m}Tc for imaging focal sites of infections.[727–729] Here 6-hydrazinonicotinic acid (HYNIC) is initially coupled through the carboxylate to an amine group of a biomolecule, such as the e-NH_2 group of lysine or the N-terminus of peptides. The labeling is usually carried out by the reaction of the HYNIC-linked biomolecule, most frequently a peptide, with $[^{99m}TcO_4]^-$ in the presence of a reducing agent, most commonly stannous chloride, and a coligand. At low biomolecule concentrations the mixture is then heated, typically to 80 °C for 30 min or to 100 °C for 10 min. The same approach is also viable for intact antibodies, but in this case higher concentrations are required, since the labeling has to be performed at room temperature. Since the pyridylhydrazine-derived ligand of HYNIC can occupy only one or two coordination sites, a coligand is essential. The actual coordination mode of HYNIC at the tracer level is not unambiguously clear, since several types of coordination mode are possible (see Section 5.2.2.3.5). Typically, coligands used are in tricine, glucoheptonate, or EDDA. Judicious choice of the coligand allows fine tuning of the hydrophilicity of the conjugate. However, the major drawbacks of this system are the instability of the Tc complexes containing HYNIC and the corresponding coligand, the formation of a mixture of species, and the occurrence of plasma–protein binding.[730] Ternary ligand systems have been proposed to improve stability and complex constitution, and these contain beside the coligand tricine an additional ligand in the form of a water-soluble phosphine. Complexes with these ternary ligand systems have very high solution stabilities. In addition to phosphines, aromatic amines have also been used and with comparable success.[731–734] Scheme 84 summarizes the chemistry of the HYNIC labeling system (Scheme 84).

The ternary ligand systems have been investigated with a number of types of biomolecule and the labeling conditions have been optimized. Problems arise only if the biomolecule is susceptible to reduction, as found for molecules with disulfide bonds, which if cleared alter the biodistribution of the vectors molecule. Although the chemical composition of the complexes with ^{99}Tc has been established by LC-MS experiments, the true oxidation state of the Tc remains unclear.[729] Even for a given composition several different formal oxidation states are possible, depending on the location of bonding electrons, and the data available do not permit unambiguous assignment.[427,428,430,631,735] Four different binding types have been established for 2-hydrazinopyridine (HYPY) (see Section 5.2.2.3.5). The variety of structural types emphasizes problems related to the characterization of complexes at the tracer level, and it should be noted that the binding modality of HYPY or HYNIC depends strongly on the nature and the availability of the coligands.

Clearly the advantages of the HYNIC approach are the high labeling efficiency and the possibility of fine tuning the physico-chemical properties of the labeled biomolecules, as well as their stabilities when the right ternary ligand combination has been chosen. The approach has been used mainly for hydrophilic peptides, such as chemotatic peptides and somatostatin analogues,[736,737] but also for antisense oligonucleotides and antibodies.[731] However, the method is not particularly suitable for lipophilic biomolecules, and there remain the problems of ambiguous characterization of the species at the no-carrier-added level.

5.2.3.2.1 Intrinsic receptor binding

A more ideal situation would emerge from the possibility of preparing a Tc complex that mimics the binding motif of a biomolecule. The topology, as well as the distribution of dipole moments and other physico-chemical characteristics of the natural lead, must be exposed by the artificial metal complex. Such an approach is highly challenging for co-ordination chemistry. Still only a very limited number of corresponding, but still very promising, approaches have been published. This approach is called the integrated design of a radiopharmaceutical, and some initial investigations have been made towards the development of steroid hormone mimics. The technetium is incorporated in a carbon skeleton in such a way as to mimic the 3-D structure of the hormone. In one approach, two different bidentate amine-thiol ligands have been chosen to prepare androgen



Scheme 84

and progesterone mimics.[738–740] In contrast to most complexes labeled with ^{99m}Tc, the approach consists of two bidentate ligands, rather than a tetradentate one. It seems that this provides an advantage, since the structural features can more easily be fine tuned as in the case of a relatively rigid tetradentate system. Although two different bidentate ligands are required, it seems that the formation of the heterodimeric complexation is formed in preference to the homodimeric compound. With ^{99m}Tc, the yield of the corresponding complexes was 40–50% by applying the glucoheptonate approach. Where it was possible to determine the stereochemistry, it could be shown that the compounds have *trans* geometry. Although bidentate only, the complexes are reasonably stable *in vitro* and showed some persistence *in vivo* as well. Stability was still not good enough for following the bidentate approach further. Instead, the mimics were expanded to tetradentate ligands, to form again a pseudosteroid structure. Despite retaining the overall size and shape, the receptor binding to the estrogen receptor was disappointing in vitro.[741] These two

approaches show that it is highly important to match not only the structural features, but also the electronic effects in a mimic. Probably, the match of steroids is very difficult and highly challenging, and other lead structures should first be chosen to prove the effectiveness of this important strategy of mimicking bioactive molecules by integrating the ^{99m}Tc into the overall structure.

5.2.4 CONCLUSION

As is obvious from this last section, coordination chemistry plays an important role in the development of novel radiopharmaceuticals. Although procedures for the efficient labeling of biomolecules, or the preparation of novel perfusion agents are available, they are still far from being sufficient to allow a rational drug design, including metal complex and targeting vector. Labeling still has to rely on a very limited number of chelators providing enough *in vivo* stability, but leaving not a great choice in influencing the properties of the radiobioconjugate. Other imaging methods like PET or MRI are competing to a large extent with the application of radiopharmaceuticals. This is not only due to better performance, but also to the difficulties in designing a useful SPECT radiopharmaceutical for ^{99m}Tc. It is the task of the coordination chemist to provide the radiopharmaceutical community with such novel methods in order to get more precise and more readily available "magic bullets." This may involve ^{99m}Tc coordination or organometallic chemistry based on what is presently available in literature but may also involve as-yet-unknown structural types.

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Alice Bizzozero for the many drawings and to his coworkers Paul Benny, Pascal Hfliger, Susanne Kunze, Philipp Kurz, Stefan Mundwiler, Chiara da Pieve, JaeKyong Pak, Bernhard Spingler and Wenwu Wang for carefully checking the manuscript.

5.2.5 REFERENCES

1. Noddack, W.; Tacke, I. *Naturwissenschaften* **1925**, *13*, 567–571.
2. Berg, O.; Tacke, I. *Naturwissenschaften* **1925**, *13*, 571–574.
3. Noddack, I.; Noddack, W. *Z. Phys. Chem.* **1927**, *125*, 264–274.
4. Mattauch, J. *Z. Phys. Chem.* **1934**, *91*, 361–371.
5. Perrier, C.; Segrè, E. *J. Chem. Phys.* **1937**, *5*, 712–716.
6. Perrier, C.; Segrè, E. *Nature (London)* **1937**, *140*, 193–194.
7. Paneth, F. *Nature* **1947**, *159*, 8–10.
8. Hahn, O.; Strassmann, F. *Naturwissenschaften* **1939**, *27*, 11–15.
9. Segrè, E.; Wu, C. S. *Phys. Rev.* **1940**, *57*, 552–552.
10. Boyd, G. E.; Sites, J. R.; Larson, Q. V.; Baldock, C. R. *Phys. Rev.* **1955**, *99*, 1030–1031.
11. Rider, B. F.; Meek, M. E. *Atomwirtschaft* June 1994, 398–400.
12. Schwochau, K. *Angew. Chem.* **1964**, *76*, 9–19.
13. Kenna, B. T.; Kuroda, P. K. *J. Inorg. Nucl. Chem.* **1961**, *23*, 142–144.
14. Kenna, B. T.; Kuroda, P. K. *J Inorg Nucl Chem* **1964**, *26*, 493–499.
15. Ruffenach, J. C.; Menes, J.; Lucas, M.; Hagemann, R.; Nief, G. *IAEA, Vienna* **1975**, 371–384.
16. Frejacques, C.; Blain, C.; Devillers, C.; Hagemann, R.; Ruffenach, J. C. *IAEA, Vienna* **1975**, 509–524.
17. Jordan, P. *Naturwissenschaften* **1953**, *40*, 407–408.
18. Arnould, M. *Ann. Astrophys.* **1968**, *31*, 179–197.
19. Takahashi, K.; Mathews, G. J.; Bloom, S. D. *Phys. Rev.* **1986**, *C33*, 296–301.
20. Merrill, P. W. *Astrophys. J.* **1952**, *116*, 21–26.
21. Merrill, P. W. *Science* **1952**, *115*, 484.
22. Van Eck, S.; Jorissen, A.; Goriely, S.; Plez, B. *Nucl. Phys. A* **2001**, *688*, 45c–48c.
23. Parker, G. W.; Martin, W. J. *Oak Ridge National Laboratory, Declassified Report ORNL-1116* **1952**, 26–27.
24. Kotegov, K. V.; Pavlov, O. N.; Shvedov, V. P. *Adv. Inorg. Chem. Radiochem.* **1968**, *2*, 1–90.
25. Schwochau, K. In *Handbuch der Präparativen Anorganischen Chemie*; Brauer, G., Ed.; Enke: Stuttgart, Germany, 1981; Vol. 3, p 1598.
26. Browne, E.; Firestone, R. B. **1986**.
27. Tuli, J. K.; Martin, M. J. E. *Nuclear Data Sheets* **1990–1993**, *60–70*.
28. *CRC Handbook of Chemistry and Physics*, 75th ed.; Lide, D. R.; Frederikse, H. P. R., Eds: 1994–1995, Chapter 11, p 60.
29. Government of the German Federal Republic, Strahlenschutzverordnung, *Bundesgesetzblatt* **1976**, *1*, 2941.
30. Office of the European Communities *Off. Bull. Eur. Comm.* **1980**, *L23*, No. 246.
31. Government of the German Federal Republic, Strahlenschutzverordnung, *Bundesgesetzblatt* **1989**, *1*, 1358.

32. Tucker, W. D.; Greene, M. W.; Weiss, A. J.; Murenhoff, A. P. *Trans. Am. Nucl. Soc.* **1958**, *1*, 160.
33. Richards, P. *Radiation and Isotope Technology in Latin American Development. Proc. of ANS Topical Mtg.* **1969**, *PRNC 135*, 252–260.
34. Richards, P. *VII Rassegna Internationale Elettronica e Nucleare, Roma, Atti Ufficiali* **1960**, 223–244.
35. Richards, P.; Atkins, H. L. *Jpn. Nucl. Med.* **1968**, *7*, 165.
36. Richards, P.; Tucker, W. D.; Srivastava, S. C. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 793–799.
37. Spitsyn, V. I. *Z. Chem.* **1981**, *21*, 131.
38. Clarke, M. J.; Fackler, P. H. *Struct. Bonding* **1982**, *50*, 57.
39. Schwochau, K. *Radiochim. Acta* **1983**, *32*, 139.
40. Russell, C. D. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 883.
41. Spitsyn, V. I.; Kuzina, A. F.; Oblova, A. A.; Kryuchkov, S. V. *Usp. Khim* **1985**, *54*, 637.
42. Melnik, M.; Van Lier, J. E. *Coord. Chem. Rev.* **1987**, *77*, 275.
43. Mazzi, U. *Polyhedron* **1989**, *8*, 1683–1688.
44. Kirmse, R.; Abram, U. *Isotopenpraxis* **1990**, *26*, 151.
45. Schwochau, K.; Pleger, U. *Radiochim. Acta* **1993**, *63*, 103.
46. Turp, J. E. *Coord. Chem. Rev.* **1982**, *45*, 281.
47. Turp, J. E. *Coord. Chem. Rev.* **1983**, *52*, 241.
48. Turp, J. E. *Coord. Chem. Rev.* **1986**, *71*, 389.
49. Turp, N.; Turp, J. E. *Coord. Chem. Rev.* **1987**, *80*, 157.
50. Constable, E. C.; Housecroft, C. E. *Coord. Chem. Rev.* **1994**, *131*, 153–175.
51. Housecroft, C. E. *Coord. Chem. Rev.* **1995**, *142*, 21–41.
52. Housecroft, C. E. *Coord. Chem. Rev.* **1997**, *162*, 305–318.
53. Housecroft, C. E. *Coord. Chem. Rev.* **1998**, *169*, 187–199.
54. Davison, A.; Jones, A. G. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 875.
55. Jones, A. G.; Davison, A. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 867.
56. Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* **1983**, *30*, 75.
57. Baldas, J. *Adv. Inorg. Chem.* **1994**, *41*, 1–123.
58. Bandoli, G.; Mazzi, U.; Roncari, E.; Deutsch, E. *Coord. Chem. Rev.* **1982**, *44*, 191–227.
59. Tisato, F.; Refosco, F.; Bandoli, G. *Coord. Chem. Rev.* **1994**, *135–136*, 325.
60. Bandoli, G.; Dolmella, A.; Porchia, M.; Refosco, F.; Tisato, F. *Coord. Chem. Rev.* **2001**, *214*, 43–90.
61. Sattelberger, A. P.; Bryan, J. C. In *Comprehensive Organometallic Chemistry II*; Carey, C. P. Ed.; Elsevier Science Inc: New York, **1996**, 151–166.
62. Alberto, R.; Herrmann, W. A.; Bryan, J. C.; Schubiger, P. A.; Baumgärtner, F.; Mihalios, D. *Radiochim. Acta* **1993**, *63*, 1453–1161.
63. Alberto, R.; Schibli, R.; Waibel, R.; Abram, U.; Schubiger, A. P. *Coord. Chem. Rev.* **1999**, *190–192*, 901–919.
64. Deutsch, E.; Barnett, B. L.; Martell, A. E., Eds.; American Chemical Society: Washington, DC, 1980; pp 103–119.
65. Deutsch, E. Libson, K. Jurisson, S. Lindoy, L. F., Ed., *Technetium Chemistry and Technetium Radiopharmaceuticals* **1983**, *30*Wiley: New York.
66. Deutsch, E.; Libson, K. *Commun. Inorg. Chem.* **1984**, *3*, 83.
67. Pinkerton, T. C.; Desilets, C. P.; Hoch, D. J.; Mikelson, M. V.; Wilson, G. M. *J. Chem. Educ.* **1985**, *62*, 965.
68. Fritzberg, A. R.; Nunn, A. D. In *Analytical and Chromatographic Techniques in Radiopharmaceutical Chemistry*; Wieland, D. M., Tobes, M. C., Mangner, T. J., Eds.; Springer-Verlag: New York, 1986, pp 183–212.
69. Blauenstein, P. *New J. Chem.* **1990**, *14*, 405.
70. Nunn, A. D. *Semin. Nucl. Med.* **1990**, *20*, 111.
71. Verbruggen, A. M. *Eur. J. Nucl. Med.* **1990**, *17*, 346–364.
72. Raynor, J. B.; Kemp, T. J.; Thyer, A. M. *Inorg. Chim. Acta* **1992**, *193*, 191–196.
73. Steigman, J.; Eckelman, W. C. *The Chemistry of Technetium in Medicine*; Nuclear Science Publication NAS-NS-3204, National Academy Press: Washington, DC, 1992.
74. Clarke, M. J.; Podbielski, L. *Coord. Chem. Rev.* **1987**, *78*, 253.
75. Kung, H. F. *Semin. Nucl. Med.* **1990**, *20*, 150.
76. Dilworth, J. R.; Parrott, S. J. *Chem. Soc. Rev.* **1998**, *27*, 43–55.
77. Jurisson, S. S.; Lydon, J. D. *Chem. Rev.* **1999**, *99*, 2205–2218.
78. Liu, S.; Edwards, D. S. *Chem. Rev.* **1999**, 1–106.
79. Schwochau, K. *Technetium: Chemistry and Radiopharmaceutical Applications*; Wiley-VCH: Weinheim, Germany, 2000.
80. *Technetium in Chemistry and Nuclear Medicine*; Mazzi, U, Nicolini, M, Bandoli, G. Eds. **1983**, Cortina International: Verona, Italy.
81. Keller, C.; Kanellakopulos, B. *Radiochim. Acta* **1963**, *1*, 107–108.
82. Schwochau, K. *Z. Naturforschg. A* **1962**, *A 17*, 630.
83. Mullen, P.; Schwochau, K.; Jorgensen, C. K. *Chem. Phys. Lett.* **1969**, *3*, 49–51.
84. Jovtschev, M.; Koch, H.; Kupsch, H. *Isotopenpraxis* **1975**, *11*, 369–378.
85. Magee, R. J.; Cardwell, T. J. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1974; Vol II, pp 125–189.
86. Russell, C. D. *Appl. Radiat. Isot.* **1982**, *33*, 883–889.
87. Boyd, G. E.; Cobble, J. W.; Nelson, C. M.; W. T. Smith, J. *J. Am. Chem. Soc.* **1952**, *74*, 556–557.
88. Harrell, A. Y.; Busey, R. H.; Gayer, K. H.; Schwochau, K.; Gutzeit, S. *Inorg. Synth.* **1977**, *17*, 155–158.
89. Smith, T. W. M. J.; Cobble, J. W.; Boyd, G. E. *J. Am. Chem. Soc.* **1953**, *75*, 5773–5776.
90. Franklin, K. J.; Lock, C. J. L.; Sayer, B. G.; Schrobilgen, G. J. *J. Fluorine Chem.* **1982**, *21*, 36.
91. Boyd, G. E. *J. Chem. Educ.* **1959**, *36*, 3–14.
92. Guest, A.; Lock, C. J. L. *Can. J. Chem.* **1972**, *50*, 1807–1810.
93. Gibson, J. K. *Radiochim. Acta* **1994**, *64*, 185–189.
94. Pershina, V. *J. Chem. Phys.* **2000**, *113*, 1441–1446.
95. Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965–969.

96. Bryan, J. C.; Burrell, A. K.; Miller, M. M.; Smith, W. H.; Burns, C. J.; Sattelberger, A. P. *Polyhedron* **1993**, *12*, 1769–1777.
97. Herrmann, W. A.; Alberto, R.; Kiprof, P.; Baumgärtner, F. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 189–191.
98. Kanellakopulos, B.; Raptis, K.; Nuber, B.; Ziegler, M. L. *Z. Naturforsch. B* **1991**, *46*, 15–18.
99. Selig, H.; Malm, J. G. *J Inorg Nucl Chem* **1963**, *25*, 349.
100. Binenboyn, J.; El–Gad, U.; Selig, H. *Inorg. Chem.* **1974**, *13*, 319–321.
101. Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **1993**, *32*, 145–151.
102. Casteel, W. J.; Dixon, D. A.; LeBlond, N.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **1998**, *37*, 340–353.
103. LeBlond, N.; Schrobilgen, G. J. *Inorg. Chem.* **2001**, *40*, 1245–1249.
104. LeBlond, N.; Schrobilgen, G. J. *Chem. Commun.* **1996**, 2479–2480.
105. LeBlond, N.; Mercier, H. P. A.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2000**, *39*, 4494–4509.
106. Davison, A.; Jones, A. G.; Abrams, M. J. *Inorg. Chem.* **1981**, *20*, 4300–4302.
107. Aronson, F. L.; Hwang, L. L. Y.; Ronca, N.; Solomon, N. A.; Steigman, J. *Inorg. Chem.* **1985**, *24*, 541–545.
108. Peters, G.; Preetz, W. *Z. Naturforsch. B* **1981**, *36*, 138–140.
109. DuPreez, J. G. H.; Gerber, T. J. A.; Gibson, M. L. *J. Coord. Chem.* **1990**, *22*, 33–42.
110. Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *7*, 1981–1989.
111. Gisdakis, P.; Rösch, N. *J. Am. Chem. Soc.* **2001**, *123*, 697–701.
112. Köstlmeier, S.; Häberlen, O. D.; Rösch, N.; Herrmann, W. A.; Solouki, B.; Bock, H. *Organometallics* **1996**, *15*, 1872.
113. Köstlmeier, S.; Pacchioni, G.; Rösch, N. *J. Organomet. Chem.* **1996**, *514*, 111.
114. Köstlmeier, S.; Nasluzov, V. A.; Herrmann, W. A.; Rösch, N. *Organometallics* **1997**, *16*, 1786.
115. Pearlstein, R. M. *Massachusetts Institute of Technology* **1988.**
116. Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Ziegler, M. L. *Z. Naturforsch. B* **1993**, *48*, 227–229.
117. Thomas, J. A.; Davison, A. *Inorg. Chim. Acta* **1991**, *190*, 231–235.
118. Banberry, H. J.; Hussain, W.; Evans, I. G.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A.; Schulte, H.-J.; Engels, B.; Kläui, W. *Polyhedron* **1990**, *9*, 2549–2551.
119. Thomas, J. A.; Davison, A. *Inorg. Chem.* **1992**, *31*, 1976–1978.
120. Baldas, J.; Colmanet, S. F.; Mackay, M. F. *J. Chem. Soc. Chem. Commun.* **1989**, *24*, 1890–1891.
121. Baldas, J.; Colmanet, S. F. *Inorg. Chim. Acta* **1990**, *176*, 1–3.
122. Baldas, J.; Colmanet, S. F.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1631–1633.
123. Abrams, M. J.; Chen, Q.; Shaikh, S. N.; Zubieta, J. *Inorg. Chim. Acta* **1990**, *176*, 11–13.
124. Burrell, A. K.; Bryan, J. C. *Organometallics* **1992**, *11*, 3501–3503.
125. Benson, M. T.; Bryan, J. C.; Burrell, A. K.; Cundari, T. R. *Inorg. Chem.* **1995**, *34*, 2348–2355.
126. Gerber, T. J. A.; Kemp, H. J.; DuPreez, J. G. H.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1992**, *202*, 191–196.
127. Baldas, J.; Boas, J. F.; Bonnyman, J.; Mackay, M. F.; Williams, G. A. *Aust. J. Chem.* **1982**, *35*, 2413–2422.
128. Colmanet, S. F.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1987**, 2305–2310.
129. Ginsberg, A. P. *Inorg. Chem.* **1964**, *3*, 567–569.
130. Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558–567.
131. Kissel, G.; Feldberg, S. W. *J. Phys. Chem.* **1969**, *73*, 3082–3088.
132. Deutsch, E.; Heineman, W. R.; Hurst, R.; Sullivan, J. C.; Mulac, W. A.; Gordon, S. *J. Chem. Soc. Chem. Commun.* **1978**, 1038–1040.
133. Astheimer, L.; Hauck, J.; Schenk, H. J.; Schwochau, K. *J. Chem. Phys.* **1975**, *63*, 1988–1991.
134. Rulfs, C. L.; Pacer, R. A.; Hirsh, R. F. *J. Inorg. Nucl. Chem.* **1967**, *29*, 681–691.
135. Fried, S.; Jaffey, A. H.; Hall, N. F.; Glendenin, L. E. *Phys. Rev.* **1951**, *81*, 741–747.
136. Selig, H.; Chernick, C. L.; Malm, J. G. *J. Inorg. Nucl. Chem.* **1961**, *19*, 377.
137. Edwards, A. J.; Hugill, D.; Peacock, R. D. *Nature* **1963**, *200*, 672.
138. Edwards, A. J.; Jones, G. R.; Sills, R. J. C. *Chem. Commun.* **1968**, 1177–1178.
139. Edwards, A. J.; Jones, G. R.; Sills, R. J. C. *J. Chem. Soc. A* **1970**, 2521–2523.
140. Holloway, J. H.; Selig, H. *J. Inorg. Nucl. Chem.* **1968**, *30*, 473–478.
141. Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1968**, *21*, 1981–1985.
142. Abram, U.; Wollert, R. *Radiochim. Acta* **1993**, *63*, 149–151.
143. Baldas, J.; F.Boas, J.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2395–2400.
144. Baldas, J.; Bonnyman, J.; Williams, G. A. *Inorg. Chem.* **1986**, *25*, 150–153.
145. Baldas, J.; Boas, J. F.; Bonnyman, J.; Colmanet, S. F.; Williams, G. A. *Inorg. Chim. Acta* **1991**, *179*, 151.
146. Mantegazzi, D.; Ianoz, E.; Lerch, P.; Tatsumi, K. *Inorg. Chim. Acta* **1990**, *167*, 195.
147. Baldas, J.; Colmanet, S. F. *Aust. J. Chem.* **1989**, *42*, 1155.
148. Kirmse, R.; Stach, J.; Abram, U. *Polyhedron* **1985**, *4*, 1403–1406.
149. Baldas, J.; Boas, J. F.; Colmanet, S. F.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 2441.
150. Abram, U.; Münze, R.; Kirmse, R.; Köhler, K.; Dietzsch, W.; Golic, L. *Inorg. Chim. Acta* **1990**, *169*, 49.
151. Baldas, J.; Boas, J. F. *J. Chem. Soc., Dalton Trans.* **1988**, 2585–2589.
152. Baldas, J.; Boas, J. F.; Bonnyman, J. *Aust. J. Chem.* **1989**, *42*, 639–648.
153. Baldas, J.; Boas, J. F.; Colmanet, S. F.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2845–2853.
154. Abram, U.; Kohler, K.; Kirmse, R.; Kalinichenko, N. B.; Marov, I. N. *Inorg. Chim. Acta* **1990**, *176*, 139–142.
155. Abram, U.; Abram, S.; Spies, H.; Kirmse, R.; Stach, J.; Köhler, K. *Z. Anorg. Allg. Chem.* **1987**, *544*, 167–180.
156. Baldas, J.; Heath, G. A.; Macgregor, S. A.; Moock, K. H.; Nissen, S. C.; Raptis, R. G. *J. Chem. Soc., Dalton Trans.* **1998**, 2303–2314.
157. Archer, C. M.; Dilworth, J. R.; Kelly, J. D.; Mcpartlin, M. *J. Chem. Soc., Chem. Commun.* **1989**, 375–376.
158. Clarke, M. J.; Lu, J. *Inorg. Chem.* **1992**, *31*, 2476–2480.
159. Lorenz, B.; Kraenke, P.; Schmidt, K.; Kirmse, R.; Huebener, R.; Abram, U. *Z. Anorg. Allg. Chem.* **1994**, *620*, 921–925.
160. Pietzsch, H.-J.; Abram, U.; Kirmse, R.; Köhler, K. *Z. Chem.* **1987**, *27*, 265–266.
161. Burgi, H. B.; Anderegg, G.; Blauenstein, P. *Inorg. Chem.* **1981**, *20*, 3829–3834.
162. Takayama, T.; Sekine, T.; Yoshihara, K. *J. Radioanal. Nucl. Chem. Letters* **1993**, *176*, 325–331.
163. Takayama, T.; Kani, Y.; Sekine, T.; Kudo, H.; Yoshihara, K. *J. Radioanal. Nucl. Chem. Letters* **1995**, *199*, 217–227.

164. Baldas, J.; Boas, J. F.; Ivanov, Z.; James, B. D. *Inorg. Chim. Acta* **1993**, *204*, 199–212.
165. Baldas, J.; Boas, J. F.; Colmanet, S. F.; Ivanov, Z.; Williams, G. A. *Radiochim. Acta* **1993**, *63*, 111.
166. Baldas, J.; Boas, J. F.; Colmanet, S. F.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1992**, 2845.
167. Ricard, L.; Martin, C.; Wiest, R.; Weiss, R. *Inorg. Chem.* **1975**, *14*, 2300.
168. Baldas, J.; Colmanet, S. F.; Mackay, M. F. *J. Chem. Soc., Dalton Trans*, **1988**, 1725–1731.
169. Lin, Z.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 3817.
170. Burrell, A. K.; Bryan, J. C. *Angew. Chem.* **1993**, *105*, 85–86.
171. Burrell, A. K.; Clark, D. L.; Gordon, P. L.; Sattelberger, A. P.; Bryan, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 3813–3821.
172. Burrell, A. K.; Bryan, J. C. *Organometallics* **1993**, *12*, 2426–2428.
173. Kirmse, R.; Stach, J.; Spies, H. *Inorg. Chim. Acta* **1980**, *45*, L251–L253.
174. Baldas, J.; Boas, J. F.; Bonnyman, J.; Pilbrow, J. R.; Williams, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 1886–1891.
175. Yamanouchi, K.; Enemark, J. H. *Inorg. Chem.* **1978**, *17*, 2911–2917.
176. deLearie, L. A.; Haltwanger, R. C.; Pierpont, C. G. *J. Am. Chem. Soc.* **1989**, *111*, 4324–4328.
177. Kawashima, M.; Koyama, M.; Fujinaga, T. *J. Inorg. Nucl. Chem.* **1976**, *38*, 801–805.
178. Abrams, M. J.; Larsen, S. K.; Zubieta, J. *Inorg. Chem.* **1991**, *30*, 2031–2035.
179. Kryuchkov, S. V.; Rakitin, Y. V.; Kazin, P. E.; Zhirov, A. I.; Konstantinov, N. Y. *Russ. J. Coord. Chem.* **1990**, *16 [Engl. 660]*, 1230.
180. Conner, K. A.; Walton, R. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 4, p 125.
181. Hugill, D.; Peacock, R. D. *J. Chem. Soc. A* **1966**, 1339–1341.
182. Frlec, B.; Selig, H.; Hyman, H. H. *Inorg. Chem.* **1967**, *6*, 1775.
183. Fergusson, J. E.; Nyholm, R. S. *Chem. Ind-London* **1960**, 347–348.
184. Glavan, K. A.; Whittle, R.; Johnson, J. F.; Deutsch, E. *J. Am. Chem. Soc.* **1980**, *102*, 2103–2104.
185. Cook, J.; Davis, W. M.; Davison, A.; Jones, A. G. *Inorg. Chem.* **1991**, *30*, 1773–1776.
186. Bandoli, G.; Gerber, T. I. A. *Inorg. Chim. Acta* **1987**, *126*, 205–208.
187. Bell, R. A.; Britten, J. F.; Guest, A.; Lock, C. J. L.; Valliant, J. F. *Chem. Commun.* **1997**, 585–586.
188. Cotton, F. A.; Davison, A.; Day, V. W.; Gage, L. D.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 3024–3029.
189. Fergusson, J. E.; Hickford, J. H. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2293–2296.
190. Rajec, P.; Macasek, F. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1607.
191. Fergusson, J. E.; Greenaway, A. M.; Penfold, B. R. *Inorg. Chim. Acta* **1983**, *71*, 29–34.
192. Preetz, W.; Peters, G. *Z. Naturforsch. B* **1980**, *35*, 1355–1358.
193. Thomas, R. W.; Davison, A.; Trop, H. S.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 2840–2842.
194. Davison, A.; Trop, H. S.; DePamphilis, B. V.; Jones, A. G. *Inorg. Synth.* **1982**, *21*, 160.
195. Huebener, R.; Abram, U. *Z. Anorg. Allg. Chem.* **1992**, *617*, 96–98.
196. Mantegazzi, D.; Ianoz, E.; Lerch, P. *Inorg. Chim. Acta* **1990**, *167*, 195–198.
197. Thomas, R. W.; Heeg, M. J.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1472–1477.
198. Kirmse, R.; Stach, J.; Abram, U. *Inorg. Chem.* **1985**, *24*, 2196–2198.
199. Baldas, J.; Boas, J. F.; Bonnyman, J.; Colmanet, S. F. In *Technetium and Rhenium in Chemistry and Nuclear Medicine*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1990, Vol. 3, p 63.
200. Davison, A.; Depamphilis, B. V.; Jones, A. G.; Franklin, K. J.; Lock, C. J. L. *Inorg. Chim. Acta* **1987**, *128*, 161–167.
201. Huber, G.; Anderegg, G.; May, K. *Polyhedron* **1987**, *6*, 1707–1708.
202. Rochon, F. D.; Melanson, R.; Kong, P.-C. *Acta Crystallogr. C* **1992**, *48*, 785–788.
203. Luo, H.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1993**, *32*, 4491–4497.
204. Sykes, A. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, U.K., 1987; Vol. 3, p 1250.
205. Jurisson, S.; Berning, D.; Jia, W.; Ma, D. S. *Chem. Rev.* **1993**, *93*, 1137–1156.
206. Hashimoto, K.; Yamada, Y.; Omori, T.; Yoshihara, K. *J. Radioanal. Nucl. Chem. Letters* **1989**, *135*, 187–197.
207. Smith, J. E.; Byrne, E. F.; Cotton, F. A.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 5571–5572.
208. Byrne, E. F.; Smith, J. E. *Inorg. Chem.* **1979**, *18*, 1832–1835.
209. Davison, A.; Orvig, C.; Trop, H. S.; Sohn, M.; DePamphilis, B. V.; Jones, A. G. *Inorg. Chem.* **1980**, *19*, 1988–1992.
210. Spies, H.; Johannsen, B.; Munze, R. *Z. Chem.* **1980**, *20*, 222–223.
211. Colmanet, S. F.; Mackay, M. F. *Aust. J. Chem.* **1987**, *40*, 1301–1307.
212. Colmanet, S. F.; Mackay, M. F. *Aust. J. Chem.* **1988**, *41*, 151–155.
213. Colmanet, S. F.; Mackay, M. F. *Inorg. Chim. Acta* **1988**, *147*, 173–178.
214. Spies, H.; Johannsen, B. *Inorg. Chim. a-Article* **1979**, *33*, L113–L113.
215. Spies, H.; Johannsen, B. *Inorg Chim, Acta* **1981**, *48*, 255–258.
216. Jones, A. G.; Depamphilis, B. V.; Davison, A. *Inorg. Chem.* **1981**, *20*, 1617–1618.
217. Depamphilis, B. V.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1983**, *22*, 2292–2297.
218. Davison, A.; Devries, N.; Dewan, J.; Jones, A. *Inorg. Chim. Acta* **1986**, *120*, L15–L16.
219. Hamor, T. A.; Hussain, W.; Jones, C. J.; McCleverty, J. A.; Rothin, A. S. *Inorg. Chim. Acta* **1988**, *146*, 181–185.
220. Abrams, M. J.; Brenner, D.; Davison, A.; Jones, A. G. *Inorg. Chim. a–Lett* **1983**, *77*, L127–L128.
221. Rochon, F. D.; Melanson, R.; Kong, P. C. *Inorg. Chim. Acta* **1992**, *194*, 43–50.
222. Bandoli, G.; Nicolini, M.; Mazzi, U.; Spies, H.; Munze, R. *Transit. Met. Chem.* **1984**, *9*, 127–129.
223. Blower, P. J.; Singh, J.; Clarke, S. E. M. *J. Nucl. Med.* **1991**, *32*, 845–849.
224. Blower, P. J.; Singh, J.; Clarke, S. E. M. *J. Nucl. Med.* **1992**, *33*, 469–469.
225. Pietzsch, H.-J.; Spies, H.; Leibnitz, P.; Reck, G.; Beger, J.; Jacobi, R. *Polyhedron* **1993**, *12*, 187–193.
226. Pietzsch, H.-J.; Spies, H.; Leibnitz, P.; Reck, G. *Polyhedron* **1995**, *14*, 1849–1853.
227. Pietzsch, H. J.; Spies, H.; Hoffmann, S. *Inorg. Chim. Acta* **1989**, *165*, 163–166.
228. Fietz, T.; Spies, H.; Pietzsch, H.-J.; Leibnitz, P. *Inorg. Chim. Acta* **1995**, *231*, 233–236.
229. Pietzsch, H. J.; Spies, H.; Hoffmann, S.; Stach, J. *Inorg. Chim. Acta* **1989**, *161*, 15–16.
230. Spies, H.; Pietzsch, H. J.; Syhre, R.; Hoffmann, S. *Isotopenpraxis* **1990**, *26*, 159–162.
231. Pietzsch, H. J.; Spies, H.; Hoffmann, S.; Scheller, D. *Appl. Radiat. Isot.* **1990**, *41*, 185–188.

232. Spies, H.; Fietz, T.; Glaser, M.; Pietzsch, H.-J.; Johannsen, B. In *Technetium and Rhenium in Chemistry and Nuclear Medicine 4*; Bandoli, M.; Mazzi, G., Nicolini, U., Eds.; **1995**, SGE: Padua, Italy, p 243.
233. Spies, H.; Fietz, T.; Pietzsch, H. J.; Johannsen, B.; Leibnitz, P.; Reck, G.; Scheller, D.; Klostermann, K. *J. Chem. Soc., Dalton Trans*. **1995**, 2277–2280.
234. Mastrostamatis, S. G.; Papadopoulos, M. S.; Pirmettis, I. C.; Paschali, E.; Varvarigou, A. D.; Stassinopoulou, C. I.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E. *J. Med. Chem*. **1994**, *37*, 3212–3218.
235. Stassinopoulou, C. I.; Pelecanou, M.; Mastrostamatis, S.; Chiotellis, E. *Magn. Reson. Chem*. **1994**, *32*, 532–536.
236. Spyriounis, D. M.; Pelecanou, M.; Stassinopoulou, C. I.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E. *Inorg. Chem*. **1995**, *34*, 1077–1082.
237. Papadopoulos, M. S.; Pirmettis, I. C.; Pelecanou, M.; Raptopoulou, C. P.; Terzis, A.; Stassinopoulou, C. I.; Chiotellis, E. *Inorg. Chem*. **1996**, *35*, 7377–7383.
238. Papadopoulos, M.; Pirmettis, I.; Tsoukalas, C.; Nock, B.; Maina, T.; Raptopoulou, C. P.; Pietzsch, H. J.; Friebe, M.; Spies, H.; Johannsen, B.; Chiotellis, E. *Inorg. Chim. Acta* **1999**, *295*, 1–8.
239. Pelecanou, M.; Pirmettis, I. C.; Papadopoulos, M. S.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E.; Stassinopoulou, C. I. *Inorg. Chim. Acta* **1999**, *287*, 142–151.
240. Maina, T.; Tsoukalas, C.; Patsis, G.; Pirmettis, I.; Nock, B.; Papadopoulos, M.; Raptopoulou, C.; Terzis, A.; Chiotellis, E. *Polyhedron* **1999**, *18*, 3545–3552.
241. Pirmettis, I.; Patsis, G.; Pelecanou, M.; Tsoukalas, C.; Papadopoulos, A.; Raptopoulou, C. P.; Terzis, A.; Papadopoulos, M.; Chiotellis, E. *Bioorg Med. Chem. Lett* **2001**, *11*, 1859–1862.
242. Papadopoulos, M. S.; Pelecanou, M.; Pirmettis, I. C.; Spyriounis, D. M.; Raptopoulou, C. P.; Terzis, A.; Stassinopoulou, C. I.; Chiotellis, E. *Inorg. Chem*. **1996**, *35*, 4478–4483.
243. Pirmettis, I. C.; Papadopoulos, M. S.; Mastrostamatis, S. G.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E. *Inorg. Chem*. **1996**, *35*, 1685–1691.
244. Johannsen, B.; Scheunemann, M.; Spies, H.; Brust, P.; Wober, J.; Syhre, R.; Pietzsch, H. J. *Nucl. Med. Biol*. **1996**, *23*, 429–438.
245. Meegalla, S.; Plossl, K.; Kung, M. P.; Svenson, D. A.; Liablesands, L. M.; Rheingold, A. L.; Kung, H. F. *J. Am. Chem. Soc*. **1995**, *117*, 11037–11038.
246. Seifert, S.; Pietzsch, H.-J.; Scheunemann, M.; Spies, H.; Syhre, R.; Johannsen, B. *Appl. Radiat. Isot*. **1997**, *49*, 5–11.
247. Bouziotis, P.; Pirmettis, I.; Pelecanou, M.; Raptopoulou, C. P.; Terzis, A.; Papadopoulos, M.; Chiotellis, E. *Chem-Eur J* **2001**, *7*, 3671–3680.
248. Bandoli, G.; Mazzi, U.; Abram, U.; Spies, H.; Münze, R. *Polyhedron* **1987**, *6*, 1547–1550.
249. Abram, U.; Spies, H. *Z. Chem*. **1984**, *24*, 74–75.
250. Kastner, M. E.; Lindsay, M. J.; Clarke, M. J. *Inorg. Chem*. **1982**, *21*, 2037–2040.
251. Kremer, C.; Gancheff, J.; Kremer, E.; Mombru, A. W.; Gonzalez, O.; Mariezcurrena, R.; Suescun, L.; Cubas, M. L.; Ventura, O. N. *Polyhedron* **1997**, *16*, 3311–3316.
252. Riché, F.; Vidal, M.; Bolzati, C.; Uccelli, L.; Marchi, A.; Duatti, A. *Inorg. Chim. Acta* **1995**, *231*, 147–151.
253. Zuckman, S. A.; Freeman, G. M.; Troutner, D. E.; Volkert, W. A.; Holmes, R. A.; Derveer, D. G. V.; Barefield, E. K. *Inorg. Chem*. **1981**, *20*, 2386–2389.
254. Fackler, P. H.; Lindsay, M. J.; Clarke, M. J.; Kastner, M. E. *Inorg. Chim. a-F-Block* **1985**, *109*, 39–49.
255. Rochon, F. D.; Melanson, R.; Kong, P. C. *Inorg. Chim. Acta* **1997**, *254*, 303–307.
256. Kuzina, A. F.; Oblova, A. A.; Spitsyn, V. I. *Russ. J. Inorg. Chem*. **1972**, *17*, 1377–1379.
257. Kastner, M. E.; Fackler, P. H.; Clarke, M. J.; Deutsch, E. *Inorg. Chem*. **1984**, *23*, 4683–4688.
258. Libson, K.; Barnett, B. L.; Deutsch, E. *Inorg. Chem*. **1983**, *22*, 1695–1704.
259. Fackler, P. H.; Kastner, M. E.; Clarke, M. J. *Inorg. Chem*. **1984**, *23*, 3968–3972.
260. Kastner, M. E.; Fackler, P. H.; Podbielski, L.; Charkoudian, J.; Clarke, M. J. *Inorg. Chim. Acta* **1986**, *114*, L11–L15.
261. Pearlstein, R. M.; Lock, C. J. L.; Faggiani, R.; Costello, C. E.; Zeng, C. H.; Jones, A. G.; Davison, A. *Inorg. Chem*. **1988**, *27*, 2409–2413.
262. Lu, J.; Clarke, M. J. *Inorg. Chem*. **1989**, *28*, 2315–2319.
263. Troutner, D. E.; Volkert, W. A.; Hoffman, T. J.; Holmes, R. A. *Int. J. Appl. Radiat. Isot*. **1984**, *35*, 467–470.
264. Holmes, R. A.; Chaplin, S. B.; Royston, K. G.; Hoffman, T. J.; Volkert, W. A.; Nowotnik, D. P.; Canning, L. R.; Cumming, S. A.; Harrison, R. C.; Higley, B.; Nechvatal, G.; Pickett, R. D.; Piper, I. M.; Neirinckx, R. D. *Nucl. Med. Commun*. **1985**, *6*, 443–447.
265. Chaplin, S. B.; Oberle, P. O.; Hoffman, T. J.; Volkert, W. A.; Holmes, R. A.; Nowotnik, D. P.; Pickett, R. D.; Neirinckx, R. *J. Nucl. Med*. **1985**, *26*, P18–P18.
266. Hoffman, T. J.; Seger, R. M.; Mckenzie, E. H.; Volkert, W. A.; Holmes, R. A.; Pettit, R. P.; Canning, L.; Cumming, S. A.; Nechvatal, G. *J. Nucl. Med*. **1985**, *26*, P129–P130.
267. Fair, C. K.; Troutner, D. E.; Schlemper, E. O.; Murmann, R. K.; Hoppe, M. L. *Acta Crystallogr. C* **1984**, *40*, 1544–1546.
268. Jurisson, S.; Schlemper, E. O.; Troutner, D. E.; Canning, L. R.; Nowotnik, D. P.; Neirinckx, R. D. *Inorg. Chem*. **1986**, *25*, 543–549.
269. Jurisson, S.; Aston, K.; Fair, C. K.; Schlemper, E. O.; Sharp, P. R.; Troutner, D. E. *Inorg. Chem*. **1987**, *26*, 3576–3582.
270. Davison, A. *Technetium in Chemistry and Nuclear Medicine*; Cortina International: Verona, Italy, 1983.
271. Lawrence, A. J.; Thornback, J. R.; Zanelli, G. D.; Lawson, A. *Inorg. Chim. Acta* **1988**, *141*, 165–166.
272. Schwochau, K.; Linse, K. H.; Pleger, P.; Pleger, U.; Kremer, C.; deGraaf, A. A. *J. Labelled Compd. Radiopharm*. **1996**, *38*, 1031–1038.
273. Thomas, R. W.; Estes, G. W.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc*. **1979**, *101*, 4581–4585.
274. Deutsch, E. A.; Elder, R. C.; Packard, A. *cited in Coord. Chem. Rev*. **1982**, *44*, 191.
275. Morgan, G. F.; Abram, U.; Evrard, G.; Durant, F.; Deblaton, M.; Clemens, P.; Vandenbroeck, P.; Thornback, J. R. *J. Chem. Soc., Chem. Commun*. **1990**, 1772–1773.
276. Morgan, G. F.; Deblaton, M.; Hussein, W.; Thornback, J. R.; Evrard, G.; Durant, F.; Stach, J.; Abram, U.; Abram, S. *Inorg. Chim. Acta* **1991**, *190*, 257–264.
277. Wilcox, B. E.; Heeg, M. J.; Deutsch, E. *Inorg. Chem*. **1984**, *23*, 2962–2967.

278. Bandoli, G.; Mazzi, U.; Clemente, D. A.; Roncari, E. *J. Chem. Soc., Dalton Trans.* **1982**, 2455–2459.
279. Mazzi, U.; Refosco, F.; Tisato, F.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1623–1628.
280. Refosco, F.; Mazzi, U.; Deutsch, E.; Kirchhoff, J. R.; Heineman, W. R.; Seeber, R. *Inorg. Chem.* **1988**, *27*, 4121–4127.
281. Bandoli, G.; Mazzi, U.; Wilcox, B. E.; Jurisson, S.; Deutsch, E. *Inorg. Chim. a-F-Block* **1984**, *95*, 217–223.
282. Dupreez, J. G. H.; Gerber, T. I. A.; Kemp, H. J. *J. Coord. Chem.* **1992**, *26*, 177–186.
283. Dupreez, J. G. H.; Gerber, T. I. A.; Jacobs, R. *J. Coord. Chem.* **1994**, *33*, 147–160.
284. Wilcox, B. E.; Cooper, J. N.; Elder, R. C.; Deutsch, E. *Inorg. Chim. Acta* **1988**, *142*, 55–58.
285. Duatti, A.; Marchi, A.; Rossi, R.; Magon, L.; Deutsch, E.; Bertolasi, V.; Bellucci, F. *Inorg. Chem.* **1988**, *27*, 4208–4213.
286. Shuter, E.; Hoveyda, H. R.; Karunaratne, V.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1996**, *35*, 368–372.
287. Jurisson, S.; Lindoy, L. F.; Dancey, K. P.; Mcpartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 227–231.
288. Abrams, M. J.; Shaikh, S. N.; Zubieta, J. *Inorg. Chim. Acta* **1991**, *186*, 87–90.
289. Luo, H. Y.; Liu, S.; Rettig, S. J.; Orvig, C. *Can. J. Chem.* **1995**, *73*, 2272–2281.
290. Pillai, M. R. A.; John, C. S.; Lo, J. M.; Schlemper, E. O.; Troutner, D. E. *Inorg. Chem.* **1990**, *29*, 1850–1856.
291. Pillai, M. R. A.; Barnes, C. L.; Schlemper, E. O. *Polyhedron* **1994**, *13*, 701–708.
292. Abram, U.; Abram, S.; Maecke, H. R.; Koch, P. *Z. Anorg. Allg. Chem.* **1995**, *621*, 854–860.
293. Duatti, A.; Marchi, A.; Magon, L.; Deutsch, E.; Bertolasi, V.; Gilli, G. *Inorg. Chem.* **1987**, *26*, 2182–2186.
294. Tisato, F.; Refosco, F.; Moresco, A.; Bandoli, G.; Mazzi, U.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 2225–2232.
295. Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1693–1699.
296. Mazzi, U.; Refosco, F.; Bandoli, G.; Nicolini, M. *Transit. Met. Chem.* **1985**, *10*, 121–127.
297. Dupreez, J. G. H.; Gerber, T. I. A.; Gibson, M. L. *J. Coord. Chem.* **1990**, *22*, 159–163.
298. Dupreez, J. G. H.; Gerber, T. I. A.; Fourie, P. J.; Vanwyk, A. J. *J. Coord. Chem.* **1984**, *13*, 173–178.
299. Davison, A.; Jones, A. G.; Orvig, C.; Sohn, M. *Inorg. Chem.* **1981**, *20*, 1629–1632.
300. Jones, A. G.; Davison, A.; Lategola, M. R.; Brodack, J. W.; Orvig, C.; Sohn, M.; Toothaker, A. K.; Lock, C. J. L.; Franklin, K. J.; Costello, C. E.; Carr, S. A.; Biemann, K.; Kaplan, M. L. *J. Nucl. Med.* **1982**, *23*, 801–809.
301. Fritzberg, A. R.; Klingensmith, W. C.; Whitney, W. P.; Kuni, C. C. *J. Nucl. Med.* **1981**, *22*, 258–263.
302. Brenner, D.; Davison, A.; Lister-James, J.; Jones, A. G. *Inorg. Chem.* **1984**, *23*, 3793–3797.
303. Kasina, S.; Fritzberg, A. R.; Johnson, D. L.; Eshima, D. *J. Med. Chem.* **1986**, *29*, 1933–1940.
304. Rao, T. N.; Brixner, D. I.; Srinivasan, A.; Kasina, S.; Vanderheyden, J. L.; Wester, D. W.; Fritzberg, A. R. *Appl Radiat. Isot.* **1991**, *42*, 525–530.
305. O'Neil, J. P.; Wilson, S. R.; Katzenellenbogen, J. A. *Inorg. Chem.* **1994**, *33*, 319–323.
306. Archer, C. M.; Dilworth, J. R.; Griffiths, D. V.; AlJeboori, M. J.; Kelly, J. D.; Lu, C. Z.; Rosser, M. J.; Zheng, Y. F. *J. Chem. Soc., Dalton Trans.* **1997**, 1403–1410.
307. Edwards, D. S.; Cheesman, E. H.; Watson, M. W.; Maheu, L. J.; Nguyen, S. A.; Dimitre, L.; Nason, T.; Watson, A. D.; Walovitch, R. In *Technetium in Chemistry and Nuclear Medicine*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1990; Vol. 3, pp 433–444.
308. Lever, S. Z.; Baidoo, K. E.; Mahmood, A. *Inorg. Chim. Acta* **1990**, *176*, 183–184.
309. Kung, H. F.; Guo, Y. Z.; Yu, C. C.; Billings, J.; Subramanyam, V.; Calabrese, J. C. *J. Med. Chem.* **1989**, *32*, 433–437.
310. Francesconi, L. C.; Graczyk, G.; Wehrli, S.; Shaikh, S. N.; McClinton, D.; Liu, S.; Zubieta, J.; Kung, H. F. *Inorg. Chem.* **1993**, *32*, 3114–3124.
311. Lock, C. J. L.; Wan, C. *Can. J. Chem.* **1975**, *53*, 1548–1553.
312. Cotton, F. A.; Lippard, S. J. *Inorg. Chem.* **1965**, *4*, 1621–1629.
313. Johnson, D. L.; Fritzberg, A. R.; Hawkins, B. L.; Kasina, S.; Eshima, D. *Inorg. Chem.* **1984**, *23*, 4204–4207.
314. Marchi, A.; Marvelli, L.; Rossi, R.; Magon, L.; Bertolasi, V.; Ferretti, V.; Gilli, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1485–1490.
315. John, C. S.; Francesconi, L. C.; Kung, H. F.; Wehrli, S.; Graczyk, G.; Carroll, P. *Polyhedron* **1992**, *11*, 1145–1155.
316. Ohmomo, Y.; Francesconi, L.; Kung, M. P.; Kung, H. F. *J. Med. Chem.* **1992**, *35*, 157–162.
317. Stassinopoulou, C. I.; Mastrostamatis, S.; Papadopoulos, M.; Vavouraki, H.; Terzis, A.; Hountas, A.; Chiotellis, E. *Inorg. Chim. Acta* **1991**, *189*, 219–224.
318. Dupreez, J. G. H.; Gerber, T. I. A.; Gibson, M. L. *J. Coord. Chem.* **1991**, *22*, 321–325.
319. Dupreez, J. G. H.; Gerber, T. I. A.; Gibson, M.; Kemp, H. J. *J. Coord. Chem.* **1992**, *25*, 53–61.
320. Nosco, D. L.; Manning, R. G.; Fritzberg, A. *J. Nucl. Med.* **1986**, *27*, 939–939.
321. Blaton, N. M.; Bormans, G.; Peeters, O. M.; Verbruggen, A. *Acta Crystallogr. C* **1997**, *53*, 449–451.
322. Grummon, G.; Rajagopalan, R.; Palenik, G. J.; Koziol, A. E.; Nosco, D. L. *Inorg. Chem.* **1995**, *34*, 1764–1772.
323. Nosco, D. L.; Tofe, A. J.; Dunn, T. J.; Lyle, L. R.; Wolfangel, R. G.; Bushman, M. J.; Grummon, G. D.; Helling, D. E.; Marmion, M. E.; Miller, K. M.; Pipes, D. W.; Strubel, T. W.; Wester, D. W.; Nicolini, M.; Bandoli, G.; Mazzi, U., Ed., *Technetium and Rhenium in Chemistry and Nuclear Medicine* **1990**, *3*, 381. Cortina International: Italy.
324. Hansen, L.; Cini, R.; Taylor, A.; Marzilli, L. G. *Inorg. Chem.* **1992**, *31*, 2801–2808.
325. Bormans, G. M.; Cleynhen, B. J.; Deroo, M. J. K.; Verbruggen, A. M. *Eur. J. Nucl. Med.* **1992**, *19*, 271–277.
326. Verbruggen, A.; Bormans, G.; Cleynhens, B.; Hoogmartens, M.; Vandecruys, A.; Deroo, M. J. K. *J. Labelled Compd. Radiopharm.* **1989**, *26*, 436.
327. Hansen, L.; Marzilli, L. G.; Eshima, D.; Malveaux, E. J.; Folks, R.; Taylor, A. *J. Nucl. Med.* **1994**, *35*, 1198–1205.
328. Bandoli, G.; Clemente, D. A.; Panttoni, C.; Dondoni, A.; Mangini, A. *J. Chem. Soc., Chem. Commun.* **1970**, 1143.
329. Johannsen, B.; Noll, B.; Leibnitz, P.; Reck, G.; Noll, S.; Spies, H. *Inorg. Chim. Acta* **1993**, *210*, 209–214.
330. Bormans, G.; Peeters, O. M.; Vanbilloen, H.; Blaton, N.; Verbruggen, A. M. *Inorg. Chim. Acta* **1996**, *35*, 6240–6244.
331. Alarabi, H.; Bell, R. A.; Faggiani, R.; Howard–Lock, H. E.; Lock, C. J. L.; Kramer, A. V. *Inorg. Chem.* **1995**, *34*, 1688–1694.
332. Wong, E.; Fauconnier, T.; Bennett, S.; Valliant, J.; Nguyen, T.; Lau, F.; Lu, L. F. L.; Pollak, A.; Bell, R. A.; Thornback, J. R. *Inorg. Chem.* **1997**, *36*, 5799–5808.

333. Valliant, J. F.; Riddoch, R. W.; Hughes, D. W.; Roe, D. G.; Fauconnier, T. K.; Thornback, J. R. *Inorg. Chim. Acta* **2001**, *325*, 155–163.
334. Wong, E.; Bennett, S.; Lawrence, B.; Fauconnier, T.; Lu, L. F. L.; Bell, R. A.; Thornback, J. R.; Eshima, D. *Inorg. Chem.* **2001**, *40*, 5695.
335. Bryson, N.; Dewan, J. C.; Lister-James, J.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 2154–2161.
336. Bryson, N.; Lister-James, J.; Jones, A. G.; Davis, W. M.; Davison, A. *Inorg. Chem.* **1990**, *29*, 2948–2951.
337. Dunn-Dufault, R.; Pollak, A.; Fitzgerald, J.; Thornback, J. R.; Ballinger, J. R. *Nucl. Med. Biol.* **2000**, *27*, 803–807.
338. Nicolini, M.; Bandoli, G.; Mazzi, U., Eds.; *Technetium and Rhenium in Chemistry and Nuclear Medicine*; Cortina International, Verona, Italy, 1990; Vol. 3. p 221.
339. Faggiani, R.; Lock, C. J. L.; Epps, L. A.; Kramer, A. V.; Brune, H. D. *Acta Crystallogr. C* **1990**, *46*, 2324–2327.
340. Rajagopalan, R.; Grummon, G. D.; Bugaj, J.; Hallemann, L. S.; Webb, E. G.; Marmion, M. E.; Vanderheyden, J.-L.; Srinivasan, A. *Bioconjugate Chem* **1997**, *8*, 407–415.
341. Spies, H.; Syhre, R.; Pietzsch, H.-J. *Plzen lek Sborn* **1990**, *62*, 85.
342. Syhre, R.; Seifert, S.; Spies, H.; Gupta, A.; Johannsen, B. *Eur. J. Nucl. Med.* **1998**, *25*, 793–796.
343. Pelecanou, M.; Pirmettis, I. C.; Nock, B. A.; Papadopoulos, M.; Chiotellis, E.; Stassinopoulou, C. I. *Inorg. Chim. Acta* **1998**, *281*, 148–152.
344. Seifert, S.; Syhre, R.; Gupta, A.; Spies, H.; Johannsen, B. In *Technetium, Rhenium and Other Metals in Chemistry and Nuclear Medicine*; Nicolini, M., Mazzi, U., Eds; SGEditorali, **1999**, 687–690, Padua, Italy.
345. Refosco, F.; Bolzati, C.; Moresco, A.; Bandoli, G.; Dolmella, A.; Mazzi, U.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1991**, 3043–3048.
346. Refosco, F.; Tisato, F.; Bandoli, G.; Bolzati, C.; Dolmella, A.; Moresco, A.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1993**, 605–618.
347. Tisato, F.; Refosco, F.; Bandoli, G. *Coord. Chem. Rev.* **1994**, *135*/*136*, 325–397.
348. Tisato, F.; Refosco, F.; Moresco, A.; Bandoli, G.; Dolmella, A.; Bolzati, C. *Inorg. Chem.* **1995**, *34*, 1779–1787.
349. Dilworth, J. R.; Griffiths, D. V.; Hughes, J. M.; Morton, S.; Archer, C. M.; Kelly, J. D. *Inorg. Chim. Acta* **1992**, *195*, 145–149.
350. Dilworth, J. R.; Hutson, A. J.; Morton, S.; Harman, M.; Hursthouse, M. B.; Zubieta, J.; Archer, C. M.; Kelly, J. D. *Polyhedron* **1992**, *11*, 2151–2155.
351. Bolzati, C.; Refosco, F.; Tisato, F.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1992**, *201*, 7–10.
352. Luo, H.; Setyawati, I.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1995**, *34*, 2287–2299.
353. Bolzati, C.; Tisato, F.; Refosco, F.; Bandoli, G. *Inorg. Chim. Acta* **1996**, *247*, 125–127.
354. Kuzina, A. F.; Oblova, A. A.; Spitsyn, V. I. *Zh. Neorganicheskoi Khim.* **1972**, *17*, 2630.
355. Roodt, A.; Leipoldt, J. G.; Deutsch, E. A.; Sullivan, J. C. *Inorg. Chem.* **1992**, *31*, 1080–1085.
356. Truffer, S.; Ianoz, E.; Lerch, P.; Kosinski, M. *Inorg. Chim. Acta* **1988**, *149*, 217–222.
357. Ianoz, E.; Mantegazzi, D.; Lerch, P.; Nicolo, F.; Chapuis, G. *Inorg. Chim. Acta* **1989**, *156*, 235–239.
358. Vanderheyden, J.-L.; Ketring, A. R.; Libson, K.; Heeg, M. J.; Roecker, L.; Motz, P.; Whittle, R.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 3184–3191.
359. Vanderheyden, J. L.; Libson, K.; Nosco, D. L.; Ketring, A. R.; Deutsch, E. *Int. J. Appl. Radiat. Isot.* **1983**, *34*, 1611–1618.
360. Kelly, J. D.; Forster, A. M.; Higley, B.; Archer, C. M.; Booker, F. S.; Canning, L. R.; Chiu, K. W.; Edwards, B.; Gill, H. K.; McPartlin, M.; Nagle, K. R.; Latham, I. A.; Pickett, R. D.; Storey, A. E.; Webbon, P. M. *J. Nucl. Med.* **1993**, *34*, 222–227.
361. Rochon, F. D.; Melanson, R.; Kong, P. C. *Inorg. Chem.* **1998**, *37*, 87–92.
362. Tisato, F.; Mazzi, U.; Bandoli, G.; Cros, G.; Darbieu, M. H.; Coulais, Y.; Guiraud, R. *J. Chem. Soc., Dalton Trans.* **1991**, 1301–1307.
363. Pillai, M. R. A.; Kothari, K.; Schlemper, E. O.; Corlija, M.; Holmes, R. A.; Volkert, W. A. *Appl. Radiat. Isot.* **1993**, *44*, 1113–1118.
364. Dupreez, J. G. H.; Gerber, T. I. A.; Jacobs, R. *J. Coord. Chem.* **1992**, *26*, 259–268.
365. Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1989**, *164*, 127–135.
366. Bandoli, G.; Nicolini, M.; Mazzi, U.; Refosco, F. *J. Chem. Soc., Dalton Trans.* **1984**, 2505–2511.
367. Trop, H. S. *cited in Int. J. Appl. Radiat. Isot.* **1982**, *33*, 875.
368. Trop, H. S.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1980**, *19*, 1993–1997.
369. Baldas, J. *Top. Curr. Chem.* **1996**, *176*, 37–76.
370. Dupreez, J. G. H.; Gerber, T. I. A.; Jacobs, R. *J. Coord. Chem.* **1994**, *33*, 147–160.
371. Davison, A.; Depamphilis, B. V.; Faggiani, R.; Jones, A. G.; Lock, C. J. L.; Orvig, C. *Can. J. Chem.* **1985**, *63*, 319–323.
372. Bryson, N. J.; Brenner, D.; Listerjames, J.; Jones, A. G.; Dewan, J. C.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3825–3828.
373. Colmanet, S. F.; Mackay, M. F. *Aust. J. Chem.* **1988**, *41*, 269–277.
374. Tisato, F.; Bolzati, C.; Duatti, A.; Bandoli, G.; Refosco, F. *Inorg. Chem.* **1993**, *32*, 2042–2048.
375. Kaden, L.; Lorenz, B.; Schmidt, K.; Sprinz, H.; Wahren, M. *Isotopenpraxis* **1981**, *17*, 174–175.
376. Abram, U.; Spies, H. *Inorg Chim a-F-Block* **1984**, *94*, L3–L6.
377. Kaden, L.; Lorenz, B.; Schmidt, K.; Sprinz, H.; Wahren, M. *Isotopenpraxis* **1981**, *17*, 174–175.
378. Baldas, J.; Bonnyman, J.; Pojer, P. M.; Williams, G. A.; Mackay, M. F. *J. Chem. Soc., Dalton Trans.* **1981**, 1798–1801.
379. Abram, U.; Lorenz, B.; Kaden, L.; Scheller, D. *Polyhedron* **1988**, *7*, 285–289.
380. Forsellini, E.; Casellato, U.; Graziani, R.; Magon, L. *Acta Crystallogr. B* **1982**, *38*, 3081–3083.
381. Williams, G. A.; Baldas, J. *J. Nucl. Med. Allied Sciences* **1989**, *33*, 327.
382. Baldas, J.; Boas, J. F.; Colmanet, S. F.; Mackay, M. F. *Inorg. Chim. Acta* **1990**, *170*, 233–239.
383. Baldas, J.; Colmanet, S. F.; Williams, G. A. *unpublished results*.
384. Baldas, J.; Ivanov, Z. *unpublished results*.
385. Marchi, A.; Rossi, R.; Magon, L.; Duatti, A.; Pasqualini, R.; Ferretti, V.; Bertolasi, V. *J. Chem. Soc., Dalton Trans.* **1990**, 1411–1416.

386. Baldas, J.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 833–837.
387. Hagenbach, A.; Abram, U. *Z. Anorg. Allg. Chem.* **2002**, *628*, 31–33.
388. Abram, U.; Dilworth, J. R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 609–612.
389. Abram, U.; Spies, H.; Görner, W.; Kirmse, R.; Stach, J. *Inorg. Chim. Acta* **1985**, *109*, L9–L11.
390. Ritter, S.; Abram, U.; Dilworth, J. R. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1975–1978.
391. Abram, U.; Abram, S.; Dilworth, J. R. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1257–1262.
392. Marchi, A.; Duatti, A.; Rossi, R.; Magon, L.; Pasqualini, R.; Bertolasi, V.; Ferretti, V.; Gilli, G. *J. Chem. Soc., Dalton Trans.* **1988**, 1743–1749.
393. Marchi, A.; Uccelli, L.; Marvelli, L.; Rossi, R.; Giganti, M.; Bertolasi, V.; Ferretti, V. *J. Chem. Soc., Dalton Trans.* **1996**, 3105–3109.
394. Marchi, A.; Marvelli, L.; Rossi, R.; Magon, L.; Uccelli, L.; Bertolasi, V.; Ferretti, V.; Zanobini, F. *J. Chem. Soc. Dalton Trans.* **1993**, 1281–1286.
395. Refosco, F.; Tisato, F.; Moresco, A.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1995**, 3475–3482.
396. Archer, C. M.; Dilworth, J. R.; Griffiths, D. V.; McPartlin, M.; Kelly, J. D. *J. Chem. Soc.* **1992**, *Dalton Transactions*, 183–189.
397. Rochon, F. D.; Melanson, R.; Kong, P.-C. *Polyhedron* **1996**, *15*, 2641–2646.
398. Abram, U.; Hartung, J.; Beyer, L.; Stach, J.; Kirmse, R. *Z. Chem.* **1990**, *30*, 180–181.
399. Marchi, A.; Rossi, R.; Magon, L.; Duatti, A.; Casellato, U.; Graziani, R.; Vidal, M.; Riche, F. *J. Chem. Soc. Dalton* **1990**, 1935–1940.
400. Kani, Y.; Takayama, T.; Inomata, S.; Sekine, T.; Kudo, H. *Chem. Lett.* **1995**, 1059–1060.
401. Kani, Y.; Takayama, T.; Sekine, T.; Kudo, H. *J. Chem. Soc., Dalton Trans.* **1999**, 209–213.
402. Dilworth, J. R.; Hubener, R.; Abram, U. *Z. Anorg. Allg. Chem.* **1997**, *623*, 880–882.
403. Abram, U.; Lang, E. S.; Abram, S.; Wegmann, J.; Dilworth, J. R.; Kirmse, R.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1997**, 623–630.
404. Pietzsch, H. J.; Spies, H.; Leibnitz, P.; Reck, G.; Beger, J.; Jacobi, R. *Polyhedron* **1993**, *12*, 187–193.
405. Pietzsch, H. J.; Spies, H.; Leibnitz, P.; Reck, G.; Johannsen, B. *Radiochim. Acta* **1993**, *63*, 163–166.
406. Marchi, A.; Rossi, R.; Marvelli, L. *Inorg. Chem.* **1993**, *32*, 4673–4674.
407. Cattabriga, M.; Marchi, A.; Marvelli, L.; Rossi, R.; Vertuani, G.; Pecoraro, R.; Scatturin, A.; Bertolasi, V.; Ferretti, V. *J. Chem. Soc., Dalton Trans.* **1998**, 1453–1460.
408. Cros, G.; Belhadj Tahar, H.; de Montauzon, D.; Gleizes, A.; Coulais, Y.; Guiraud, R.; Bellande, E.; Pasqualini, R. *Inorg. Chim. Acta* **1994**, *227*, 25–31.
409. Bolzati, C.; Boschi, A.; Uecelli, L.; Malago, E.; Bandoli, G.; Tisato, F.; Refosco, F.; Pasqualini, R.; Duatti, A. *Inorg. Chem.* **1999**, *38*, 4473–4479.
410. Bolzati, C.; Uccelli, L.; Boschi, A.; Malago, E.; Duatti, A.; Tisato, F.; Refosco, F.; Pasqualini, R.; Piffanelli, A. *Nucl. Med. Biol.* **2000**, *27*, 369–374.
411. Bolzati, C.; Boschi, A.; Duatti, A.; Prakash, S.; Uccelli, L. *J. Am. Chem. Soc.* **2000**, *122*, 4510–4511.
412. Boschi, A.; Bolzati, C.; Benini, E.; Malago, E.; Uccelli, L.; Duatti, A.; Piffanelli, A.; Refosco, F.; Tisato, F. *Bioconjugate Chem* **2001**, *12*, 1035–1042.
413. Nicholson, T.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1990**, *168*, 227–231.
414. Nicholson, T.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1991**, *187*, 51–57.
415. Nicholson, T.; Cook, J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1994**, *218*, 97–101.
416. Archer, C. M.; Dilworth, J. R.; Jobanputra, P.; Thompson, R. M.; McPartlin, M.; Povey, D. C.; Smith, G. W.; Kelly, J. D. *Polyhedron* **1990**, *9*, 1497–1502.
417. Nicholson, T.; Storm, S. L.; Davis, W. M.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1992**, *196*, 27–34.
418. Nicholson, T.; Davison, A.; Zubieta, J. A.; Chen, Q.; Jones, A. G. *Inorg. Chim. Acta* **1995**, *230*, 205–208.
419. Hirsch-Kuchma, M.; Nicholson, T.; Davison, A.; Jones, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 3189–3192.
420. Rochon, F. D.; Melanson, R.; Kong, P.-C. *Inorg. Chem.* **1995**, *34*, 2273–2277.
421. Archer, C. M.; Dilworth, J. R.; Jobanputra, P.; Thompson, R. M.; Mcpartlin, M.; Hiller, W. *J. Chem. Soc., Dalton Trans.* **1993**, 897–904.
422. Nicholson, T.; Devries, N.; Davison, A.; Jones, A. G. *Inorg. Chem.* **1989**, *28*, 3813–3819.
423. Dilworth, J. R.; Jobanputra, P.; Thompson, R. M.; Povey, D. C.; Archer, C. M.; Kelly, J. D. *J. Chem. Soc., Dalton Trans.* **1994**, 1251–1256.
424. Abrams, M. J.; Shaikh, S. N.; Zubieta, J. *Inorg. Chim. Acta* **1990**, *171*, 133–134.
425. Nicholson, T.; Hirsch–Kuchma, M.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1998**, *271*, 191–194.
426. Nicholson, T.; Mahmood, A.; Morgan, G.; Jones, A. G.; Davison, A. *Inorg. Chim. Acta* **1991**, *179*, 53–57.
427. Nicholson, T.; Cook, J.; Davison, A.; Rose, D. J.; Maresca, K. P.; Zubieta, J. A.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *252*, 421–426.
428. Hirsch-Kuchma, M.; Nicholson, T.; Davison, A.; Davis, W. M.; Jones, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 3185–3188.
429. Nicholson, T.; HirschKuchma, M.; Davison, A.; Davis, W. M.; Jones, A. G. *Inorg. Chim. Acta* **1998**, *267*, 165–168.
430. Rose, D. J.; Maresca, K. P.; Nicholson, T.; Davison, A.; Jones, A. G.; Babich, J.; Fischman, A.; Graham, W.; DeBord, J. R. D.; Zubieta, J. *Inorg. Chem.* **1998**, *37*, 2701–2716.
431. Abram, U.; Hagenbach, A. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1719–1720.
432. Katti, K. V.; Singh, P. R.; Barnes, C. L.; Katti, K. K.; Kopicka, K.; Ketring, A. R.; Volkert, W. A. *Z. Naturforsch. B* **1993**, *48*, 1381–1385.
433. Eble, B.; Berning, D.; Barnes, C. L.; Katti, K. V.; Jurisson, S. *J. Chem. Crystallogr.* **1999**, *29*, 39–43.
434. Colton, R. In *The Chemistry of Rhenium and Technetium* **1965**, Interscience Publishers, London.
435. Elder, M.; Penfold, B. R. *Inorg. Chem.* **1966**, *5*, 1197–& .
436. Abram, U.; Wollert, R.; Hiller, W. *Radiochim. Acta* **1993**, *63*, 145–147.
437. Peacock, R. D. *The Chemistry of Technetium and Rhenium* **1966**, Elsevier: Amsterdam.
438. Nelson, C. M.; Boyd, G. E.; Smith, W. T. *J. Am. Chem. Soc.* **1954**, *76*, 348–352.
439. Dalziel, J.; Gill, N. S.; Nyholm, R. S.; Peacock, R. D. *J. Chem. Soc.* **1958**, 4012–4016.
440. Elder, M.; Fergusson, J. E.; Gainsfor, G. J.; Hickford, J. H.; Penfold, B. R. *J. Chem. Soc. A* **1967**, 1423–1425.

441. Schwochau, K. *Z Naturforsch Pt A* **1964**, *A 19*, 1237–1238.
442. Alberto, R.; Anderegg, G. *Polyhedron* **1985**, *4*, 1067.
443. Elder, R. C.; Estes, G. W.; Deutsch, E. *Acta Crystallogr. B* **1979**, *35*, 136–137.
444. Baldas, J.; Bonnyman, J.; Samuels, D. L.; Williams, G. A. *Acta Crystallogr. C* **1984**, *40*, 1343–1346.
445. Kozmin, N. A.; Kuzina, A. F.; Novitska, G. *Zh. Strukt. Khim.* **1972**, *13*, 941–948.
446. Shepelkov, S. V.; Konarev, M. I.; Chebotarev, N. T.; Zaitseva, L. L.; Vinogradov, I. V. *Zh. Neorganicheskoi Khim.* **1975**, *20*, 3310–3313.
447. Kryuchkov, S. V.; Grigorev, M. S.; Kuzina, A. F.; Spitsyn, V. I. *Russ. J. Inorg. Chem.* **1987**, *32*, 1714.
448. Kryuchkov, S. V.; Grigorev, M. S.; Kuzina, A. F.; Spitsyn, V. I. *Russ. J. Inorg. Chem.* **1987**, *32*, 1708.
449. Jorgense, Ck; Schwochau, K. *Z Naturforsch Pt A* **1965**, *A 20*, 65–75.
450. Schenk, H. J.; Schwochau, K. *Z Naturforsch Pt A* **1973**, *A 28*, 89–97.
451. Verdonck, E.; Vanquickenborne, L. G. *Inorg. Chim. Acta* **1977**, *23*, 67–76.
452. Trop, H. S.; Davison, A.; Carey, G. H.; Depamphilis, B. V.; Jones, A. G.; Davis, M. A. *J. Inorg. Nucl. Chem.* **1979**, *41*, 271–272.
453. Huber, E. W.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1987**, *26*, 3718–3722.
454. Zaitseva, L. L.; Kruglov, A. A.; Romanov, A. V.; Samsonov, V. E.; Teterin, E. G. *Zh. Neorganicheskoi Khim.* **1987**, *32*, 2958–2962.
455. Zaitseva, L. L.; Kruglov, A. A.; Romanov, A. V.; Samsonov, V. E.; Teterin, E. G. *Zh. Neorganicheskoi Khim.* **1988**, *33*, 2536–2540.
456. Wendt, A.; Preetz, W. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1669–1671.
457. Crouthamel, C. E. *Anal. Chem.* **1957**, *29*, 1756–1760.
458. Foster, R. E.; Maeck, W. J.; Rein, J. E. *Anal. Chem.* **1967**, *39*, 563–&.
459. Schwochau, K.; Astheimer, L.; Schenk, H. J. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2249–2257.
460. Trop, H. S.; Davison, A.; Jones, A. G.; Davis, M. A.; Szalda, D. J.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 1105–1110.
461. Williams, G. A.; Bonnyman, J.; Baldas, J. *Aust. J. Chem.* **1987**, *40*, 27–33.
462. Alberto, R.; Anderegg, G.; May, K. *Polyhedron* **1986**, *5*, 2107.
463. Edwards, D. S.; Liu, S.; Poirier, M. J.; Zhang, Z.; Webb, G. A.; Orvig, C. *Inorg. Chem.* **1994**, *33*, 5607–5609.
464. Abrams, M. J.; Davison, A.; Jones, A. G.; Costello, C. E. *Inorg Chim. a–Lett* **1983**, *77*, L235–L236.
465. Mazzi, U.; Roncari, E.; Bandoli, G.; Magon, L. *Transit. Met. Chem.* **1979**, *4*, 151–155.
466. Mazzi, U.; Roncari, E.; Bandoli, G.; Clemente, D. A. *Transit. Met. Chem.* **1982**, *7*, 163–166.
467. Breikss, A. I.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1990**, *170*, 75–79.
468. Levanda, O. Y.; Oblova, A. A.; Kuzina, A. F.; Belyaeva, L. I.; Spitsyn, V. I. *Zh. Neorganicheskoi Khim.* **1985**, *30*, 930–934.
469. Rochon, F. D.; Melanson, R.; Kong, P. C. *Inorg. Chim. Acta* **2000**, *300–302*, 43–48.
470. Clarke, M. J.; Kastner, M. E.; Podbielski, L. A.; Fackler, P. H.; Schreifels, J.; Meinken, G.; Srivastava, S. C. *J. Am. Chem. Soc.* **1988**, *110*, 1818–1827.
471. Dupreez, J. G. H.; Gerber, T. I. A.; Knoesen, O. *Inorg Chim. a–F–Block* **1985**, *109*, L17–L18.
472. Bush, C. D.; Hamor, T. A.; Hussain, W.; Jones, C. J.; Mccleverty, J. A.; Rothin, A. S. *Acta Crystallogr. C* **1987**, *43*, 2088–2091.
473. Colmanet, S. F.; Mackay, M. F. *J. Chem. Soc. Chem. Commun.* **1987**, 705–706.
474. Fergusson, J. E.; Hickford, J. H. *Aust. J. Chem.* **1970**, *23*, 453–461.
475. Mazzi, U.; Depaoli, G.; Rizzardi, G.; Magon, L. *Inorg. Chim. Acta* **1974**, *10*, L2–L2.
476. Bandoli, G.; Clemente, D. A.; Mazzi, U.; Roncari, E. *J. Chem. Soc., Dalton Trans.* **1982**, 1381–1384.
477. Mazzi, U.; Depaoli, G.; Dibernardo, P.; Magon, L. *J. Inorg. Nucl. Chem.* **1976**, *38*, 721–725.
478. Rochon, F. D.; Melanson, R.; Kong, P. C. *Acta Crystallogr. C* **1991**, *47*, 732–737.
479. Cotton, F. A.; Day, C. S.; Diebold, M. P.; Roth, W. J. *Acta Crystallogr. C* **1990**, *46*, 1623–1624.
480. Cotton, F. A.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chim. Acta* **1998**, *271*, 187–190.
481. Refosco, F.; Bandoli, G.; Mazzi, U.; Tisato, F.; Dolmella, A.; Nicolini, M. *Inorg. Chem.* **1990**, *29*, 2179–2180.
482. Anderegg, G.; Muller, E.; Zollinger, K.; Burgi, H. B. *Helv. Chim. Acta* **1983**, *66*, 1593–1598.
483. Alberto, R.; Anderegg, G.; Albinati, A. *Inorg. Chim. Acta* **1990**, *178*, 125–130.
484. Linder, K. E.; Dewan, J. C.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3820–3825.
485. Abrams, M. J.; Davison, A.; Jones, A. G.; Costello, C. E.; Pang, H. *Inorg. Chem.* **1983**, *22*, 2798–2800.
486. Farr, J. P.; Abrams, M. J.; Costello, C. E.; Davison, A.; Lippard, S. J. *Organometallics* **1985**, *4*, 139–142.
487. Hurst, R. W.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1981**, *20*, 3298–3303.
488. Ichimura, A.; Heineman, W. R.; Vanderheyden, J.-L.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 1272–1278.
489. Ichimura, A.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 2134–2139.
490. Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1987**, *26*, 3108–3113.
491. Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 3608–3614.
492. Rochon, F. D.; Kong, P.-C. *Inorg. Chem.* **2000**, *39*, 5757–5762.
493. Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1976**, 125–130.
494. Watson, P. L.; Albanese, J. A.; Calabrese, J. C.; Ovenall, D. W.; Smith, R. G. *Inorg. Chem.* **1991**, *30*, 4638–4643.
495. Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1978**, 373–380.
496. Mazzi, U.; Bismondo, A.; Kotsev, N.; Clemente, D. A. *J. Organomet. Chem.* **1977**, *135*, 177–182.
497. Rochon, F. D.; Melanson, R.; Kong, P. C. *Can. J. Chem.* **1991**, *69*, 397–403.
498. Trop, H. S., Ph.D. Thesis, Massachusetts Institute of Technology, 1979..
499. Archer, C. M.; Dilworth, J. R.; McPartlin, R. M. T. M.; Povey, D. C.; Kelly, J. D. *J. Chem. Soc., Dalton Trans.* **1993**, 461–466.
500. Pearlstein, R. M.; Davis, W. M.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1989**, *28*, 3332–3334.
501. Lu, J.; Yamano, A.; Clarke, M. J. *Inorg. Chem.* **1990**, *29*, 3483–3487.
502. Barrera, J.; Burrell, A. K.; Bryan, J. C. *Inorg. Chem.* **1996**, *35*, 335–341.
503. Lu, J.; Hiller, C. D.; Clarke, M. J. *Inorg. Chem.* **1993**, *32*, 1417–1423.
504. Barrera, J.; Bryan, J. C. *Inorg. Chem.* **1996**, *35*, 1825–1830.
505. Wilcox, B. E.; Ho, D. M.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 1743–1751.

506. Jurisson, S. S.; Dancey, K.; McPartlin, M.; Tasker, P. A.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 4743–4749.
507. Gerson, M. C.; Lukes, J.; Deutsch, E.; Biniakiewicz, D.; Rohe, R. C.; Washburn, L. C.; Fortman, C.; Walsh, R. A. *J. Nucl. Cardiol.* **1994**, *1*, 499–508.
508. Gerson, M. C.; Lukes, J.; Deutsch, E.; Biniakiewicz, D.; Washburn, L. C.; Walsh, R. A. *J. Nucl. Cardiol.* **1995**, *2*, 224–230.
509. Hendel, R. C.; Verani, M. S.; Miller, D. D.; Wackers, F. J. T.; McMahon, M.; Cerqueira, M. D.; Botvinick, E. H.; Kvols, L.; Gerson, M. C. *J. Nucl. Cardiol.* **1996**, *3*, 291–300.
510. Marmion, M. E.; Woulfe, S. R.; Neumann, W. L.; Nosco, D. L.; Deutsch, E. *Nucl. Med. Biol.* **1999**, *26*, 755–770.
511. Treher, E. N.; Francesconi, L. C.; Gougoutas, J. Z.; Malley, M. F.; Nunn, A. D. *Inorg. Chem.* **1989**, *28*, 3411–3416.
512. Linder, K. E.; Malley, M. F.; Gougoutas, J. Z.; Unger, S. E.; Nunn, A. D. *Inorg. Chem.* **1990**, *29*, 2428–2434.
513. Linder, K. E.; Nowotnik, D. P.; Malley, M. F.; Gougoutas, J. Z.; Nunn, A. D. *Inorg. Chim. Acta* **1991**, *190*, 249–255.
514. Jurisson, S.; Halihan, M. M.; Lydon, J. D.; Barnes, C. L.; Nowotnik, D. P.; Nunn, A. D. *Inorg. Chem.* **1998**, *37*, 1922–1928.
515. HirschKuchma, M.; Nicholson, T.; Davison, A.; Davis, W. M.; Jones, A. G. *Inorg. Chem.* **1997**, *36*, 3237–3241.
516. Bryan, J. C.; Cotton, F. A.; Daniels, L. M.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chem.* **1995**, *34*, 1875–1883.
517. Bandoli, G.; Clemente, D. A.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1977**, 1837–1844.
518. Bandoli, G.; Clemente, D. A.; Mazzi, U.; Roncari, E. *Acta Crystallogr. B* **1978**, *34*, 3359–3361.
519. Hashimoto, K.; Kabuto, C.; Omori, T.; Yoshihara, K. *Chem. Lett.* **1988**, 1379–1380.
520. Leesmeister, K.; Schwochau, K. *Nucl. Med. Biol.* **1992**, *19*, 73–78.
521. Kido, H.; Hatakeyama, Y. *Inorg. Chem.* **1988**, *27*, 3623–3625.
522. Mutalib, A.; Sekine, T.; Omori, T.; Yoshihara, K. *J. Radioanal. Nucl. Chem.* **1994**, *178*, 311–318.
523. Spies, H.; Abram, U.; Uhlemann, E.; Ludwig, E. *Inorg. Chim. Acta* **1985**, *109*, L3–L4.
524. Bandoli, G.; Mazzi, U.; Spies, H.; Munze, R.; Ludwig, E.; Ulhemann, E.; Scheller, D. *Inorg. Chim. Acta* **1987**, *132*, 177–185.
525. Abrams, M. J.; Davison, A.; Faggiani, R.; Jones, A. G.; Lock, C. J. L. *Inorg. Chem.* **1984**, *23*, 3284–3288.
526. Pietzsch, H. J.; Spies, H.; Leibnitz, P.; Reck, G.; Beger, J.; Jacobi, R. *Polyhedron* **1992**, *11*, 1623–1628.
527. Mevellec, F.; Tisato, F.; Refosco, F.; Roucoux, A.; Noiret, N.; Patin, H.; Bandoli, G. *Inorg. Chem.* **2002**, *41*, 598–601.
528. Konno, T.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 4113–4121.
529. Munze, R.; Abram, U.; Stach, J.; Hiller, W. *Inorg. Chim. Acta* **1991**, *186*, 151–154.
530. Konno, T.; Kirchhoff, J. R.; Heeg, M. J.; Heineman, W. R.; Deutsch, E. *J. Chem. Soc., Dalton Trans.* **1992**, 3069–3075.
531. Refosco, F.; Bandoli, G.; Deutsch, E.; Duatti, A.; Mazzi, U.; Moresco, A.; Nicolini, M.; Tisato, F. In *Technetium and Rhenium in Chemistry and Nuclear Medicine*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1990; Vol. 3, p 221.
532. Bolzati, C.; Uccelli, L.; Refosco, F.; Tisato, F.; Duatti, A.; Giganti, M.; Piffanelli, A. *Nucl. Med. Biol.* **1998**, *25*, 71–76.
533. Tisato, F.; Refosco, F.; Bandoli, G.; Bolzati, C.; Moresco, A. *J. Chem. Soc., Dalton Trans.* **1994**, 1453–1461.
534. Vries, N. d.; Dewan, J. C.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1988**, *27*, 1574–1580.
535. Vries, N. d.; Cook, J.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1991**, *30*, 2662–2665.
536. Spies, H.; Glaser, M.; Pietzsch, H.-J.; Hahn, F. E.; Kintzel, O.; Luegger, T. *Angew. Chem.* **1994**, *106*, 1416–1419.
537. Spies, H.; Glaser, M. *Inorg. Chim. Acta* **1995**, *240*, 465–478.
538. Pietzsch, H. J.; Tisato, F.; Refosco, F.; Leibnitz, P.; Drews, A.; Seifert, S.; Spies, H. *Inorg. Chem.* **2001**, *40*, 59–64.
539. Pietzsch, H. J.; Spies, H.; Hoffmann, S. *Inorg. Chim. Acta* **1990**, *168*, 7–9.
540. Seifert, S.; Drews, A.; Gupta, A.; Pietzsch, H. J.; Spies, H.; Johannsen, B. *Appl. Radiat. Isot.* **2000**, *53*, 431–438.
541. Nicholson, T.; Thornback, J.; Oconnell, L.; Morgan, G.; Davison, A.; Jones, A. G. *Inorg. Chem.* **1990**, *29*, 89–92.
542. Lorenz, B.; Schmidt, K.; Hiller, W.; Abram, U.; Hubener, R. *Inorg. Chim. Acta* **1993**, *208*, 195–199.
543. Baldas, J.; Bonnyman, J.; Pojer, P. M.; Williams, G. A.; Mackay, M. F. *J. Chem. Soc., Dalton Trans.* **1982**, 451–455.
544. Mullen, G. E. D.; Blower, P. J.; Price, D. J.; Powell, A. K.; Howard, M. J.; Went, M. J. *Inorg. Chem.* **2000**, *39*, 4093–4098.
545. Mullen, G. E. D.; Went, M. J.; Wocadlo, S.; Powell, A. K.; Blower, P. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1205–1207.
546. Cotton, F. A.; Curtis, N. F.; Johnson, B. F. G.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 326–330.
547. Cotton, F. A.; Harris, C. B. *Inorg. Chem.* **1965**, *4*, 330–333.
548. Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334–336.
549. Eakins, J. D.; Humphreys, D. G.; Mellish, C. E. *J. Chem. Soc.* **1963**, 6012–6016.
550. Cotton, F. A.; Bratton, W. K. *J. Am. Chem. Soc.* **1965**, *87*, 921.
551. Bratton, W. K.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 789–793.
552. Cotton, F. A.; Shive, L. W. *Inorg. Chem.* **1975**, *14*, 2032–2035.
553. Cotton, F. A.; Davison, A.; Day, V. W.; Fredrich, M. F.; Orvig, C.; Swanson, R. *Inorg. Chem.* **1982**, *21*, 1211–1214.
554. Cotton, F. A.; Fanwick, P. E.; Gage, L. D.; Kalbacher, B.; Martin, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5642–5645.
555. Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 383–387.
556. Hedwig, K.; Linse, K. H.; Schwochau, K. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 199.
557. Schwochau, K. *Chemiker-Zeitung* **1978**, *102*, 329–337.
558. Schwochau, K.; Hedwig, K.; Schenk, H. J.; Greis, O. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 77–80.
559. Preetz, W.; Peters, G. *Z. Naturforsch. B* **1980**, *35*, 797–801.
560. Cotton, F. A.; Daniels, L.; Davison, A.; Orvig, C. *Inorg. Chem.* **1981**, *20*, 3051–3055.
561. Cotton, F. A.; Gage, L. D. *New J. Chem.* **1977**, *1*, 441–442.
562. Cotton, F. A.; Fanwick, P. E.; Gage, L. D. *J. Am. Chem. Soc.* **1980**, *102*, 1570–1577.
563. Zaitseva, L. L.; Kotelnikova, A. S.; Rezvov, A. A. *Zhurnal Neorganicheskoi Khimii* **1980**, *25*, 2624–2628.
564. Baturin, N. A.; German, K. E.; Grigoriev, M. S.; Kryuchkov, S. V. *Russ. J. Coord. Chem.* **1991**, *17*, 1375–1383.
565. Grigoriev, M. S.; Kryutchkov, S. V. *Radiochim. Acta* **1993**, *63*, 187–193.
566. Skowronek, J.; Preetz, W. *Z. Naturforsch. B* **1992**, *47*, 482–490.
567. Skowronek, J.; Preetz, W.; Jessen, S. M. *Z. Naturforsch. B* **1991**, *46*, 1305–1314.
568. Skowronek, J.; Preetz, W. *Z. Anorg. Allg. Chem.* **1992**, *615*, 73–76.

569. Burns, C. J.; Burrell, A. K.; Cotton, F. A.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chem.* **1994**, *33*, 2257–2264.
570. Cotton, A. F.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chem.* **1996**, *35*, 1831–1838.
571. Cotton, A. F.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chem.* **1996**, *35*, 7350–7357.
572. Armstrong, R. A.; Taube, H. *Inorg. Chem.* **1976**, *15*, 1904–1909.
573. Jones, A. G.; Davison, A. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 867–874.
574. Orvig, C.; Davison, A.; Jones, A. G. *J. Labelled Compd. Radiopharm.* **1981**, *18*, 148–148.
575. Brown, D. S.; Newman, J. L.; Thornback, J. R.; Davison, A. *Acta Crystallogr. C* **1987**, *43*, 1692–1694.
576. Baldas, J.; Boas, J. F.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 827–831.
577. Brown, D. S.; Newman, J. L.; Thornback, J. R.; Pearlstein, R. M.; Davison, A.; Lawson, A. *Inorg. Chim. Acta* **1988**, *150*, 193–196.
578. Abram, U.; Hübener, R.; Wollert, R.; Kirmse, R.; Hiller, W. *Inorg. Chim. Acta* **1993**, *206*, 9–14.
579. Kirmse, R.; Lorenz, B.; Schmidt, K. *Polyhedron* **1983**, *2*, 935–939.
580. Abram, U.; Kirmse, R.; Kohler, K.; Lorenz, B.; Kaden, L. *Inorg. Chim. Acta* **1987**, *129*, 15–20.
581. Kaden, L.; Lorenz, B.; Kirmse, R.; Stach, J.; Behm, H.; Beurskens, P. T.; Abram, U. *Inorg. Chim. Acta* **1990**, *169*, 43–48.
582. Schwochau, K.; Linse, K. H.; Su, Z. F. *Appl. Radiat. Isot.* **1992**, *43*, 1079–1082.
583. Thomas, J. A.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1991**, *184*, 99–105.
584. Bandoli, G.; Clemente, D. A.; Mazzi, U.; Tondello, E. *Cryst. Struct. Commun.* **1974**, *3*, 293.
585. Mazzi, U.; Clemente, D. A.; Bandoli, G.; Magon, L.; Orio, A. A. *Inorg. Chem.* **1977**, *16*, 1042–1048.
586. Fergusson, J. E.; Nyholm, R. S. *Nature* **1959**, *183*, 1039–1040.
587. Konno, T.; Heeg, M. J.; Stuckey, J. A.; Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1992**, *31*, 1173–1181.
588. Konno, T.; Kirchhoff, J. R.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 1174–1179.
589. Konno, T.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 1694–1700.
590. Bandoli, G.; Mazzi, U.; Ichimura, A.; Libson, K.; Heineman, W. R.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 2898–2901.
591. Wilcox, B. E.; Ho, D. M.; Deutsch, E. *Inorg. Chem.* **1989**, *28*, 3917–3923.
592. Wilcox, B. E.; Deutsch, E. *Inorg. Chem.* **1991**, *30*, 688–693.
593. Breikss, A. I.; Nicholson, T.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1990**, *29*, 640–645.
594. Seifert, S.; Muenze, R.; Leibnitz, P.; Reck, G.; Stach, J. *Inorg. Chim. Acta* **1992**, *193*, 167–172.
595. Okamoto, K.-I.; Chen, B.; Kirchhoff, J. R.; Ho, D. M.; Elder, R. C.; Heineman, W. R.; Deutsch, E. *Polyhedron* **1993**, *12*, 1559–1568.
596. Rochon, F. D.; Melanson, R.; Kong, P.-C. *Can. J. Chem.* **1994**, *72*, 2183–2187.
597. Freiberg, E.; Davis, W. M.; Davison, A.; Jones, A. G. *Inorg. Chem.* **2002**, *41*, 3337–3339.
598. White, D. J.; Kuppers, H. J.; Edwards, A. J.; Watkin, D. J.; Cooper, S. R. *Inorg. Chem.* **1992**, *31*, 5351–5352.
599. Mullen, G. E. D.; Fässler, T. F.; Went, M. J.; Howland, K.; Stein, B.; Blower, P. J. *J. Chem. Soc., Dalton Trans.* **1999**, 3759–3766.
600. Cotton, F. A.; Haefner, S. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1996**, *118*, 5486–5487.
601. Cotton, F. A.; Haefner, S. C.; Sattelberger, A. P. *Inorg. Chim. Acta* **1997**, *266*, 55–63.
602. Schwochau, K.; Herr, W. *Z. Anorg. Allg. Chem.* **1962**, *319*, 148–158.
603. Herr, W.; Schwochau, K. *Angew. Chem., Int. Ed. Engl.* **1961**, *73*, 492–495.
604. Tulip, T. H.; Calabrese, J. C.; Kronauge, J. F.; Davison, A.; Jones, A. G. In *Technetium in Chemistry and Nuclear Medicine*; Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1986; Vol. 2, pp 119–122.
605. Kaden, L.; Lorenz, B.; Schmidt, K.; Sprinz, H.; Wahren, M. *Z. Chem.* **1979**, *19*, 305–306.
606. Abram, U.; Abram, S.; Beyer, R.; Muenze, R.; Kaden, L.; Lorenz, B.; Findeisen, M. *Inorg. Chim. Acta* **1988**, *148*, 141–142.
607. Kaden, L.; Pombeiro, A. J. L.; Wang, Y.; Abram, U. *Inorg. Chim. Acta* **1995**, *230*, 189–192.
608. Abram, U.; Beyer, R.; Munze, R.; Findeisen, M.; Lorenz, B. *Inorg. Chim. Acta* **1989**, *160*, 139–142.
609. O'Connell, L. A.; Davison, A. *Inorg. Chim. Acta* **1990**, *176*, 7–9.
610. Rochon, F. D.; Melanson, R.; Kong, P. C. *Inorg. Chim. Acta* **1996**, *245*, 251–256.
611. O'Connell, L. A.; Dewan, J.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1990**, *29*, 3539–3547.
612. Linder, K. E.; Davison, A.; Dewan, J. C.; Costello, C. E.; Maleknia, S. *Inorg. Chem.* **1986**, *25*, 2085–2089.
613. Wester, D. W.; White, D. H.; Miller, F. W.; Dean, R. T. *Inorg. Chem.* **1984**, *23*, 1501–1502.
614. Burrell, A. K.; Bryan, J. C.; Kubas, G. J. *J. Am. Chem. Soc.* **1994**, *116*, 1575–1576.
615. Burrell, A. K.; Bryan, J. C.; Kubas, G. J. *Organometallics* **1994**, *13*, 1067–1069.
616. Huebener, R. A. Ulrich; Hiller, Wolfgang. *Acta Crystallogr. C* **1994**, *C50*, 188–190.
617. Struchkov, Y. T.; Bazanov, A. S.; Kaden, L.; Lorenz, B.; Wahren, M.; Meyer, H. *Z. Anorg. Allg. Chem.* **1982**, *494*, 91–97.
618. Kaden, L.; Findeisen, M.; Lorenz, B.; Schmidt, K.; Wahren, M. *Inorg. Chim. Acta* **1992**, *193*, 213–215.
619. Joachim, J. E.; Apostolidis, C.; Kanellakopulos, B.; Maier, R.; Meyer, D.; Rebizant, J.; Ziegler, M. L. *J. Organomet. Chem.* **1993**, *455*, 137–141.
620. Castro, H. H. K.; Hissink, C. E.; Teuben, J. H.; Vaalburg, W. *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 105–108.
621. Marchi, A.; Rossi, R.; Duatti, A.; Magon, L.; Bertolasi, V.; Ferretti, V.; Gilli, G. *Inorg. Chem.* **1985**, *24*, 4744–4748.
622. Rossi, R.; Marchi, A.; Magon, L. *Inorg. Chim. Acta* **1989**, *160*, 23–28.
623. Alberto, R.; Herrmann, W. A.; Kiprof, P.; Baumgärtner, F. *Inorg. Chem.* **1992**, *31*, 895–899.
624. Tsutsui, M.; Hrung, C. O. *J. Coord. Chem.* **1973**, *3*, 193–195.
625. Tsutsui, M.; Hrung, C. P.; Ostfeld, D.; Srivastava, T. S.; Cullen, D. L.; Meyer, E. F. *J. Am. Chem. Soc.* **1975**, *97*, 3952–3965.
626. Lu, J.; Clarke, M. J. *Inorg. Chem.* **1990**, *29*, 4123–4125.
627. Cheah, C. T.; Newman, J. L.; Nowotnik, D. P.; Thornback, J. R. *Nucl. Med. Biol.* **1987**, *14*, 573–577.
628. Rossi, R.; Marchi, A.; Magon, L.; Casellato, U.; Graziani, R. *J. Chem. Res.-S.* **1990**, 78–79.
629. Blanchard, S. S.; Nicholson, T.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *241*, 95–100.
630. Blanchard, S. S.; Nicholson, T.; Davison, A.; Davis, W.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *244*, 121–130.
631. Nicholson, T.; Hirsch-Kuchma, M.; Freiberg, E.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1998**, *279*, 206–209.

632. Alberto, R.; Schibli, R.; Schubiger, P. A. *Polyhedron* **1996**, *15*, 1079–1089.
633. Alberto, R.; Schibli, R.; Abram, U.; Hubener, R.; Berke, H.; Kaden, T. A.; Schubiger, P. A. *J. Chem. Soc., Chem. Commun.* **1996**, 1291.
634. Alberto, R.; Schibli, R.; Egli, A.; Abram, U.; Abram, S.; Kaden, T. A.; Schubiger, P. A. *Polyhedron* **1998**, *17*, 1133.
635. Egli, A.; Hegetschweiler, K.; Alberto, R.; Abram, U.; Schibli, R.; Hedinger, R.; Gramlich, V.; Kissner, R.; Schubiger, P. A. *Organometallics* **1997**, *16*, 1833.
636. Schibli, R.; Alberto, R.; Abram, U.; Egli, A.; Kaden, T. A.; Schubiger, P. A. *Inorg. Chem.* **1998**, *37*, 3509.
637. Alberto, R.; Schibli, R.; Egli, A.; Abram, U.; Kaden, T. A.; Schubiger, P. A. *J. Am. Chem. Soc.* **1998**, *120*, 7987.
638. Alberto, R.; Ortner, K.; Wheatley, N.; Schibli, R.; Schubiger, A. P. *J. Am. Chem. Soc.* **2001**, *123*, 3135–3136.
639. Kidd, R. G. *J. Magn. Reson.* **1981**, *45*, 88–93.
640. O'Connell, L. A.; Pearlstein, R. M.; Davison, A. *Inorg. Chim. Acta* **1989**, *161*, 39–43.
641. Findeisen, M.; Lorenz, B.; Wahren, M. *Isotopenpraxis* **1990**, *26*, 520–523.
642. Piwnicaworms, D.; Kronauge, J. F.; LeFurgey, A.; Backus, M.; Hockett, D.; Ingram, P.; Lieberman, M.; Holman, B. L.; Jones, A. G.; Davison, A. *Magn. Reson. Chem.* **1994**, *12*, 641–652.
643. Walchli, H.; Livingston, R.; Martin, W. J. *Phys. Rev.* **1952**, *85*, 479–479.
644. Buckingham, M. J.; Hawkes, G. E.; Thornback, J. R. *Inorg. Chim. Acta* **1981**, *56*, L41–L42.
645. Franklin, K. J.; Lock, C. J. L.; Sayer, B. G.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1982**, *104*, 5303–5306.
646. Wester, D. W.; White, D. H.; Miller, F. W.; Dean, R. T.; Schreifels, J. A.; Hunt, J. E. *Inorg. Chim. Acta* **1987**, *131*, 163–169.
647. Davison, A.; Kronauge, J. F.; Jones, A. G.; Pearlstein, R. M.; Thorback, J. R. *Inorg. Chem.* **1988**, *27*, 3245–3246.
648. Findeisen, M.; Kaden, L.; Lorenz, B.; Rummel, S.; Wahren, M. *Inorg. Chim. Acta* **1987**, *128*, L15–L16.
649. Findeisen, M.; Kaden, L.; Lorenz, B.; Wahren, M. *Inorg. Chim. Acta* **1988**, *142*, 3–4.
650. Lorenz, B.; Findeisen, M.; Olk, B.; Schmidt, K. *Z. Anorg. Allg. Chem.* **1988**, *566*, 160–168.
651. Kaden, L.; Findeisen, M.; Lorenz, B.; Schmidt, K.; Wahren, M. *Isotopenpraxis* **1991**, *27*, 265–266.
652. Kaden, L.; Findeisen, M.; Schmidt, K. *Isotopenpraxis* **1991**, *27*, 266–267.
653. Aebischer, N.; Schibli, R.; Alberto, R.; Merbach, A. E. *Angew. Chem.* **2000**, *39*, 254–256.
654. Sands, H.; Delano, M. L.; Camin, L. L.; Gallagher, B. M. *Biochim Biophys Acta* **1985**, *812*, 665–670.
655. Deutsch, E.; Glavan, K. A.; Sodd, V. J.; Nishiyama, H.; Ferguson, D. L.; Lukes, S. J. *J. Nucl. Med.* **1981**, *22*, 897–907.
656. Deutsch, E.; Bushong, W.; Glavan, K. A.; Elder, R. C.; Sodd, V. J.; Scholz, K. L.; Fortman, D. L.; Lukes, S. J. *Science* **1981**, *214*, 85–86.
657. Gerson, M. C.; Deutsch, E. A.; Nishiyama, H.; Libson, K. F.; Adolph, R. J.; Grossman, L. W.; Sodd, V. J.; Fortman, D. L.; Vanderheyden, J. L. E.; Williams, C. C.; Saenger, E. L. *Eur. J. Nucl. Med.* **1983**, *8*, 371–374.
658. Jones, A. G.; Abrams, M. J.; Davison, A.; Brodack, J. W.; Toothaker, A. K.; Adelstein, S. J.; Kassis, A. I. *Nucl. Med. Biol.* **1984**, *11*, 225.
659. Narahara, K. A.; Villanuevameyer, J.; Thompson, C. J.; Brizendine, M.; Mena, I. *Am. J. Cardiol.* **1990**, *66*, 1438–1444.
660. McGoron, A. J.; Gerson, M. C.; Biniakiewicz, D. S.; Roszell, N. J.; Washburn, L. C.; Millard, R. W. *Eur. J. Nucl. Med.* **1997**, *24*, 1479–1486.
661. Carvalho, P. A.; Chiu, M. L.; Kronauge, J. F.; Kawamura, M.; Jones, A. G.; Holman, B. L.; Piwnicaworms, D. *J. Nucl. Med.* **1992**, *33*, 1516–1521.
662. Platts, E. A.; North, T. L.; Pickett, R. D.; Kelly, J. D. *J. Nucl. Cardiol.* **1995**, *2*, 317–326.
663. Piwnicaworms, D.; Kronauge, J. F.; Delmon, L.; Holman, B. L.; Marsh, J. D.; Jones, A. G. *J. Nucl. Med.* **1990**, *31*, 464–472.
664. Piwnicaworms, D.; Holman, B. L. *J. Nucl. Med.* **1990**, *31*, 1166–1167.
665. Schaefer, W. M.; Moka, D.; Brockmann, H. A.; Schomaecker, K.; Schicha, H. *Nucl. Med. Biol.* **2002**, *29*, 243–254.
666. Bernard, B. F.; Krenning, E. P.; Breeman, W. A. P.; Ensing, G.; Benjamins, H.; Bakker, W. H.; Visser, T. J.; de Jong, M. *Nucl. Med. Biol.* **1998**, *25*, 233–240.
667. Mansi, L.; Rambaldi, P. F.; Marino, G. *J. Nucl. Med.* **1995**, *36*, 83.
668. deJong, M.; Bernard, B. F.; Breeman, W. A. P.; Ensing, G.; Benjamins, H.; Bakker, W. H.; Visser, T. J.; Krenning, E. P. *Eur. J. Nucl. Med.* **1996**, *23*, 1361–1366.
669. Jurisson, S. *Drug. Future* **1990**, *15*, 1085.
670. Narra, R. K.; Nunn, A. D.; Kuczynski, B. L.; Feld, T.; Wedeking, P.; Eckelman, W. C. *J. Nucl. Med.* **1989**, *30*, 1830–1837.
671. Jurisson, S. S.; Hirth, W.; Linder, K. E.; Dirocco, R. J.; Narra, R. K.; Nowotnik, D. P.; Nunn, A. D. *Nucl. Med. Biol.* **1991**, *18*, 735–744.
672. Pasqualini, R.; Duatti, A. *J. Chem. Soc., Chem. Commun.* **1992**, 1354–1355.
673. Brodie, B. B.; Hogben, C. A. M. *J. Pharm. Pharmacol.* **1957**, *9*, 345–380.
674. Troutner, D. E.; Volkert, W. A.; Hoffman, T. J.; Holmes, R. A. *J. Nucl. Med.* **1983**, *24*, P10–P10.
675. Ell, P. J.; Jarritt, P. H.; Cullum, I.; Hocknell, J. M. L.; Costa, D. C.; Lui, D.; Jewkes, R. F.; Steiner, T. J.; Nowotnik, D. P.; Pickett, R. D.; Neirinckx, R. D. *Lancet* **1985**, *2*, 50–51.
676. Leonard, J. P.; Nowotnik, D. P.; Neirinckx, R. D. *J. Nucl. Med.* **1986**, *27*, 1819–1823.
677. Neirinckx, R. D.; Canning, L. R.; Piper, I. M.; Nowotnik, D. P.; Pickett, R. D.; Holmes, R. A.; Volkert, W. A.; Forster, A. M.; Weisner, P. S.; Marriott, J. A.; Chaplin, S. B. *J. Nucl. Med.* **1987**, *28*, 191–202.
678. Sharp, P. F.; Smith, F. W.; Gemmell, H. G.; Lyall, D.; Evans, N. T. S.; Gvozdanovic, D.; Davidson, J.; Tyrrell, D. A.; Pickett, R. D.; Neirinckx, R. D. *J. Nucl. Med.* **1986**, *27*, 171–177.
679. Walovitch, R. C.; Hill, T. C.; Garrity, S. T.; Cheesman, E. H.; Burgess, B. A.; Oleary, D. H.; Watson, A. D.; Ganey, M. V.; Morgan, R. A.; Williams, S. J. *J. Nucl. Med.* **1989**, *30*, 1892–1901.
680. Holman, B. L.; Hellman, R. S.; Goldsmith, S. J.; Mena, I. G.; Leveille, J.; Gherardi, P. G.; Moretti, J. L.; Bischofdelaloye, A.; Hill, T. C.; Rigo, P. M.; Vanheertum, R. L.; Ell, P. J.; Buell, U.; Deroo, M. C.; Morgan, R. A. *J. Nucl. Med.* **1989**, *30*, 1018–1024.
681. Leveille, J.; Demonceau, G.; Deroo, M.; Rigo, P.; Taillefer, R.; Morgan, R. A.; Kupranick, D.; Walovitch, R. C. *J. Nucl. Med.* **1989**, *30*, 1902–1910.

682. Vallabhajosula, S.; Zimmerman, R. E.; Picard, M.; Stritzke, P.; Mena, I.; Hellman, R. S.; Tikofsky, R. S.; Stabin, M. G.; Morgan, R. A.; Goldsmith, S. J. *J. Nucl. Med.* **1989**, *30*, 599–604.
683. Carroll, T. R. *Advances in Metals in Medicine*, 1993; Vol. 1, pp 1–27.
684. Narra, R. K.; Nunn, A. D.; Kuczynski, B. L.; Dirocco, R. J.; Feld, T.; Silva, D. A.; Eckelman, W. C. *J. Nucl. Med.* **1990**, *31*, 1370–1377.
685. Morgan, G. F.; Deblaton, M.; Clemens, P.; Vandenbroeck, P.; Bossuyt, A.; Thornback, J. R. *J. Nucl. Med.* **1991**, *32*, 500–505.
686. Bossuyt, A.; Morgan, G. F.; Deblaton, M.; Pirotte, R.; Chirico, A.; Clemens, P.; Vandenbroeck, P.; Thornback, J. R. *J. Nucl. Med.* **1991**, *32*, 399–403.
687. Morgan, G.; Deblaton, M.; Clemens, P.; Van den Broeck, P.; Hussain, W.; Bossuyt, A.; Thornback, J.; In *Technetium and Rhenium in Chemistry and Nuclear Medicine;* Nicolini, M., Bandoli, G., Mazzi, U., Eds.; Cortina International: Verona, Italy, 1990; Vol. 3, pp 419–423.
688. Chilton, H. M.; J. H., In *Pharmaceuticals in Medical Imaging*; Swanson, D., H., C., Thrall, J., Eds.; Macmillan: New York, 1990, p 305.
689. Eckelman, W. C.; Richards, P.; Meinken, G. *J. Nucl. Med.* **1972**, *13*, 577–581.
690. Fritzberg, A. R.; Kasina, S.; Eshima, D.; Johnson, D. L. *J. Nucl. Med.* **1986**, *27*, 111–116.
691. Rao, T. N.; Adhikesavalu, D.; Camerman, A.; Fritzberg, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 5798–5804.
692. Singh, J.; Powell, A. K.; Clarke, S. E. M.; Blower, P. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1115–1117.
693. Ikeda, I.; Inoue, O.; Kurata, K. *Int. J. Appl. Radiat. Isot.* **1976**, *27*, 681–688.
694. Moretti, J. L.; Rapin, J. R.; Saccavini, J. C.; Lageron, A.; Leponcin, M.; Bardy, A. *Int. J. Nucl. Med. Biol.* **1984**, *11*, 270–274.
695. Garcia, R.; Galvez, J.; Moreno, J. L. *Int. J. Appl. Radiat. Isot.* **1982**, *33*, 521–524.
696. Delange, M. J.; Piers, D. A.; Kosterink, J. G. W.; Vanluijk, W. H. J.; Meijer, S.; Dezeeuw, D.; Vanderhem, G. K. *J. Nucl. Med.* **1989**, *30*, 1219–1223.
697. Saha, G. B. 3rd edn. *Fundamentals of Nuclear Pharmacy* **1992**, Springer: New York.
698. Wilson, G. M.; Pinkerton, T. C. *Anal. Chem.* **1985**, *57*, 246–253.
699. Pinkerton, T. C.; Desilets, C. P.; Hoch, D. J.; Mikelsons, M. V.; Wilson, G. M. *J. Chem. Educ.* **1985**, *62*, 965–973.
700. Pinkerton, T. C.; Heineman, W. R.; Deutsch, E. *Anal. Chem.* **1980**, *52*, 1106–1110.
701. Vanlicrazumenic, N.; Jankovic, D.; Veselinovic, D. *J. Radioanal. Nucl. Chem. Articles* **1995**, *190*, 149–154.
702. Libson, K.; Deutsch, E.; Barnett, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 2476–2478.
703. Mikelsons, M. V.; Pinkerton, T. C. *Appl. Radiat. Isot* **1987**, *38*, 569–570.
704. Fogelman, I.; Tofe, A. J.; Francis, M. D. *J. Nucl. Med.* **1981**, *22*, P78–P78.
705. Wackers, F. J. T.; Berman, D. S.; Maddahi, J.; Watson, D. D.; Beller, G. A.; Strauss, H. W.; Boucher, C. A.; Picard, M.; Holman, B. L.; Fridrich, R.; Inglese, E.; Delaloye, B.; Bischofdelaloye, A.; Camin, L.; Mckusick, K. J. *Nucl. Med.* **1989**, *30*, 301–311.
706. Higley, B.; Smith, F. W.; Smith, T.; Gemmell, H. G.; Dasgupta, P.; Gvozdanovic, D. V.; Graham, D.; Hinge, D.; Davidson, J.; Lahiri, A. *J. Nucl. Med.* **1993**, *34*, 30–38.
707. Rossetti, C.; Vanoli, G.; Paganelli, G.; Kwiatkowski, M.; Zito, F.; Colombo, F.; Bonino, C.; Carpinelli, A.; Casati, R.; Deutsch, K.; Marmion, M.; Woulfe, S. R.; Lunghi, F.; Deutsch, E.; Fazio, F. *J. Nucl. Med.* **1994**, *35*, 1571–1580.
708. Crankshaw, C. L.; Marmion, M.; Luker, G. D.; Rao, V.; Dahlheimer, J.; Burleigh, B. D.; Webb, E.; Deutsch, K. F.; Piwnicaworms, D. *J. Nucl. Med.* **1998**, *39*, 77–86.
709. Piwnicaworms, D.; Chiu, M. L.; Budding, M.; Kronauge, J. F.; Kramer, R. A.; Croop, J. M. *Cancer Res.* **1993**, *53*, 977–984.
710. Rao, V. V.; Chiu, M. L.; Kronauge, J. F.; Piwnicaworms, D. *J. Nucl. Med.* **1994**, *35*, 510–515.
711. Iyer, R. V.; Engelhardt, E. L.; Stobbe, C. C.; Schneider, R. F.; Chapman, J. D. *Int. J. Radiat. Oncol.* **1998**, *42*, 741–745.
712. Hockel, M.; Schlenger, K.; Aral, B.; Mitze, M.; Schaffer, U.; Vaupel, P. *Cancer Res.* **1996**, *56*, 4509–4515.
713. Linder, K. E.; Chan, Y. W.; Cyr, J. E.; Malley, M. F.; Nowotnik, D. P.; Nunn, A. D. *J. Med. Chem.* **1994**, *37*, 9–17.
714. Dirocco, R. J.; Kuczynski, B. L.; Pirro, J. P.; Bauer, A.; Linder, K. E.; Ramalingam, K.; Cyr, J. E.; Chan, Y. W.; Raju, N.; Narra, R. K.; Nowotnik, D. P.; Nunn, A. D. *J. Cerebr. Blood F. Met.* **1993**, *13*, 755–762.
715. Ramalingam, K.; Raju, N.; Nanjappan, P.; Linder, K. E.; Pirro, J.; Zeng, W.; Rumsey, W.; Nowotnik, D. P.; Nunn, A. D. *J. Med. Chem.* **1994**, *37*, 4155–4163.
716. Johnson, G.; Nguyen, K. N.; Liu, Z. G.; Okada, R. D. *J. Nucl. Cardiol.* **1998**, *5*, 285–294.
717. Kniess, T.; Spies, H.; Brandau, W.; Johannsen, B. *J. Labelled Compd. Radiopharm.* **1998**, *41*, 605–614.
718. Seifert, S.; Pietzsch, H. J.; Scheunemann, M.; Spies, H.; Syhre, R.; Johannsen, B. *Appl. Radiat. Isot.* **1998**, *49*, 5–11.
719. Wust, F.; Spies, H.; Johannsen, B. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2729–2734.
720. Wust, F.; Carlson, K. E.; Katzenellenbogen, J. A.; Spies, H.; Johannsen, B. *Steroids* **1998**, *63*, 665–671.
721. Johannsen, B.; Pietzsch, H. J. *Eur. J. Nucl. Med. Mol. Imaging* **2002**, *29*, 263–275.
722. Kung, H. F. *Nucl. Med. Biol.* **2001**, *28*, 505–508.
723. Madras, B. K.; Jones, A. G.; Mahmood, A.; Zimmerman, R. E.; Garada, B.; Holman, B. L.; Davison, A.; Blundell, P.; Meltzer, P. C. *Synapse* **1996**, *22*, 239–246.
724. Kung, M. P.; Stevenson, D. A.; Plossl, K.; Meegalla, S. K.; Beckwith, A.; Essman, W. D.; Mu, M.; Lucki, I.; Kung, H. F. *Eur. J. Nucl. Med.* **1997**, *24*, 372–380.
725. Heimbold, I.; Drews, A.; Syhre, R.; Kretzschmar, M.; Pietzsch, H. J.; Johannsen, B. *Eur. J. Nucl. Med.* **2002**, *29*, 82–87.
726. Kung, H. F.; Meegalla, S.; Kung, M. P.; Plossl, K. *Transit. Met. Chem.* **1998**, *23*, 531–536.
727. Abrams, M. J.; Juweid, M.; Tenkate, C. I.; Schwartz, D. A.; Hauser, M. M.; Gaul, F. E.; Fuccello, A. J.; Rubin, R. H.; Strauss, H. W.; Fischman, A. J. *J. Nucl. Med.* **1990**, *31*, 2022–2028.
728. Larson, S. K.; Solomon, H. F.; Caldwell, G.; Abrams, M. J. *Bioconjugate Chem.* **1995**, *6*, 635–638.
729. Schwartz, D. A.; Abrams, M. J.; Hauser, M. M.; Gaul, F. E.; Larsen, S. K.; Rauh, D.; Zubieta, J. A. *Bioconjugate Chem.* **1991**, *2*, 333–336.
730. Ono, M.; Arano, Y.; Mukai, T.; Uehara, T.; Fujioka, Y.; Ogawa, K.; Namba, S.; Nakayama, M.; Saga, T.; Konishi, J.; Horiuchi, K.; Yokoyama, A.; Saji, H. *Nucl. Med. Biol.* **2001**, *28*, 155–164.
731. Liu, S.; Edwards, D. S.; Harris, A. R. *Bioconjugate Chem.* **1998**, *9*, 583–595.

732. Liu, S.; Edwards, D. S.; Looby, R. J.; Harris, A. R.; Poirier, M. J.; Barrett, J. A.; Heminway, S. J.; Carroll, T. R. *Bioconjugate Chem.* **1996**, *7*, 63–71.
733. Zhang, Y.-M.; Liu, N.; Zhu, Z.-H.; Rusckowski, M.; Hnatowich, K. J. *Eur. J. Nucl. Med.* **2000**, *27*, 1700–1707.
734. Liu, S.; Edwards, D. S.; Harris, A. R. *J. Nucl. Med.* **1998**, *39*, 215–216.
735. Nicholson, T.; Cook, J.; Davison, A.; Rose, D. J.; Maresca, K. P.; Zubieta, J. A.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *252*, 427–430.
736. Edwards, D. S.; Liu, S.; Harris, A. R.; Poirier, M. J.; Ewels, B. A. *Bioconjugate Chem.* **1999**, *10*, 803–807.
737. Decristoforo, C.; Mather, S. J. *Nucl. Med. Biol.* **1999**, *26*, 389–396.
738. Chi, D. Y.; Oneil, J. P.; Anderson, C. J.; Welch, M. J.; Katzenellenbogen, J. A. *J. Med. Chem.* **1994**, *37*, 928–937.
739. Chi, D. Y.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 7045–7046.
740. Hom, R. K.; Chi, D. Y.; Katzenellenbogen, J. A. *J. Org. Chem.* **1996**, *61*, 2624–2631.
741. Hom, R. K.; Katzenellenbogen, J. A. *J. Org. Chem.* **1997**, *62*, 6290–6297.

Comprehensive Coordination Chemistry II
ISBN (set): 0-08-0437486

Volume 5, (ISBN 0-08-0443273); pp 127–270

5.3
Rhenium

U. ABRAM
Freie Universität Berlin, Germany

5.3.1 INTRODUCTION

Rhenium was the last naturally occurring chemical element to be discovered in 1925 by Noddack, Tacke, and Berg in the mineral gadolinite.[1] The name of this extremely rare element (the estimated occurrence in the earth's crust is about 0.7 ppb[2]) is derived from the Rhine river. Residues from the processing of molybdenum ores represent the main source of the metal.

Naturally occurring rhenium is a mixture of two isotopes: ^{185}Re (natural abundance: 37.07%) and the ^{187}Re (natural abundance: 62.93%).[3] Although representing the main constituent in natural rhenium sources, ^{187}Re is weakly radioactive with a β^--emission with the very long half-life of 5×10^{10} yr.[4] The ^{187}Re/^{187}Os isotope system is used in geology[5,6] and cosmology[7] to determine the age of minerals or meteorites. Other radioactive rhenium isotopes are known with mass numbers between 161 and 192 and physical half-lifes between 10 ms and 71 d.[4] A part of the Nuclide Chart[4] showing main isotopes of rhenium and its neighbors together with some of their nuclear properties is shown in Figure 1. The isotopes ^{186}Re (β^- emitter, $T_{1/2} = 89.25$ h, $E_{max} = 1.1$ MeV) and ^{188}Re (β^- emitter, $T_{1/2} = 16.98$ h, $E_{max} = 2.1$ MeV) have physical properties that make them attractive for the radiotherapeutic treatment of cancer via antibody mediated targeting.[8,9] Particular attention has been paid to ^{188}Re which can be obtained from an isotope generator system from ^{188}W ($T_{1/2} = 69$ d).[10–12] Excellent reviews introducing nuclear medical applications of rhenium compounds and describing their perspectives are available.[13–20] A summary of recent developments in this sector will be given in Section 5.3.3, but structurally well-characterized rhenium compounds with potential nuclear medical applications will also be mentioned along with the systematic treatment of the rhenium coordination chemistry.

The outstanding overview of Connor and Walton in Comprehensive Coordination Chemistry (*CCC*, 1987) [21] covers all relevant rhenium coordination chemistry up to early 1984. The present article starts at this time and is restricted to basic coordination chemistry. It does not include compounds with metal–metal bonds, which are extensively described in Chapter 4.7. The organometallic chemistry of rhenium has been reviewed extensively in the companion series *Comprehensive Organometallic Chemistry*[22] and, thus, here compounds with rhenium–carbon bonds will only be mentioned in exceptional cases, particularly when the "organometallic part" of the molecule does not dominate the properties of the compound. The following review is based on a number of excellent annual surveys of the rhenium chemistry which have been compiled by the *Royal Society of Chemistry* in the series of *Annual Reports*[23–30] and articles appearing in *Coordination Chemistry Reviews*.[31–36] Additional reviews are available which cover special fields and aspects of rhenium chemistry, such as catalysis,[37–42] structural chemistry,[43,44] electrochemistry[45] and cluster chemistry[46–54] as well as complexes with particular ligands[55] or structural motifs.[37,56–59]

Coordination compounds of rhenium are known with the metal in the oxidation states +1 up to +7. The oxidation state with the by far most representatives is that of +5. The d^2 configuration is readily stabilized by multiply bonded ligands such as oxo, nitrido, or imido.

5.3.2 SYSTEMATIC CHEMISTRY

5.3.2.1 Oxidation State VII

Following general trends in the transition metal series the redox potentials of complexes of the third row element rhenium are lower than those of manganese and (to a smaller extent) techne-

	^{181}Os 1.8 h ε , β^+, γ	^{182}Os 22.1 h ε , γ	^{183}Os 13.0 h ε , β^+,γ	^{184}Os stable	^{185}Os 94 d ε ,γ	^{186}Os 2·10^{15}a α	^{187}Os stable	^{188}Os stable	^{189}Os stable	^{190}Os stable	^{191}Os 15.4 d β^-	^{192}Os stable	^{193}Os 30.1 h β^- ,γ	^{194}Os 6.0 a β^-; γ;e^-	^{194}Os 6.5m β^-	
	^{180}Re 2.4 m ε , β^+,γ	^{181}Re 20 h ε , γ	^{182}Re 13 h ε , β^+,γ	^{183}Re 71 d ε, γ	^{184}Re 38 d ε , γ	^{185}Re stable	^{186}Re 89.2 h ε , β^-, γ	^{187}Re 5 10^{10}a β^-	^{188}Re 16.9 h β^- , γ	^{189}Re 24.3 h β^- ,γ	^{190}Re 3.1 m β^- ,γ	^{191}Re 9.8 m β^-	^{192}Re 16 s β^- ,γ			
	^{179}W 38 m ε , γ	^{180}W stable	^{181}W 121 d ε,γ, e^-	^{182}W stable	^{183}W stable	^{184}W stable	^{185}W 75.1 d β^-, γ	^{186}W stable	^{187}W 23.7 d β^-, γ	^{188}W 69 d β^-, γ	^{189}W 11 m β^-, γ	^{190}W 30 m β^-, γ				

Figure 1 Part from the Nuclide Chart with basic properties of important isotopes of rhenium and its neighbors in the periodic table of elements.

tium. Perrhenate is only a weak oxidizing agent which permits a developed coordination chemistry of rhenium(VII). As for other higher oxidation states, the chemistry of rhenium(VII) is dominated by the presence of multiply bonded ligands such as O^{2-}, N^{3-}, or NR^{2-}. A comprehensive review summarizing all aspects of the inorganic and organometallic chemistry of rhenium(VII) oxo and imido complexes has been published recently.[37]

5.3.2.1.1 Complexes with oxo ligands

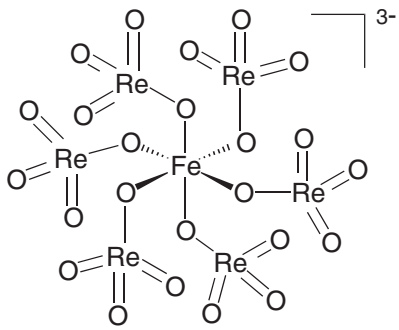
(i) Perrhenate complexes

The aqueous chemistry of rhenium(VII) is dominated by the perrhenate ion, $[ReO_4]^-$, which is easily formed by the dissolution of Re_2O_7 in alkaline solutions. The kinetics of oxygen exchange between $[ReO_4]^-$ and solvent water have been examined at 25 °C using ^{17}O NMR measurements.[60] The data suggest a very slow exchange with an acid independent rate constant of 1.4×10^{-8} $mol^{-1}s^{-1}$. This value is a factor of two smaller than that for $[TcO_4]^-$. However, $[ReO_4]^-$ shows a dramatically increased rate for H_2O exchange in the presence of complexing citrate ions. This suggests an exchange mechanism that involves a coordination number expansion.

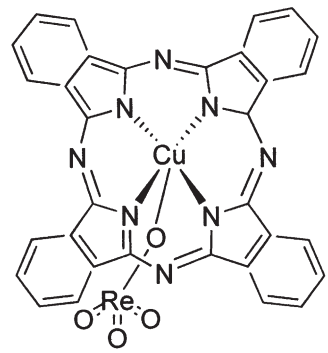
The tetrahedral perrhenate ion is a stronger base than $[ClO_4]^-$ and should coordinate to metal ions more readily than the latter.[59] The place of the $[ReO_4]^-$ ligand in the spectrochemical series has been estimated by the chemical and spectroscopic properties of five-coordinate iron(III) porphyrin complexes of the general formula [Fe(TPP)X] (TPP = dianion of tetraphenylporphyrin, $X = Cl^-$, $[B_{11}CH_{12}]^-$, $[ClO_4]^-$, $[ReO_4]^-$, AcO^-, F^-) supporting the assumption that perrhenate is a stronger ligand than perchlorate.[61] Complexes with monodentately bonded perrhenate ligands have been observed for numerous metal ions including sodium, where Na—O—ReO_3 units with Na—O bond lengths between 2.29 Å and 2.55 Å were found for sodium complexes with crown ethers of various ring sizes.[62–66] The Re—O bond lengths are almost unaffected by the coordination of the $[ReO_4]^-$ ion. Three forms of coordinated perrhenate are observed for caesium complexes with calix[4]arene bis(crown-6) (BC6) in the 1,3-alternate conformation of the ligand. $[Cs_2(ReO_4)(BC6)][ReO_4]$, $[Cs_2(ReO_4)(H_2O)(BC6)][ReO_4]$, and $[Cs_3(ReO_4)_2(BC6)_2][ReO_4]$ differ one from the other in the coordination mode of the perrhenate ions (monodentate, bidentate, and bridging) and the position of the caesium ions in the crown.[67] Molecular adducts of various composition are formed between M^{2+} ions ($M = Ca^{2+}$, Cd^{2+}), urea, or thiourea, perrhenate, and aqua ligands when the metal perrhenates are mixed with the ligands in different ratios.[68–70] Supramolecular arrays were derived from very similar reaction mixtures with bivalent metal ions such as Ca^{2+}, Pb^{2+}, Ba^{2+}, or Cd^{2+}.[71–74] They will be described in Section 5.3.2.1.4.

Reaction of perrhenic acid with ferrocene yields complex anions of the composition $[Fe(OReO_3)_6]^{3-}$ (**1**) and $[Fe(OReO_3)_4(H_2O)_2]^-$ which have been isolated as ferrocenium salts and characterized by crystallography and Mössbauer spectroscopy.[75] The neutral complex *mer*-$[Fe(OReO_3)_3(H_2O)_3]$ is obtained by the reaction of iron(III) hydroxide with perrhenic acid.[76] Electrochemical oxidation of copper phthalocyanine, [Cu(pc)], in the presence of $[Bu_4N][ReO_4]$ yielded [Cu(pc)] units with one and two $[ReO_4]^-$ co-ligands (**2**). EPR spectroscopy verifies that both compounds contain Cu^{II}.[77,78] The heterometallic μ-oxo Os^{VI}–Re^{VII} complex $[OsN\{N(SPPh_2)_2\}_2(OReO_3)]$ ($\{N(SPPh_2)_2\}^-$ = imidobis(diphenylphosphinothiolate)) is prepared by the reaction of $[OsN\{N(SPPh_2)_2\}_2](BF_4)$ with $[Bu_4N][ReO_4]$.[79] $[Ta_2(OMe)_8(OReO_3)]$, a compound with two bis-methoxo-bridged tantalum(V) ions, displays a close analogy to the homometallic $[M_2(OMe)_{10}]$ (M = Mo, W) complexes.[80]

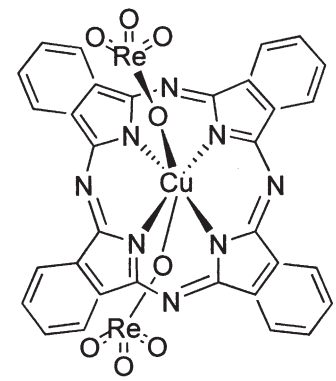
Perrhenate coordination at rhenium centers is in most cases a result of either incomplete reduction when starting from rhenium(VII) precursors or partial oxidation of rhenium in the course of complex reactions. It has been observed for different rhenium cores containing the metal in various oxidation states. A fascinating example is the oxidation of the metalloorganic rhenium(V) complex $[(\eta^5\text{-}C_5Me_5)ReO(OCH_2CH_2O)]$ which produces a tetranuclear compound (**3**) containing two asymmetric Re^V fragments and two $[ReO_4]^-$ ligands in *trans* position to each other.[81] The perrhenate ligands in $[Re^I(CO)(OReO_3)(Ph_2PCH_2PPh_2)]$ (**4**),[82] $[Re(CO)_5(OReO_3)]$,[83] $[Re(CO)_3(Ph_3P)_2(OReO_3)]$,[84] $[Re^{II}(NO)Cl_2(PPh_3)\text{-}(OPPh_3)(OReO_3)]$ (**5**),[85] $[Re^{II}(NO)Cl_2(OPPh_3)_2\text{-}(OReO_3)]$,[85] $(Bu_4N)[Re^{VI}(NCPh_3)\text{-}Cl_4(OReO_3)]$,[85] $[ReO(TPP)(OReO_3)]$,[87] $[ReO(Ph_2PC_6H_4S)_2\text{-}(OReO_3)]$,[88] $[ReO_3(eg)(OReO_3)]$,[89] and $[Re(NPh)I_2(PhNH_2)(PPh_3)(OReO_3)]$[90] coordinate *trans* to carbonyl, nitrosyl, triphenylmethaneimido, oxo-, or phenylimido-ligands.



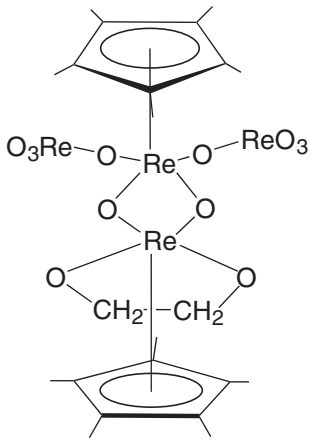
(1)



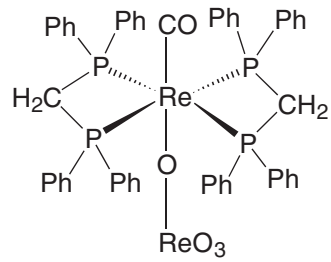
(2a)



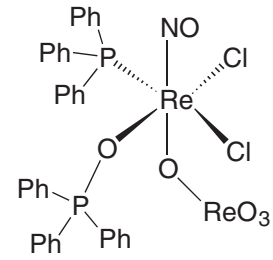
(2b)



(3)



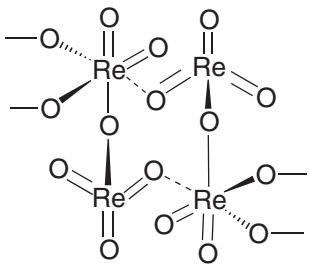
(4)



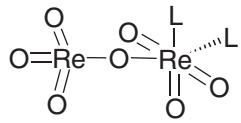
(5)

(ii) Compounds derived from Re_2O_7

Re_2O_7 is readily soluble in some organic solvents. This is somewhat surprising for a polymeric compound, but can be attributed to the unique structure of this oxide which contains tetrameric rings with octahedral [ReO_6] and tetrahedral [ReO_4] units (**6**).[91] These units can easily be cleaved from the polymer by donor solvents giving reactive [Re_2O_7] units having two vacant coordination positions which are occupied by solvent molecules or bidentate ligands. This was demonstrated in an early report on the isolation and characterization of "solid perrhenic acid",[92,93] which has two aqua ligands in the coordination sphere of one of the rhenium atoms. This arrangement remains unchanged when the compound is co-crystallized with dioxane[94] or diglyme.[95] Further adducts of the general formula [$Re_2O_7L_2$] (**7**) are formed when Re_2O_7 is dissolved in polar solvents such as MeCN,[96,97] THF,[98] or propionitrile.[89] When Re_2O_7 was treated with DME or bidentate bases such as 2,2′-bipyridyl (bipy), 4,4′-di-*t*-butyl-2,2′-bipyridine (Bu^t-bipy), 2,2′-bis(pyrazolyl)propane ((pz)$_2$-prop) or *N*,*N*′-dicyclohexyl-1,4-diazabuta-1,3-diene (cydab) is added to a solution of [$Re_2O_7(THF)_2$] in THF, the adducts [$Re_2O_7(L^{\frown}L)$] are formed (**8**).[89] Similarly to the compounds of the type (**7**) one tetrahedral and one octahedral rhenium center is observed. Addition of a ligand to the tetrahedral site of the molecule occurred with pyridine.[99] The moisture-sensitive [$Re_2O_7py_3$] (**9**) deposits from solutions of Re_2O_7 in dry pyridine. Hydrolysis of the complex gives [Hpy][ReO_4].[100] The extremely oxygen-rich peroxo compound [$Re_2O_3(H_2O)_2(O_2)_4$] (**10**) which can be prepared from rhenium oxide and H_2O_2 in diethyl ether shows considerable catalytic activity in oxidation reactions but decomposes during these processes. Hydrolysis yields "perrhenic acid", [$Re_2O_7(H_2O)_2$].[101]

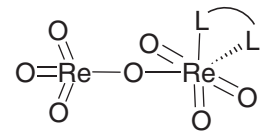


(**6**)



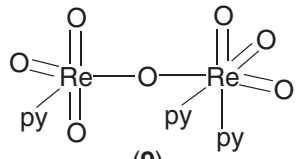
L = H_2O, MeCN, THF, EtCN

(**7**)

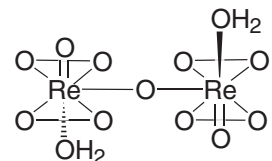


L L = bipy, Bu^tbipy, $(pz)_2$-prop cydab

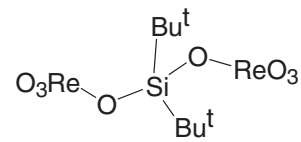
(**8**)



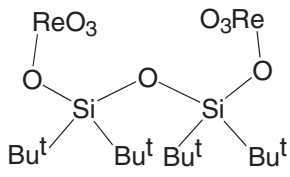
(**9**)



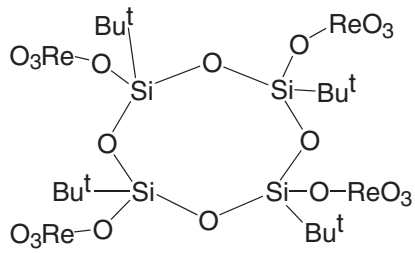
(**10**)



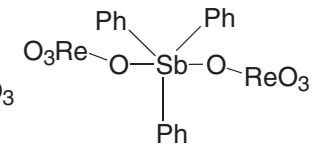
(**11**)



(**12**)



(**13**)



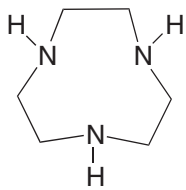
(**14**)

Cleavage of the Re–O–Re units and the formation of oxo bridges to other elements generates numerous novel compounds which can be regarded as derivatives of dirhenium heptoxide. Thus, stimulated by the great synthetic potential of [TMS($OReO_3$)] and the promising catalytic properties of [$O_3ReOSiR_3$] compounds,[102,103] novel silicon compounds such as [Ph_3Si-($OReO_3$)],[104] [(O_3ReO)($Bu^t{}_2Si$)($OReO_3$)] (**11**),[105] [(O_3ReO)(Bu_2Si)O(Bu_2Si)($OReO_3$)] (**12**),[106,107] or the cyclic [$OSi(Bu^t)(OReO_3)]_4$ (**13**) have been prepared.[108,109] Whereas [$Ph_3SiOReO_3$] is easily accessible from Re_2O_7 and Ph_3SiOH, a similar reaction with (2,4,6-$Me_3C_6H_2)_3GeOH$ which leads to [(2,4,6-$Me_3C_6H_2)_3Ge(OReO_3)$] requires longer reaction times.[104] Ph_3SnOH and Re_2O_7 do not yield the tin analogue but give a tetrameric compound of the composition [(O_3ReO)$Ph_2SnOPh_2SnOH]_2$.[104] [(O_3ReO)$SnMe_3$] and [(O_3ReO)$PbMe_3$] are formed from dirheniumheptoxide and tetramethyltin[110] or tetramethyllead.[111] The tin compound has a zigzag chain structure which originates from catenation of the molecules via the tin atom to the perrhenate group of the neighboring molecule. The trinuclear [$(O_3ReO)_2SbPh_3O$] (**14**) can be prepared from Re_2O_7 and the dimeric $(Ph_3SbO)_2$.[107] When the reaction is performed in a 1:2 molar ratio [(O_3ReO)$SbPh_3$–O–$SbPh_3(OReO_3)$] is formed. These reactions show that one of the antimony—oxygen bonds in triphenylstibane oxide can be selectively cleaved.

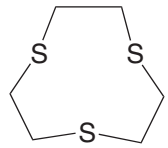
$$Re_2O_7 \rightarrow \text{“}ReO_3{}^+\text{”} + [ReO_4]^- \qquad (1)$$

Re_2O_7 undergoes a formal heterolytic Re—O—Re bond cleavage upon reaction with strongly chelating ligands such as 1,4,7-triazacyclononane (tacn) (**15a**), 1,4,7-trithiacyclononane (9S3) (**15b**), or 1,4,7-trimethyl-*N*,*N*′,*N*″-triazacyclononane (Me_3tacn) (**15c**).[89,112,113] The resulting $ReO_3{}^+$ building blocks (Equation (1)) form stable cationic complexes of the general formula $[LReO_3]^+$ with the tridentate ligands and perrhenate anions serve as counter ions. The driving force of these reactions is most probably the formation of the stable octahedral $[LReO_3]^+$ units and has also been observed for open-chain ligands such as *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylene-

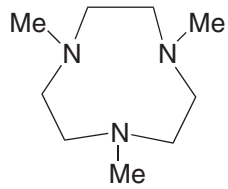
triammine or tris(pyrazolyl)methane.[89] The extraordinary stability of the trioxorhenium(VII) core is demonstrated by the large number of derivatives containing this core.



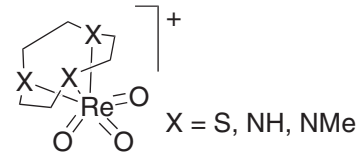
(**15a**)



(**15b**)



(**15c**)



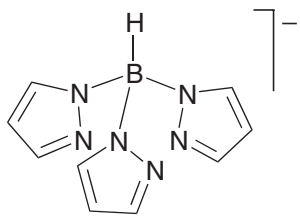
(**16**)

(iii) Trioxo complexes

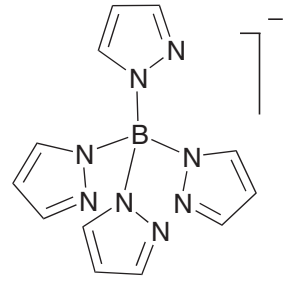
Stable trioxorhenium(VII) complexes have been isolated with various ligands. A dominating motif is a tripodal donor atom arrangement which stabilizes $[ReO_3L]^{0,+}$ complexes perfectly.

The heterolytic cleavage of rhenium heptoxide with ligands of type (**15**) has been discussed above. The resulting $[ReO_3L]^+$ cations (**16**) are also accessible from perrhenate,[114] or by the oxidation of rhenium(I) tricarbonyl[115–118] or rhenium(V) oxo complexes.[116–119] Whereas the ionic complexes $[ReO_3(tacn)]^+$ and $[ReO_3(Me_3tacn)]^+$ are water stable, $[ReO_3(9S3)]^+$ slowly decomposes in water. A more rapid hydrolysis is observed with open chain ligands.[89,120] Due to the formation of perrhenic acid, the solutions become strongly acidic and $(HL)ReO_4$ salts can be isolated from the resulting solutions. The $[ReO_3(tacn)]^+$ cation deprotonates in alkaline solutions ($pK_a = 10.3$, 25 °C) to give the neutral $[ReO_3(tacn)]$.[116] A coordination behavior which is very similar to that of tacn has been found for *tris*-(2-pyridyl)amine, which reacts with Re_2O_7 under formation of a light-blue solid which has been identified as the cationic rhenium(VII) complex $[ReO_3(L)][ReO_4]$.[121] In contrast to $[ReO_3(tacn)]^+$, however, the *tris*-(2-pyridyl)amine compound does not convert alkenes into alcohols. Nevertheless, a complex which is the potential product of this conversion of ethene, $[ReO(OCH_2CH_2O)(L)]Cl$, has been prepared by a ligand exchange procedure starting from the rhenium(V) precursor $[ReOCl_3(PPh_3)_2]$.

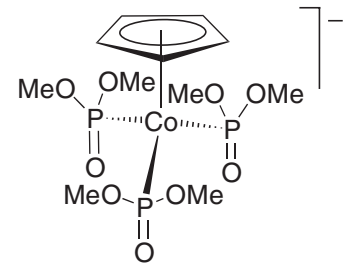
Neutral $[ReO_3L]$ complexes are formed with monoanionic tripodal ligands such as hydrotris-(pyrazolyl)borate ($HB(pz)_3^-$) (**17**), tetrakis(pyrazolyl)borate ($B(pz)_4^-$) (**18**), and the phosphite-based *Kläui* ligand ($[cpCo\{PO(OR)_2\}_3]^-$) (**19**) and their derivatives.



(**17**)



(**18**)



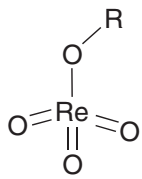
(**19**)

$[ReO_3\{HB(pz)_3\}]$ as well as the methyl substituted analogues can be prepared from Re_2O_7,[122,123] $[NH_4][ReO_4]$,[124] by nitric acid oxidation of $[ReOCl_2\{HB(pz)_3\}]$ or by thermolysis of the rhenium(V) complex $[ReO(eg)\{HB(pz)_3\}]$ (eg = ethylene glycolate).[124] The latter reaction can be attributed to the loss of ethylene and is the reverse reaction pathway observed for technetium. Thus, $[TcO_3\{HB(pz)_3\}]$ readily reacts with ethylene to form the technetium(V) complex $[TcO\{HB(pz)_3\}(eg)]$ and is a representative of a class of compounds which dihydroxylate alkenes.[124,125] $[ReO_3\{HB(pz)_3\}]$ is easily reduced to rhenium(V) species, the composition of which are dependent on the reducing agent used. Similar behavior is observed for $[ReO_3\{B(pz)_4\}]$.[126,127]

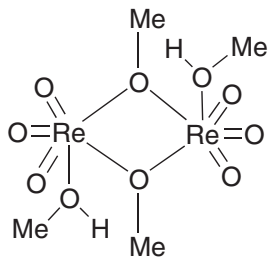
Rhenium(VII) trioxo-complexes with derivatives of the Kläui ligand (**19**) are stable in air and organic solvents, but slowly decompose in aqueous solutions yielding perrhenic acid.[128,129] $[ReO_3(cpCo\{PO(OR)_2\}_3)]$ can be prepared from Re_2O_7, perrhenate, or by oxidation of the corresponding Re^I tricarbonyl complex. Reduction with phosphines in the presence of HBr

gives access to the rhenium(V) complex $[ReOBr_2(cpCo\{PO(OR)_2\}_3)]$. This reaction, however, is completely reversible.[128]

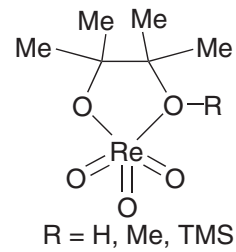
The observed conversion of oxo ligands to glycolate in technetium and rhenium complexes[125] containing the metals in their higher oxidation states promoted interest in alkoxy complexes, little being known about complexes of the type $[ROReO_3]$ (**20**).[130,131] Tetracoordinate species are unstable at room temperature, whereas the higher coordinated compounds $[RO\text{-}ReO_3L_2]$ are thermally stable.[130] The alkoxy complexes $[ReO_3(OMe)(MeOH)]_2$ (**21**) and $[ReO_3(OCMe_2\text{-}CMe_2OR)]$ (R = H, Me, TMS) (**22**) have fluxional structures in solution at room temperature.[132] The protic hydrogen atom in $[ReO_3(OCMe_2CMe_2OH)]$ ((**22**) with R = H) can be abstracted to yield the lithium salt $Li[ReO_3(OCMe_2CMe_2O)]$.[132] The yellow solutions of $[ReO_3(OCMe_2C\text{-}Me_2OH)]$ or $[ReO_3\{OC(C_6H_{10})C(C_6H_{10})OH\}]$ (C_6H_{10} = cyclohexyl) (**23**) in CH_2Cl_2 slowly become orange and red crystals of the rhenium(VI) complex $[ReO(diolate)_2]$ may be isolated.[133]



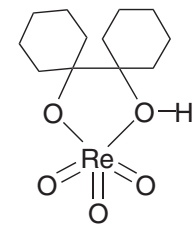
(**20**)



(**21**)

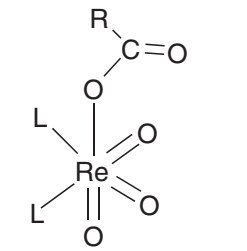


(**22**)

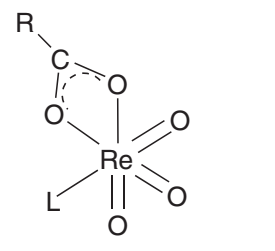


(**23**)

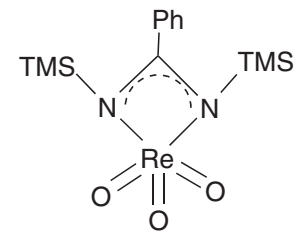
Treatment of Re_2O_7 with carboxylic anhydrides $(RCO)_2O$ in THF or MeCN yields two types of perrhenic anhydrides. Strongly electron-withdrawing groups (e.g., $R = CF_3$) lead to complexes of the type $[RC(O)OReO_3L_2]$ (L = THF, MeCN) (**24**) exhibiting η^1-coordinated carboxylato groups and octahedral coordination of the metal. By way of contrast, anhydrides of weak carboxylic acids (e.g., R = Me) yield $[RC(O)OReO_3L]$ (L = THF, MeCN) (**25**) complexes with η^2-bonded carboxylato groups.[134]



(**24**)



(**25**)



(**26**)

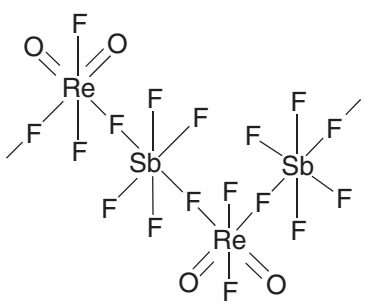
Compounds which can formally be regarded as derivatives of $[ReO_3Cl]$ or the $[ReO_3Cl_2]^-$ anion, which can be isolated from mixtures of ReO_3Cl and $(Ph_4P)Cl$,[135] are formed with imine ligands or phenothiazines.[136–138] $[ReO_3Cl(phen)]$[136] (phen = 1,1-phenanthroline) and $[ReO_3Br\text{-}(Bu^tbipy)]$[137] precipitate from solutions of perrhenate, the ligands and HCl or HBr. The five-coordinate complex $[ReO_3(oxinate)]$[139] (oxinate = 8-hydroxyquinolinate) has been studied for its photoluminescence properties, showing a green fluorescence at $\lambda = 511$ nm and a very weak one at $\lambda = 645$ nm. Both emissions originate from the lowest-energy intraligand π to π^* transition on the oxinate ligand.[140] Five-coordination of the rhenium atom was also observed in $[ReO_3\{(TMSN)_2CPh\}]$ ($(TMSN)_2CPh$ = bis(trimethylsilyl)- benzamidinate) (**26**) which is obtained from reaction of Re_2O_7 with the zinc salt of the ligand.[141] The metal exhibits an irregular trigonal

bipyramidal environment. An unusual trioxorhenium(VII) compound containing the metal with the coordination number 4 can be made from the organometallic $[ReO_2(mes)_2]$ (mes = 2,4,6-$Me_3C_6H_2$) and NO gas. This reactions gives orange crystals of the imido complex $[ReO_3(NMes)]$.[142]

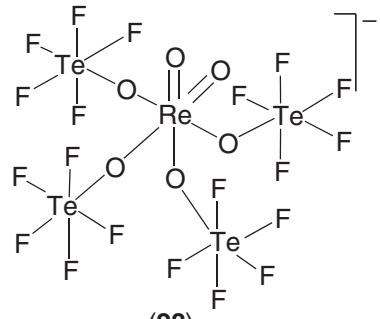
(iv) Dioxo and monoxo complexes

Compared with the large number of rhenium(VII) trioxo complexes there are relatively few reports on dioxo and monoxo compounds. They are mainly derived from rhenium(VII) oxyfluorides or contain catecholato ligands.

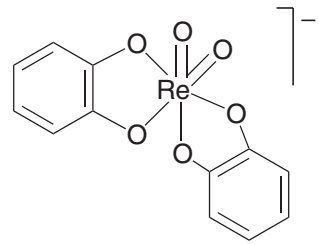
Reactions of ReO_2F_3 with AsF_5 or SbF_5 lead to compounds of the compositions $[ReO_2\text{-}F_3(AsF_5)]$ or $[ReO_2F_3(SbF_5)]$ which have solid-state structures consisting of infinite chains of octahedral $[ReO_2F_4]$ and $[AsF_6]$ or $[SbF_6]$ units.[143] The oxo ligands are in *cis* position to each other (**27**). $[ReO_2F_3(SbF_5)]$ ionizes in SO_2ClF solvent to give the novel $[Re_2O_4F_5]^+$ cation and the $[Sb_2F_{11}]^-$ anion. The $[ReO_2F_2(MeCN)_2][SbF_6]$ complex salt is formed upon dissolution of $[ReO_2F_3(SbF_5)]$ in acetonitrile. The $[ReO_2F_2(MeCN)_2]^+$ cation has a pseudooctahedral *cis*-dioxo-arrangement in which the MeCN ligands are *trans* to the oxygen atoms.[143] *cis*-Coordination of two oxo ligands can also be found in complexes with the pentafluorooxotellurato ligand, $OTeF_5^-$, which resembles fluorine in its ability to stabilize the high oxidation states of the elements. $[ReO_2(OTeF_5)_3]$ can be prepared from a reaction of ReO_2F_3 with $B(OTeF_5)$.[144] NMR and vibrational spectroscopic results are consistent with a trigonal bipyramidal arrangement in which the oxygen atoms and an $OTeF_5^-$ group occupy the equatorial plane. Fluorine-19 and ^{125}Te NMR spectra show that the axial and the equatorial $OTeF_5^-$ ligands are fluxional and are consistent with intramolecular exchange by means of a pseudorotation. $[ReO_2(OTeF_5)_3]$ shows Lewis acid behavior as can be seen by its reaction with $OTeF_5^-$ which yields the $[ReO_2(OTeF_5)_4]^-$ anion (**28**) which can be isolated in form of its tetraalkylammonium salt.[144] The *cis* arrangement of the oxo ligands is preserved during this reaction. A monooxo complex, the pseudooctahedral $[ReO(OTeF_5)_5]$ is formed when the rhenium(VI) compound $[ReO(OTeF_5)_4]$ is oxidized with $Xe(OTeF_5)$.[145]



(**27**)



(**28**)



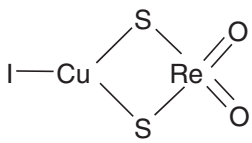
(**29**)

Oxidation of rhenium(V) to rhenium(VII) is observed when $[ReOCl_3(PPh_3)_2]$ reacts with excess catechol (H_2cat) in air and the complex anion $[ReO_2(cat)_2]^-$ (**29**) can be isolated from these reaction mixtures.[146] Cyclic voltammetry coupled with convolution analysis showed that the rhenium(VII) complex undergoes a reversible diffusion-controlled one-electron reduction. Another approach to complexes of the type (**29**) is the reaction of monoprotonated catecholates with rhenium pentacarbonyl triflate.[147] The formation of oxobridged dimeric $[Re_2O_6\text{-}(SO_3Cl)_2]$ complexes has been suggested from spectroscopic studies on solvolytic reactions of perrhenates with chlorosulfuric acid.[148]

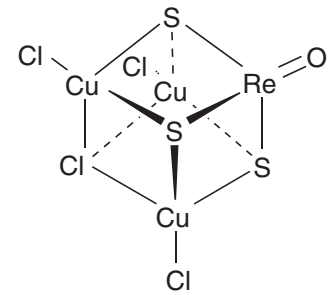
5.3.2.1.2 Sulfido complexes

Transition metal sulfide units occur in minerals in nature and play an important role in the catalytic activity of enzymes such as hydrogenase and nitrogenase. Industrial processes use transition metal sulfides in hydroprocessing catalysis. Both the metal and the sulfur sites in these compounds can undergo redox reactions which are an important part of their reactivity. Thus, the electronic situation of the ReS_4^- anion and related complexes is of considerable interest and has been evaluated applying quantum chemical methods.[149,150]

Tetrathioperrhenate, ReS_4^-, has been the subject of a number of studies including both synthetic and structural aspects. $[Et_4N][ReS_4]$ is formed upon heating ReO_4^- in a methanolic ammonium polysulfide solution. A change of the solvent and/or the cation leads to reduction of the metal and complexes containing rhenium(V) or rhenium(IV) centers such as $[ReS_9]^-$, $[Re_4S_{22}]^{4-}$ or $[Re_2S_{16}]^{2-}$ are formed.[151,152] Stable transition metal complexes with the tetrahedral $[ReS_4]^-$ ligand and related species are formed with iron which partially mimic biological reaction centers.[151,153–156] The reaction of $[Et_4N][ReS_4]$ with $[Re(CO)_5Cl]$ gives di- and trinuclear complexes with sulfido bridges between rhenium atoms in both low and high oxidation states.[157] Multinuclear copper complexes with $[ReS_4]^-$ ligands are available from mixtures containing $[Et_4N][ReS_4]$ and copper(I) halides.[151,158,159] The reaction with CuNCS yields anions with complicated (partially polymeric) structures in which parts of the solid-state structure of CuNCS are linked by tetrathioperrhenate units.[160] Complexes containing oxothioperrhenato ligands have been prepared from copper(I) halides, Ph_3P, and $[Et_4N][ReS_4]$ in acetone or CH_2Cl_2 in air.[161] The copper atoms in the products are exclusively bonded by halogen and sulfur atoms forming monomeric $[CuI(S_2ReO_2)]^-$ units (**30**) and the heterocubane anion $[Cu_3Cl_4(ReOS_3)]^{2-}$ (**31**).



(**30**)

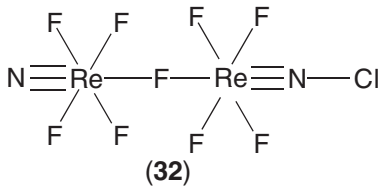


(**31**)

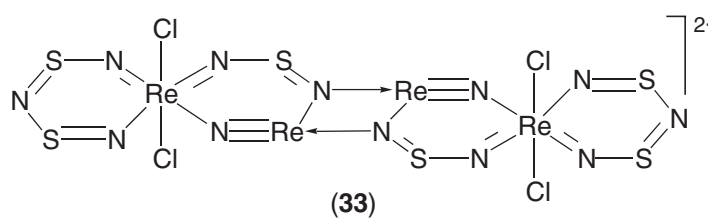
An interesting feature of the $[ReS_4]^-$ anion is its reactivity, which gives access to a number of new sulfur-rich compounds. $[ReS_4]^-$ undergoes addition and cycloaddition reactions with alkenes, alkynes, or isocyanides yielding a large variety of rhenium(V), rhenium(IV), or rhenium(III) sulfido, perthiolato, and thiolato complexes.[162–170] Details will be described in the sections which cover the chemistry of the corresponding oxidation states.

5.3.2.1.3 Nitrido and imido and related complexes

In addition to oxo and sulfido groups, multiply bonded nitrogen ligands are able to stabilize rhenium in its highest oxidation state. The dinuclear $[NRe_2F_9(NCl)]$ (**32**) is the product of direct fluorination of $ReNCl_4$.[171] The fluoro bridge between the two rhenium(VII) centers is strongly asymmetric (Re—F: 1.88 Å vs. 2.28 Å) which is a consequence of the different *trans* directing influences of the nitrido and the chloroimido ligands. Another approach to $[Re(NX)F_5]$ complexes is given by reactions of $ReNF_4$ with XeF_2, ClF_3, or BrF_3.[172] The dianionic $[Cl_2Re(N_3S_2)(\mu\text{-NSN})(\mu\text{-N}{\equiv}ReCl_3)]_2^{2-}$ (**33**) is formed during the reaction of $[ReCl_4(NSCl)_2]$ with $N(TMS)_3$ in dichloromethane.[173] The complex anion consists of a planar ReN_3S_2-heterocycle which is connected with a second rhenium atom by a μ-nitrido bridge as well as by a μ-dinitridosulfato(II) ligand. Two of these $[Cl_2Re(N_3S_2)(\mu\text{-NSN})(\mu\text{-N}{\equiv}ReCl_3)]$ units dimerize via one of the *N*-atoms of the $(NSN)^{4-}$ ligand to give a centrosymmetric R_2N_2 four-membered ring.



(**32**)



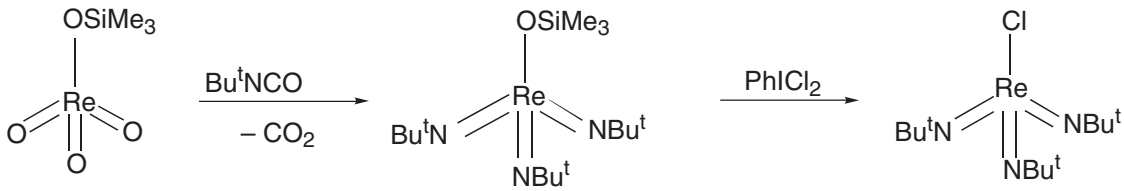
(**33**)

The formation of N^{3-} ligands by decomposition of hydrazine or hydrazine derivatives in acidic media provides one of the standard procedures for the synthesis of rhenium nitrido complexes.[174]

The mechanisms of these reactions, however, are still not completely clear. Hydrazido complexes as possible intermediates in nitride formation have been obtained from the reaction of the rhenium(V) compound $[ReOCl_3(PPh_3)_2]$ with $MePhNNH_2$.[175] The reaction in methanol under reflux gives the rhenium(VII) bis(hydrazido) cation $[ReCl_2(NNMePh)_2(PPh_3)_2][BPh_4]$ which can be used as precursor for the synthesis of further hydrazido–rhenium(VII) complexes with various co-ligands. When Ph_2NNH_2 is used instead of $MePhNNH_2$, a mixture of the rhenium(V) hydrazide $[ReCl_3(NNPh_2)(PPh_3)_2]$ and the mixed nitrido/hydrazido rhenium(VII) complex $[ReCl_2(N)(NNPh_2)(PPh_3)]$ is formed. In the presence of a base, the rhenium(VII) cation $[ReCl_2(NNPh_2)_2(PPh_3)_2]^+$ is the preferred product.[176]

Imido-ligands, NR^{2-}, are isoelectronic with the oxo ligand and should produce complexes of similar types. However, there are two important differences between NR^{2-} and O^{2-}. The imido-group has better electron-donating capabilities and the fact that with the substituent R the steric requirements of this ligand can be controlled within a wide range. This allows the stabilization of imido species with low coordination numbers and with ligands which are easily oxidized.

Key compounds in rhenium(VII) imido-chemistry are $[Re(OTMS)(NBu^t)_3]$ (**34**) and its derivatives $[Re(OER_3)(NR_3)]$ (E = C, Sn; R = Ph, 2,6-$C_6H_3Me_2$, 2,6-$C_6H_3Pr^i_2$) which can be prepared from the parent rhenium(VII) oxo compounds and isocyanates (Scheme 1).[104,177] The corresponding halides can be made by reactions of the trimethylsiloxo compounds with PhICl[177] (*t*-butyl compounds (**35**)) or by a simple single-pot reaction from rhenium(VII) oxide, $ArNH_2$, and TMSCl in the presence of a base (aryl derivatives).[178] Both types of compounds are versatile precursors which allow access to numerous novel imido complexes (Scheme 2). The amido-derivative $[Re(NBu^t)_3(NHBu^t)]$ (**36**) is obtained upon reaction of (**35**) with $LiNHBu^t$ and can undergo deprotonation to yield $[Re(NBu^t)_4]^-$, the imido-analogue of the perrhenate ion (**37**).[177,179] Further protonation gives cationic $[Re(NBu^t)_3(NH_2Bu^t)]^+$ (**38**) which is frequently used for ligand exchange reactions.[180] In the resulting complexes the high oxidation state of the metal is also stabilized in the presence of reducing ligands such as Ph_3P (**39**). Similar products can be obtained directly from $[Re(NBu^t)_3Cl]$ and include pyrazolato (**40**), phosphido, and amido ligands (**41**).[181,182] Phosphoraneiminato complexes (**42**) are formed during the reaction with $LiN=PR_3$.[182] A chemistry which is comparable to that of $[Re(NBu^t)_3X]$ has been developed for arylimido-analogues.[183,184] This also includes complexes containing different imido ligands at the same metal center,[185] and the structure of *cis*,*trans*-$[Re(NC_6H_3\text{-}2,6\text{-}Pr^i_2)_2Cl_2(benzoate\text{-}O,O')]$ has been determined.[186]



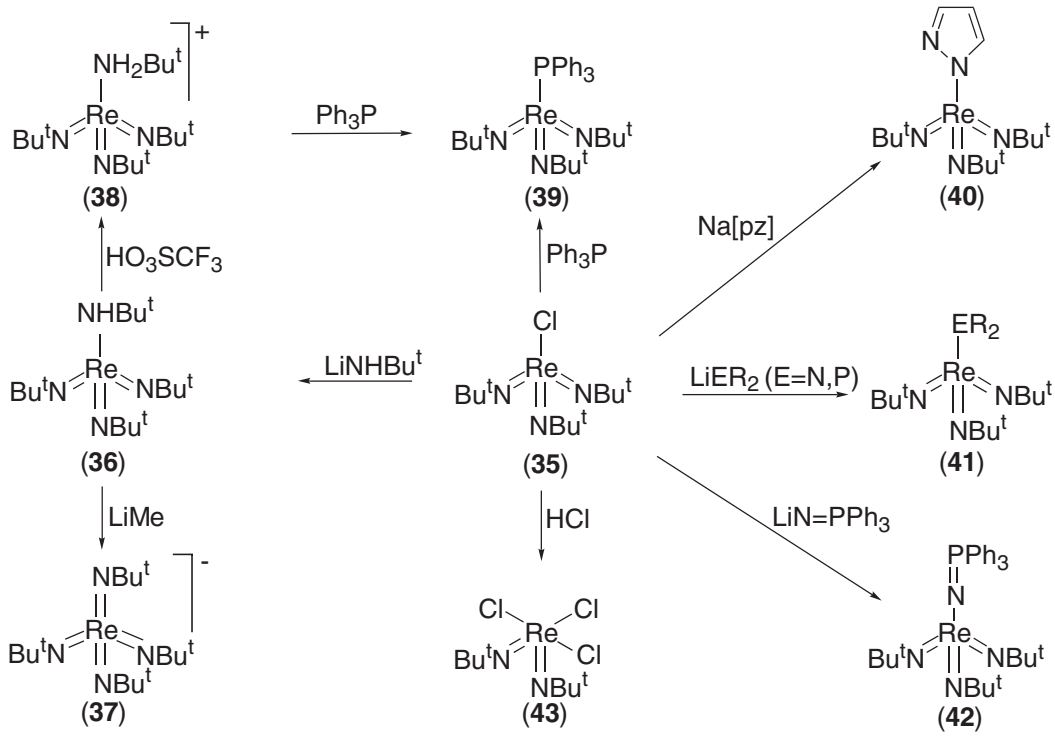
(**34**) (**35**)

Scheme 1

Bis-imido complexes which can be regarded as derivatives of $[Re(NBu^t)_2X_3]$ (**43**) (X = Cl, Br)[187] have been described with pyridine ($[Re(NBu^t)_2Cl_3py]$)[188] and tripodal ligands of the type (**15**).[189,190]

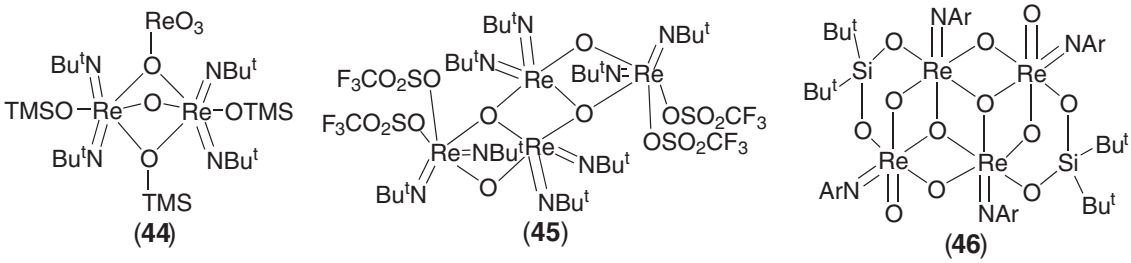
Several organometallic mixed imido/oxo compounds are known. They can be synthesized by mixing oxo- and imido-complexes and oxo/imido-ligand exchange takes place via bridging ligand groups. In solution there is an equilibrium between monomers and dimers, in the solid-state dimeric compounds with bridging oxygen atoms can be isolated.[191] An example without a rhenium–carbon bond, is the trimethystannyl-substituted aminorhenium trioxide $(Me_3Sn)_2$-$NReO_3$, prepared from $TMSOReO_3$ and $N(SnMe_3)_3$.[107]

The formation of polynuclear compounds is often observed as a competing reaction when a deficiency of reactants is used or ligands are provided which can easily act as bridges between metal centers. Thus, the trinuclear $[\{Re(NBu^t_2(OTMS)\}_2(\mu\text{-}O)(\mu\text{-}OTMS)(\mu\text{-}OReO_3)]$ (**44**) is obtained when $[ReO_3(OTMS)]$ is exposed to a deficient amount of Bu^tHTMS.[192] The bridging perrhenato ligand can easily be replaced by F_3CCOO^-.[181] A tetrameric compound with a rather complex structure, $[Re_4(NBu^t)_8(\mu\text{-}O)(\mu_3\text{-}O)_2(OSO_2CF_3)_4]$ (**45**) is obtained as a side-product upon



Scheme 2

protonation of $[Re(NBu^t)_3(NHBu^t)]$ with CF_3SO_3H.[180] The reaction of $[Bu^t{}_2Si(OReO_3)_2]$ with an arylisocyanate, however, yields the tetrameric, mixed oxo/imido compound $[(Bu^t{}_2SiO_2)_2(\mu\text{-}O)_4(\mu_3\text{-}O)_2\{ReO(NAr)\}\{Re(NAr)\}_2]$ (**46**).[193]

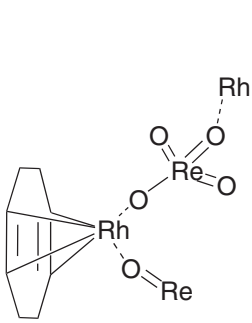


Phosphoraneiminato complexes of rhenium(VII) have been isolated from reactions of Re_2O_7 with $TMSNPR_3$ (R = Ph, Et) or $TMSNP(Ph)_2C_2H_4PPh_2NTMS$,[194,195] whereas attempts starting from $[NH_4][ReO_4]$ only yield the ion pair $[TMSNHPPh_3][ReO_4]$.[196] A quantum chemical analysis of $[(Ph_3PN)ReO_3]$ and complexes with the isolobal cyclopentadienyl ligand suggests differences in metal–ligand bond strengths.[197] The formation of compounds of the composition $[ReO_2(OTMS)_2\{N(Ph_2)PCH_2PPh_2\}]$ and $[ReO_2(OTMS)_2\{N(Ph_2)PCH_2AsPh_2\}]$ from $[(TMSO)ReO_3]$ and the trimethylsilyl protected chelating ligand has been concluded from spectroscopic studies; however, X-ray structural data was not reported.[198] Well characterized are the mixed phosphoraneiminato/arylimido compound, $[(Ph_3PN)Re(NC_6H_3Pr^i{}_2\text{-}2,6)_3]$,[199] and structurally related cyclophosphazene imido complexes which were prepared from silylated diphosphazenes and Re_2O_7 followed by the reaction of the resulting oxo-species with ArNCO ($Ar = 2,6\text{-}C_6H_3Pr^i{}_2$).[200,201]

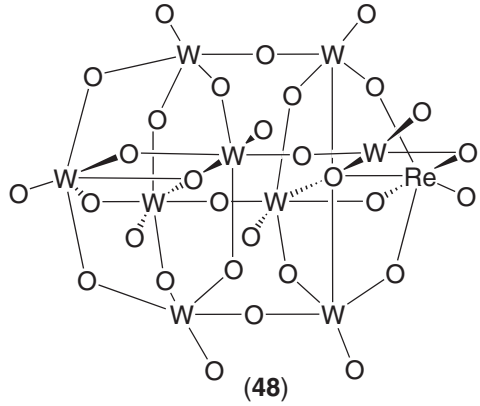
5.3.2.1.4 Supramolecular compounds

The role of perrhenate as bridging ligand in the coordination chemistry of bivalent cations such Ca^{2+}, Ba^{2+}, Cd^{2+}, or Pb^{2+} has already been mentioned in Section 5.3.2.1.1(i). Three-dimensional

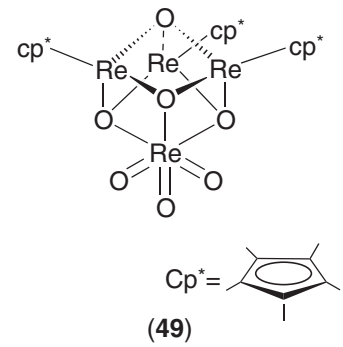
networks are formed with urea or thiourea as co-ligands. Perrhenato ligands act as bi- or tridentate bridges or complete the coordination sphere of the M^{2+} cations as monodentate $OReO_3^-$ building blocks.[71–74] A similar structural pattern can be observed in the paramagnetic gadolinium(III) complex $[Gd(H_2O)_2(OReO_3)_3]$ where distorted tricapped trigonal prisms of the $\{Gd(H_2O)_2(OReO_3)_{6/2}\}$ subunits are interconnected via ReO_4^- ligands.[202] Infinite chains of $[Ho(OReO_3)_3(TDTD)_4(H_2O)]$ (TDTD = 1,4-dithiane 1,4-dioxide) are formed when hydrated holmium perrhenate is mixed with TDTD in a molar ratio of 1:4.[203] Similar structures are also known for other lanthanides.[204] Supramolecular assemblies are known with tetranuclear $[Ag_4(pyrimidine)_4]$ subunits interconnected by $[ReO_4]^-$ ions to give a coordination polymer. The perrhenate is bonded via hydrogen bonds and long range Ag–O contacts of between 2.8 Å and 3.0 Å.[205] Infinite chains in which square-planar rhodium and tetrahedral rhenium centers are linked by oxygen bridges to form a $(–ReO_2–O–Rh(COD)–O–)_n$ polymer are the result of the reaction of $[(COD)Rh(\mu\text{-Cl})]_2$ (COD = 1,5-C_8H_{12}) (**47**) with two equivalents of $AgReO_4$.[206]



(**47**)



(**48**)



(**49**)

Another class of supramolecular arrays containing rhenium is the group of tungstorhenate heteropolyanions. They can be isolated from reaction mixtures of sodium tungstate and various rhenium starting materials. Besides complexes of the Keggin structure type,[207] compounds with $[W_9ReO_{32}]^{n-}$ ($n = 3$–5)[208] (**48**) or $[\alpha_2\text{-}ReOP_2W_{17}O_{61}]^{n-}$ ($n = 5$–7)[209] subunits have been studied. The resulting polyanions undergo redox reactions at the rhenium centers yielding cavities containing rhenium atoms in the oxidation states +5, +6, or +7. ESR studies of $[W_9ReO_{32}]^{4-}$ suggest that the Re atom occupies one of the eight identical equatorial positions in the anion.[208]

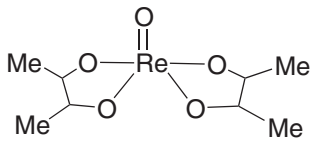
Perrhenate and related building blocks are constituents of several cluster compounds where they act as terminal groups in organometallic rhenium oxides such as in $[(cp^*Re)_3(\mu_2\text{-}O)_3(\mu_3\text{-}O)_3ReO_3]^+$ (**49**)[210] or in heterometallic clusters such as the structurally related $[(Re)_3(\mu^2\text{-dppm})_3(\mu^3\text{-}O)_3ReO_3]^+$ (dppm = bis(diphenylphosphino)methane)[211] and $[Pt_4\{P(C_6H_{11})_3\}_4\ (\mu\text{-}CO)_2(ReO_4)_2]$.[212] A series of platinum–rhenium and platinum–rhenium–mercury clusters with Pt–Re multiple bonds has been isolated from reactions of Pt_3 precursors with Re_2O_7 or perrhenate.[213,214]

5.3.2.2 Oxidation State VI

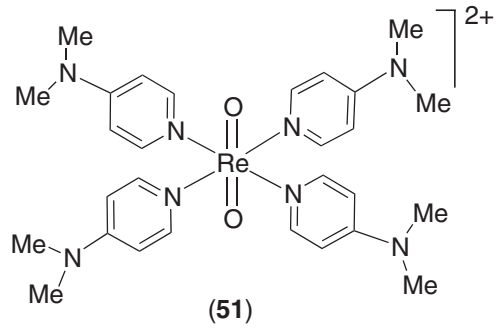
Rhenium(VI) complexes which contain the metal in a d^1 configuration are comparatively rare. They are often formed as transient states during the reduction of rhenium(VII) or oxidation of rhenium(V) compounds and readily undergo further redox processes. Stable Re^{VI} complexes can be obtained with strongly donating ligands such as oxo-, nitrido-, or imido- groups or by stabilization of the metal center by a trigonal prismatic coordination sphere. The monomeric, paramagnetic d^1 compounds are often studied by EPR spectroscopy, which is particularly suitable for complexes with axial symmetry, where well-resolved ^{185,187}Re hyperfine interactions ($I = 5/2$) can be expected. Despite specific problems due to the large Re hyperfine couplings and the occurrence of "forbidden" $\Delta M_I = \pm 1, \pm 2, \ldots$ transitions detailed information about the delocalization of the unpaired electron and the composition of the first coordination sphere can be derived.[209,215] By means of EPR spectroscopy unstable paramagnetic intermediates can be detected as has been demonstrated for a number of oxohalide complexes[216] or the electrochemically generated $[ReOCl_2(OEt)(py)_2]^+$.[217] Diamagnetism is observed for dimeric rhenium(VI) complexes where spin-pairing is obtained by the formation of a metal–metal bond.

5.3.2.2.1 Oxo complexes

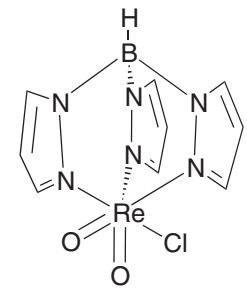
Oxo complexes of rhenium(VI) are preferably stabilized by "hard" donor atom ligands such as oxygen or nitrogen. Rhenium(VI) oxo-complexes with alkoxo ligands including $[Re_2O_3(OMe)_6]$, $[ReO(OPr^i)_5]^-$, and $ReO(OBu^t)_4]$ were isolated early.[218] These are unstable as is their homoleptic analogue $[Re(OMe)_6]$[219,220] and decompose even at moderate temperatures. Thermally more stable compounds can be obtained with chelating alkoxides such as 2,3-dimethylbutane-2,3-diol (pinacol, H_2pin) or 1,1′-bicyclohexane-1,1′-diol (H_2bicyc).[133] $[ReO(pin)_2]$ (**50**) and $[ReO(bicyc)_2]$ are formed upon reduction of the corresponding trioxo hydrogendiolato rhenium(VII) complexes with Ph_3P. They possess a distorted square-pyramidal coordination geometry and are not oxidized by dry air.



(**50**)



(**51**)



(**52**)

$ReCl_5$ or $ReOCl_4$ react with $ClOTeF_5$ to give blue paramagnetic $[ReO(OTeF_5)_4]$. In the solid state the geometry is square pyramidal with the doubly bonded oxygen atom in the apical position. The rhenium(VI) compound can be oxidized with $Xe(OTeF_5)_2$ to give the yellow rhenium(VII) complex $[ReO(OTeF_5)_5]$.[145]

Another approach to rhenium(VI) compounds is the oxidation of appropriate rhenium(V) precursors. Dioxorhenium(VI) complexes with (substituted) pyridine ligands are formed upon photochemical or electrochemical oxidation of *trans*-$[ReO_2(Rpy)_4]^+$ complexes (R = H or 4-NMe_2).[221,222] The *trans*-configuration of the oxo ligands is maintained in the products. Structural and EPR studies on *trans*-$[ReO_2(4\text{-}NMe_2py)_4]^{2+}$ (**51**) show that the oxidation of *trans*-$[ReO_2(4\text{-}NMe_2py)_4]^+$ results in considerable shortening of the Re—N bond lengths whereas the Re—O bond lengths are virtually the same in the rhenium(V) and rhenium(VI) compounds. The structural data confirm that an electron is removed from the d_{xy} orbital upon oxidation of Re^V as suggested by the EPR data.[222]

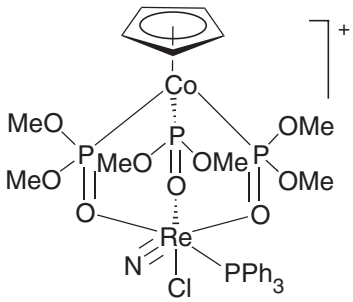
Although a *trans*-configuration of the oxo-ligands in the pyridine complexes is observed, a *cis*-dioxo arrangement occurs in $[ReO_2X\{HB(pz)_3\}]$ (X = Cl, Br, I) (**52**).[223] These compounds are the result of the reactions of [ReO(X)(triflate){HB(pz)$_3$}] complexes with one equivalent of pyridine *N*-oxide. The reactions most probably occur by initial formation of the d^0 rhenium(VII) cations $[ReO_2(X)\{HB(pz)_3\}]^+$ by oxygen atom transfer, followed by a one electron reduction. The rhenium(VI) compounds are fairly stable in the solid state, but in solution they slowly disproportionate with formation of $[Re^{VII}O_3\{HB(pz)_3\}]$ and $[Re^VO(X_2)\{HB(pz)_3\}]$.

5.3.2.2.2 Nitrido and imido complexes

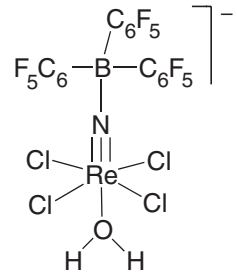
The neutral rhenium(VII) nitride chloride $ReNCl_4$ is reduced to the tetrachloronitridorhenate(VI), $[ReNCl_4]^-$, by the reaction with $[Ph_4As]Cl$.[224] However, the hazardous synthesis of $ReNCl_4$ from $ReCl_5$ and nitrogen trichloride or chlorine azide, restricted the use of the Re^{VI} anion for further ligand exchange experiments. A more facile synthesis of $[Bu_4N][ReNCl_4]$ is achieved by the reaction of $[ReO_4]^-$ with sodium azide and HCl.[225] The electronic structure of the $[ReNX_4]^-$ anions (X = Cl, Br, F) has been studied extensively by EPR showing that the experimental results can readily be reproduced by quantum chemical (Extended Hücker Theory, Density Functional Theory) techniques.[215,226,227] $[ReNCl_4]^-$ reacts with reduction of the metal with numerous ligand systems having phosphorus, sulfur, nitrogen, or oxygen atoms as donors.[225] The 6+ oxidation state is maintained during ligand exchange reactions with halides or pseudohalides.[225–227] The existence of the unstable $[ReNF_4]^-$ anion and the mixed-ligand complexes $[ReNCl_{4-n}F_n]^-$ ($n = 0$–4) has been proved conclusively by EPR studies.[228] EPR spectra of axially symmetric rhenium(VI)

complexes consist of six ^{185,187}Re hyperfine lines (Figure 2a) due to the interaction of the unpaired electron with the nuclear spin of rhenium ($I = 5/2$). Anisotropic frozen solution spectra show patterns with two pairs of six lines each in the parallel and perpendicular part in which additional (superhyperfine) couplings can be observed. These couplings patterns as well as the $\tilde{g}$ and $\tilde{a}$ values of the spectra give direct information on the composition of the coordination sphere of the metal. Figure 2b shows a frozen-solution spectrum of $[ReNF_4]^-$ with well-resolved ^{19}F-superhyperfine quintets as expected for the equatorial $[ReF_4]$ coordination.[227]

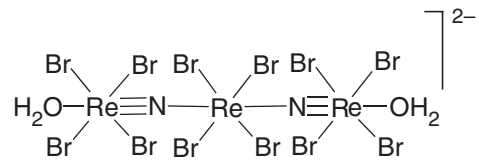
Rhenium(VI) nitride compounds can be generated by oxidation of rhenium(VI) complexes with chlorine or bromine. The products formed are often unstable and ligand exchange reactions with Cl^- or Br^- lead to a complex mixture of Re^{VI} compounds. Oxidation of the rhenium(V) complex $[ReN(PPh_3)Cl(cpCo\{PO(OR)_2\}_3)]$ with $Ag(BF_4)$, however, yields $[ReN(PPh_3)Cl(cpCo\{PO(OR)_2\}_3)](BF_4)$ (**53**) in good yields.[229]



(**53**)



(**54**)



(**55**)

The terminal nitrido-ligands are nucleophilic and react with Lewis acids. The isolated bimetallic products which contain rhenium in the 5+ oxidation state are treated in Section 5.3.2.3.3. Rhenium(VI) compounds are obtained when $[Bu_4N][ReNCl_4]$ reacts with $B(C_6F_5)_3$ or BBr_3.

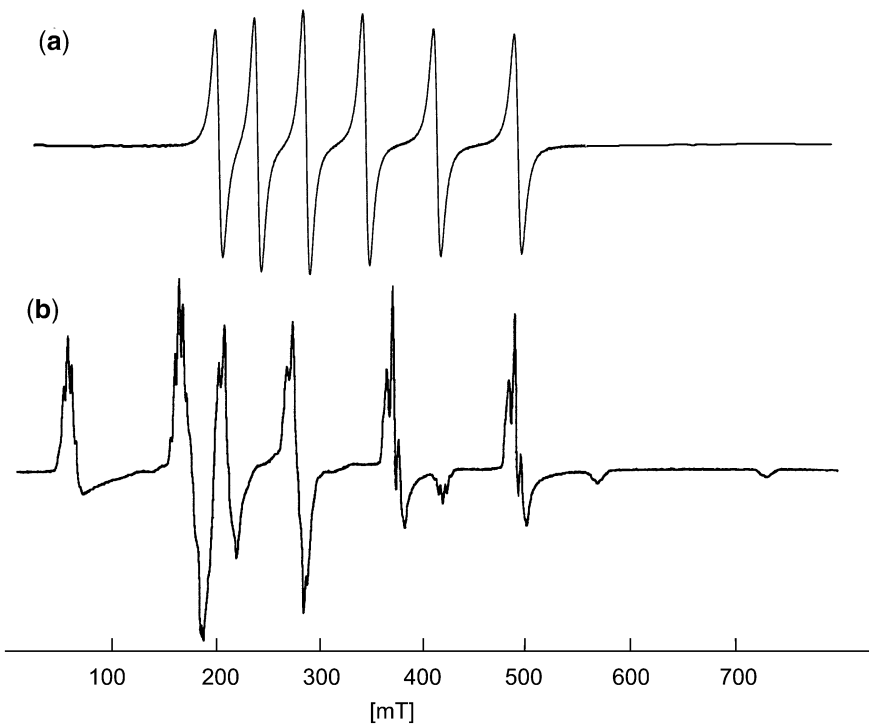


Figure 2 EPR spectra of rhenium(VI) complexes: a) liquid solution spectum of $[NBu_4][ReNCl_4]$ showing exclusively the six hyperfine lines due to the nuclear spin of 5/2 of the ^{185,187}Re nuclei and b) well resolved ^{18}F superhyperfine couplings in the axially symmetric frozen solution spectrum $[ReNF_4]^-$ showing two pairs of ^{185,187}Re sextets in parallel and perpendicular part.

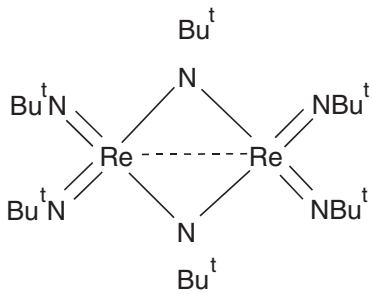
Whereas simple adduct formation is observed with the borane and the $[Re\{NB(C_6F_5)_3\}Cl_4(H_2O)]^-$ anion (**54**) is obtained as its $[Bu_4N]^+$ salt in good yields,[230] the trimeric compound $[(H_2O)Br_4ReNReBr_4ReBr_4N(H_2O)]^{2-}$ (**55**) is the product of the reaction with boron tribromide.[231] Both compounds are paramagnetic and have been characterized by EPR spectroscopy. The spectral parameters indicate a decrease of the $^{185,187}Re$ coupling constants upon the formation of the nitrido-bridge.

An unusual synthesis of a rhenium(VI) nitrido complex has been observed with the ligand reaction of the rhenium(V) precursor $[ReNCl_2(PPh_3)_2]$ with 2,4,6-tri-isopropylbenzenethiolate, $tipt^-$, which gave the green rhenium(VI) complex $[ReN(tipt)_4]^-$, when the reaction mixture was exposed to air, whereas the pale orange rhenium(V) compound $[ReN(tipt)_4]^{2-}$ was obtained in an inert atmosphere.[232]

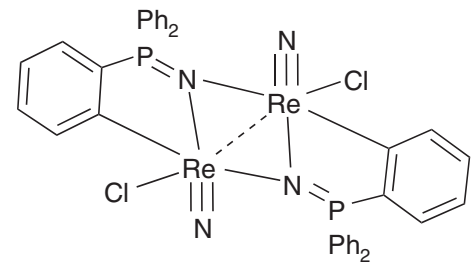
The addition of electrophilic agents to terminal nitride ligands can be applied to the synthesis of imido complexes. This has been demonstrated with triphenylcarbonium salts[86] and compounds of the formula $[Re\{NC(C_6H_5)_3\}X_4]$ (X = Cl, Br, F, NCS)[233] have been studied by EPR spectroscopy and show similar spectroscopic features to their $[Re\{NB(C_6F_5)_3\}X_4]^-$ analogues.[234]

$ReOCl_4$ reacts with PhNCO to give the rhenium(VI) compound $[Re(NPh)Cl_4]$ which forms adducts with donor solvents such as THF or acetonitrile.[235] Anionic $[Re(NPh)Cl_5]^-$ is obtained when $[Re(NPh)Cl_4]$ is treated with $[Me_4N]Cl$.[235] Two other approaches to rhenium(VI) arylimido compounds include an azo splitting reaction starting from 2-(arylazo)pyridines[236] and the oxidation of rhenium(V) imides by nitric acid.[237,238]

The dimeric homoleptic rhenium(VI) imide $[\{(Bu^tN)_2Re(\mu\text{-}NBu^t)\}_2]$ (**56**) is product of the reduction of $[Re(NBu^t)_3(TMS)]$ or $[Re(NBu^t)_3I]$ by sodium amalgam.[177,239] The compound reacts with electrophiles with protonation or the formation of multinuclear, heterometallic aggregates.[239]



(**56**)



(**57**)

An unusual dimeric complex has been synthesized by the reaction of $[ReNCl_4]$ with $TMSNPPh_3$ in acetonitrile. The rhenium atoms in $[\{Re(N)Cl(NPPh_3C_6H_4)\}_2]$ (**57**), which possesses a Re—Re bond, are μ_2-bridged via the *N*-atoms of the phosphoraneiminato ligands and the coordination spheres of the metal atoms are completed by nitrido and chloro ligands as well as by a Re—C bond to one phenyl group.[240]

5.3.2.2.3 Miscellaneous

The stabilization of high oxidation states by catecholato ligands has been described in Sections 5.3.2.1.1(iii) and 5.3.2.2.1. This is also possible in the absence of oxo ligands. Tris-complexes with 3,5-di-*t*-butyl-1,2-catecholate and tetrachloro-1,2-catecholate have been described.[241,242] The coordination sphere of the metal in these compounds are distorted octahedra which is also reflected in the well-resolved axial EPR spectra. This structure contrasts with that of the crystallographically characterized trigonal-prismatic rhenium(VI) complexes with dithiolene-type ligands and $[Re(NHNC(S)Ph)_3]$.[243] The latter compound is obtained when a mixture of perrhenate and HCl is mixed with thiobenzoylhydrazine or $[ReOCl_3(PPh_3)_2]$ reacts with the ligand in air. A trigonal prismatic geometry was also suggested for a *tris*-*o*-phenylenediamine complex[244] and a product which is obtained from the oxidation of $[Re(C_3S_5)_3]^-$ ($C_3S_5^{2-}$ = 4,5-dithio-1,3-dithiole-2-dithionate dianion) with iodine.[245] The oxidation state of the metal is ambiguous in all such complexes and in the absence of specific magnetic or PES (Photo Electron Spectroscopy) measurements assignment is entirely formal.

The redox behavior of $[W_9ReO_{32}]^{n-}$ ($n = 3$–5) (**48**) or $[\alpha_2\text{-}ReOP_2W_{17}O_{61}]^{n-}$ ($n = 5$–7) heteropolyanions[208,209] has been mentioned in Section 5.3.2.1.3. ESR studies at $[W_9ReO_{32}]^{4-}$ suggest that the Re^{VI} ion occupies one of the eight identical equatorial positions in the anion.[208]

Homo- and heterometallic rhenium oxomethoxide clusters with a $[M_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4]$ (M = Re, Nb, Ta) planar core have been obtained by anodic oxidation of Re metal in methanol. $[Re_4O_6(OMe)_{12}]$ has been studied crystallographically. The molecule is built up of a planar rectangular tetranuclear $[Re_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4O_4(OMe)_8]$ unit.[246] The heterometallic members of the family $[Re_{4-x}M_xO_{6-y}(OMe)_{12+y}]$ (M = Mo, W) have been obtained by interaction of Re_2O_7 with $MO(OMe)_4$ or $M(OMe)_6$ in toluene at reflux.

5.3.2.3 Oxidation State V

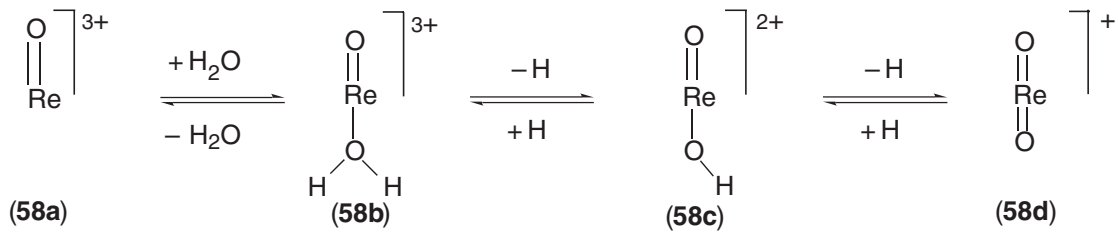
By far, the largest number of structurally characterized rhenium complexes contain the metal in the oxidation state "+5". This can be attributed to the high stability of the rhenium(V) oxo, nitrido, and imido cores with a great variety of ligand systems, but is doubtlessly also related to the fact that rhenium complexes are frequently used as nonradioactive model compounds for the development of technetium radiopharmaceuticals. The dominance of "O^{2-}", "N^{3-}", and "NR^{2-}" ligands can be rationalized by the fact that they are excellent π-donors and, therefore, stabilize high oxidation states. The strong *trans*-influence of these ligands often leads to five-coordinate complexes of square-pyramidal geometry or six-coordinate compounds having a strong tetragonal distortion. A quantum chemical analysis of the electronic structure of rhenium oxo and nitrido complexes shows that the ReO and ReN multiple bonds are strongly covalent.[247] The σ and π contributions to the ReO bonds are strongly polarized towards oxygen. The ReN bonds are much less polarized and should be regarded as triple bonds. The bonding to the equatorial ligands has mainly M(d) character. These bonding properties lead to spin pairing in the b_2 orbital and rhenium(V) oxo, nitrido, and imido complexes are diamagnetic or show an only slightly temperature dependent paramagnetism.

5.3.2.3.1 Oxo complexes

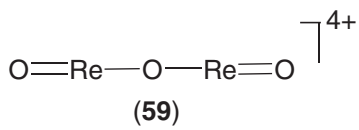
General approaches to oxo complexes of rhenium(V) are given via ligand exchange procedures starting from the readily available precursors $[ReOCl_3(PPh_3)_2]$ or $[Bu_4N][ReOCl_4]$ or by simultaneous reduction and substitution starting directly from $[ReO_4]^-$.

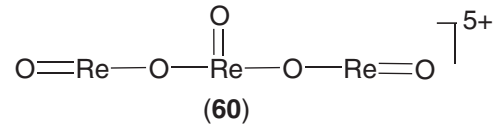
Oxo ligands can be found in various cores which are related to each other by the addition (and subsequent deprotonation) of water ligands in the empty sixth position of square-pyramidal monoxo rhenium(V) complexes. Subsequently the $[ReO]^{3+}$, $[ReO(OH_2)]^{3+}$, $[ReO(OH)]^{2+}$, and $[ReO_2]^+$ cores (**58**) can be formed (Scheme 3). *cis*-Dioxorhenium(V) complexes are much more rare than the corresponding *trans* complexes. An EHMO explanation of this fact has been suggested indicating that bidentate ligands with small bite angles and good σ-donor and π-acceptor properties should allow the formation of the *cis* isomer.[248] Condensation of the monomeric units may yield dimeric or trimeric oxo-bridged cores with the linear $[O{=}Re{-}O{-}Re{=}O]^{4+}$ (**59**) or $[O{=}Re{-}O{-}Re(O){-}O{-}Re{=}O]^{5+}$ (**60**) cores. Rhenium oxo cores therefore possess a marked flexibility and form stable complexes with ligands with various steric and electronic demands. Depending on the net charge of the ligands applied different central units will be formed for optimal charge compensation. Thus, neutral ligands will generally prefer $[ReO_2]^+$ centers whereas ligands which carry two or more negative charges will preferably be coordinated to the $[ReO]^{3+}$ core. Of course there are exceptions to this rule and the prevailing bonding situation is controlled by the individual σ- and π-bonding properties of the ligands and their interactions with the metal. Common starting materials for the synthesis of rhenium(V) oxo complexes are the readily available complexes $[ReOCl_3(PPh_3)_2]$, $[Bu_4N][ReOCl_4]$, or $[ReO_2(py)_4]Cl$. The nature of the resulting rhenium oxo core (**58**)–(**60**), however, is mainly determined by the incoming ligand, not by the structure of the oxorhenium precursor.

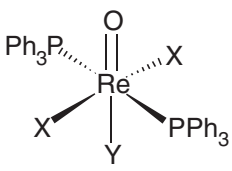
A remarkable aspect of the rhenium oxo complex chemistry is the ability of terminal oxo functions to act as nucleophiles. This has been used to incorporate dioxo complexes such as $[ReO_2(py)_4]^+$ or $[ReO_2(CN)_4]^{3-}$ between the negatively charged interlayers of silicates like hectorite (pyridine complex) or between the positive layers of a hydrotalcite-like Mg/Al double hydroxide.[249] The same concept has been applied for the isolation of molecular units containing Re–O–M bridges where M is a Lewis acid.[250,251]

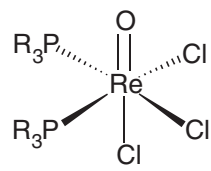


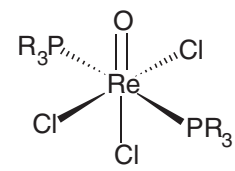
Scheme 3











In the following systematic overview the ligands are distinguished by their denticity and the nature of their donor atoms. The ligands discussed first will later be treated as co-ligands in mixed-ligand complexes. A similar approach is adopted for mixed-ligand complexes containing at least one chelating ligand where monodentate ligands will be regarded as co-ligands.

(i) Complexes containing exclusively monodentate ligands

(a) Halide and pseudohalide ligands. Oxoanions with halide ligands are versatile precursors for the preparation of numerous other rhenium(V) compounds. Several syntheses of $[ReOX_4]^-$, $[ReOX_5]^{2-}$, or $[ReOX_4(solvent)]^-$ anions (X = Cl, Br) are known,[21] but most of them suffer from the contamination of the products by paramagnetic species such as $[ReOX_5]^-$ or $[ReX_6]^{2-}$. Improved synthetic procedures for the preparation of pure $[Bu_4N]$ $[ReOCl_4]$ and $[Bu_4N]$ $[ReOBr_4(H_2O)]$ in high yield have been reported by the reduction of perrhenate with HCl gas in methanol,[252] or by the reaction of $[ReO_4]^-$ with Bu_3PBr_2 on air.[253] That the occupation of the coordination position *trans* to the oxo ligand with a fifth halide or a solvent molecule depends on the conditions of crystallization and the cation used as has been demonstrated crystallographically for a number of new examples.[254–257] A comparative study summarizes the vibrational spectra of pentahalooxorhenates and their technetium analogues.[258]

Extensive mechanistic studies on the ligand exchange behavior of tetracyanodioxorhenate with other monodentate nucleophiles[259,260] have been performed by means of ^{13}C-, ^{15}N-, and ^{17}O-NMR spectroscopy and are summarized in Figure 3. The results have been compared with the behavior of similar molybdenum(IV), tungsten(IV), and technetium(V) complexes. The cyanide exchange at the rhenium(V) center contrasts to the behavior of the other metals and shows a pH dependence which cannot be attributed to the protonation of either an oxo ligand or to the pK_a value of HCN and possibly results from protonation of a bound cyano ligand in $[ReO_2(CN)_4]^{3-}$ or an outer-sphere interaction.[261] The oxygen exchange is unique for all these metal centers and follows an acid-catalyzed pathway[262] whereas the proton exchange is manifested by the inversion induced on the coordination polyhedron via protolysis.[263] The cyanide exchange processes are the slowest. The kinetic studies are accompanied by the X-ray crystallographic characterization of several intermediates and related compounds.[264–267] Ligand exchange reactions on $[ReOX_4]^-$ (X = Cl, Br) with NH_4SCN in DMSO gave several mixed-ligand complexes with coordinated

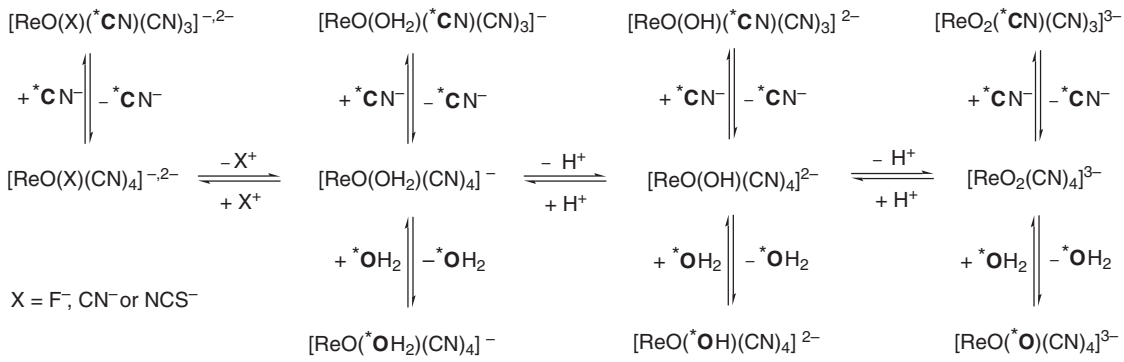


Figure 3 Ligand exchange and protonation/deprotonation reactions at $[ReO_2(CN)_4]^{3-}$.

dimethylsulfoxide molecules[268] whereas $[ReO(SCN)_5]^{2-}$ was formed during electrochemical reduction of $[ReO_4]^-$ in H_2SO_4 in the presence of SCN^-.[269]

(b) Phosphorus and arsenic donor ligands. Although known for decades, rhenium(V) oxo complexes with tertiary phosphines still arouse considerable interest. This is due to their outstanding importance as starting materials for the synthesis of rhenium(V) oxo compounds with chelating ligands. Special attention has been paid to compounds of the type $[ReOX_2(Y)(PPh_3)_2]$ (X = Cl, Br, I; Y = X, OR, F) (**61**). The existence of two polymorphs of the key compound of this class, *trans*-$[ReOCl_3(PPh_3)_2]$, has been established crystallographically and explains the fact that the color and solubility of this frequently used precursor is dependent on the mode of preparation.[270] The chloro ligand in *trans* position to the oxo oxygen is very labile and can easily be exchanged with incoming ligands which are preferentially directed to this position as has been demonstrated for the mixed-halide complex *trans*-$[ReOCl_2F(PPh_3)_2]$.[271] Substitution of meridional PPh_3 ligands by the released Cl^- has only been observed in the case of bulky incoming ligands such as $OPPh_3$, where *mer*,*cis*-$[ReOCl_3(PPh_3)(OPPh_3)]$ is formed.[272] Simple heating of *trans*-$[ReOCl_3(PPh_3)_2]$ in alcohols yields *trans*-$[ReOCl_2(OR)(PPh_3)_2]$ complexes in almost quantitative yields.[273–275] *trans*-$[ReOBr_2(OEt)(PPh_3)_2]$[276] and *trans*-[ReO-$(NCS)_2(OEt)(PPh_3)_2$][277] have been prepared in a similar way and their molecular structures have been determined. A considerable degree of multiple bond character has been found for the Re-alkoxo bonds for all $[ReOX_2(OR)(PPh_3)_2]$ derivatives.

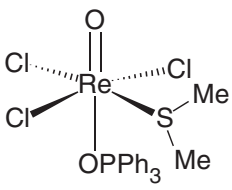
The reaction of $KReO_4$ with HI and PPh_3 in ethanol yields $[ReOI_2(EtO)(PPh_3)_2]$ which reacts with water to give $[ReO_2I(PPh_3)_2]$.[278] The iodo derivatives $[ReOI_2Cl(PPh_3)_2]$[279] and $[ReO_2I(PMe_2Ph)_3]$[280] have been prepared from $[ReOCl_3(PPh_3)_2]$ and KI and from $[ReO_2I(PPh_3)_2]$ and PMe_2Ph, respectively. The reaction of $[ReO_2I(PPh_3)_2]$ with PhNCO in toluene, which finally yields arylimido complexes (see Section 5.3.2.3.4(i)), forms a trimeric intermediate in which the PhNCO moiety is added to one of the oxo ligands to form an *N*-phenylcarbamato group. This group acts as a bridging ligand chelating one rhenium atom via its N and one O atom and coordinating another Re atom by its second O atom.[90]

Reactions of $[ReOCl_3(PPh_3)_2]$ with the less bulky phosphines PMe_2Ph, PEt_2Ph or PMe_3 give mixtures of *fac–cis* (**62a**) and *mer–trans* (**62b**) isomers as has been discussed for $[ReOCl_3(PEt_2Ph)_2]$[281] and $[ReOCl_3(PMe_3)_3]$.[282]

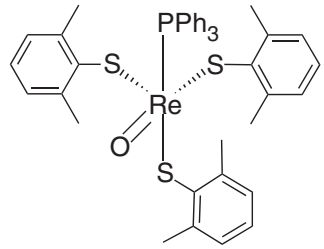
The formation of phosphinite and phosphine oxide has been observed during the reduction of perrhenate with PBu^t_2Cl in ethanol and finally the mixed phosphinite/phosphine oxide complex $[ReOCl_2(OEt)\{PBu^t_2(OEt)(OPBu^t_2H)]$ was isolated.[283] Mononuclear and dinuclear complexes with phosphite ligands derived from the spirophosphorane $\{(OCMe_2CMe_2O)POCMe_2CMe_2O\}^-$ are known and have been studied spectroscopically and by X-ray crystallography.[284,285] The formation of the phosphonato complex $[ReOCl(OMe)\{P(O)(OMe)_2\}(PPh_3)_2]$ has been reported from a reaction with $[ReOCl_3(PPh_3)_2]$ with P(OMe)(O)H in methanol in the presence of a base. In absence of a base only $[ReOCl_2(OMe)(PPh_3)_2]$ could be isolated. Hence, the phosphonato ligand was probably derived by deprotonation of the pentavalent tautomeric form of the dialkyl phosphate, $P(OMe)_2(O)H$, which predominates over the trivalent form $P(OMe)_2(OH)$.[286]

$[ReOCl_3(AsPh_3)_2]$, which is obtained almost quantitatively from reaction between perrhenate, $AsPh_3$ and HCl in glacial acid, serves as versatile starting material for the synthesis of $[ReOCl_3L_2]$ complexes (L = $P(C_6H_4–CF_3\text{-}4)_3$, $P(C_6H_4–OMe_3\text{-}4)_3$, PPh_2OMe, PPh_2OEt, PPh_2Pr^i, $PPh(OEt)_2$, $PPh(OPr^i)_2$), and a number of hydrido compounds.[287,288]

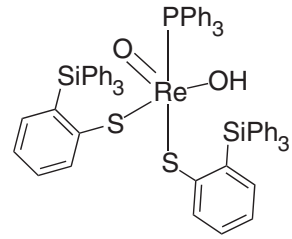
(c) Sulfur and oxygen donor ligands. $[ReOCl_3(PPh_3)_2]$ reacts with DMSO to form $OPPh_3$ and $[ReOCl_3(OPPh_3)(SMe_2)]$.[289] The two rhenium complexes act as catalysts for the oxygen transfer from DMSO to $OPPh_3$. The rhenium oxo group does not appear to be involved in the mechanism of the reaction based on an ^{18}O NMR study. $[ReOCl_3(OPPh_3)(SMe_2)]$ (**63**) is an excellent starting material for the synthesis of other rhenium(V) oxo complexes. A number of isocyanide derivatives have been prepared by ligand exchange procedures which mainly replace the $OPPh_3$ and Me_2S ligands.[289] The rhenium-catalyzed reduction of sulfoxides has been studied for various derivatives including sterically hindered and such with organic functional groups. Aryl sulfoxides are reduced faster than aliphatic analogues.[290]



(**63**)



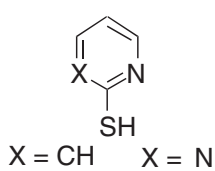
(**64**)



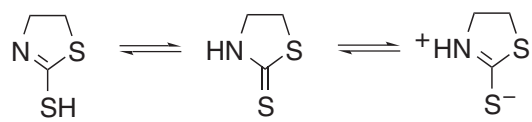
(**65**)

Sterically hindered thiolates such as $(SC_6H_4$–TMS-2$)^-$, $(SC_6H_4$–$SiPh_3$-2$)^-$, $\{SC_6H_3$–$(TMS)_2$-2,6$\}^-$, or $(SC_6H_2$–Me_3-2,4,6$)^-$ form stable $[ReOL_4]^-$ anions which can be isolated with bulky cations.[291–293] Complexes of this type have been prepared by ligand exchange starting from $[ReOCl_3(PPh_3)_2]$ or $[ReCl_6]^{2-}$. Whereas the latter reaction is accompanied by air oxidation, some intermediate complexes have been isolated and structurally characterized from reactions of the triphenylphosphine starting complex. Due to the steric demand of the contributing ligands these compounds are five-coordinate with a trigonal bipyramidal structure. The trigonal axis is formed by a PPh_3 and a thiolate ligand as is demonstrated for two examples in (**64**)[294] and (**65**).[295] A complex of structure (**64**) has also been isolated with fluorinated benzenethiols.[296]

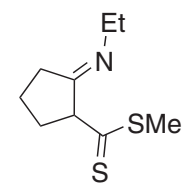
N-Heterocyclic thiols such as pyridine-2-thiol (**66a**), pyrimidine-2-thiol (**66b**), or thiazoline-2-thiol (**67**) can act as monodentate *S*-donor ligands or as *S*,*N*-chelating ligands (Scheme 4). The mode of coordination is controlled by the properties of the metal core and the reaction conditions. The compounds can act as neutral *S*-bonded ligands in their tautomeric thione form, as monodentate or chelating thiolates or as zwitterionic thiolates as is illustrated for thiazoline thiolate (**67a**–**c**). Additionally to the *N*,*S*-chelated complexes which will be discussed in Section 5.3.2.3(i)(f) a number of rhenium(V) oxo complexes of the composition $[ReOCl_3(L)(OPPh_3)]$ (L = (**66b**) and (**67**)) with monodentately *S*-bonded ligands have been isolated.[297,298] Similar behavior has been described for benzimidazole thione and benzoxazole thione[299] and unexpectedly for 2-(*N*-ethylamino)-1-cyclopentenedithiocarboxylate (**68**) which coordinated via the sulfur atom of the thiocarbonyl function.[300]



(**66a**) (**66b**)



(**67a**) (**67b**) (**67c**)



(**68**)

Scheme 4

Early reports on the formation of thiourea rhenium(V) oxo complexes by simple reduction of $[ReO_4]^-$ with HCl in the presence of thiourea (tu)[301] could not be verified. A detailed study of this reaction clearly indicates that this reaction (as with other thiourea derivatives) yields the rhenium(III) complex $[Re(tu)_6]^{3+}$ in excellent yields.[302] Details will be discussed in Section 5.3.2.5.2(ii). However, a stable rhenium(V) oxo complex could be isolated with the bulky tetramethylthiourea (Me_4tu).[303] The red compound represents one of the rare examples of a triply positive charged rhenium(V) monoxo complex. Quantum chemical studies (semiempirical MNDO–PM3 level and

DFT) suggest steric hindrance as the reason for the stabilization of the ReO^{3+} center in preference to the Re^{III} one.

Monodentate oxygen-donor ligands frequently act as co-ligands in mixed-ligand compounds such as the alkoxo ligands in the $[ReOCl_2(OR)(PPh_3)_2]$ complexes mentioned in Section 5.3.3.2.1(i)(b) or trialkylphosphane oxides.[253] Other examples are trimethylsiloxo ligands as in $[ReO(OTMS)Cl_2py_2]$[304] or 2-(dimethylaminomethyl)-4-methylphenol which acts as a zwitterionic, neutral monodentate ligand in $[ReOCl_3(L)(PPh_3)]$.[305]

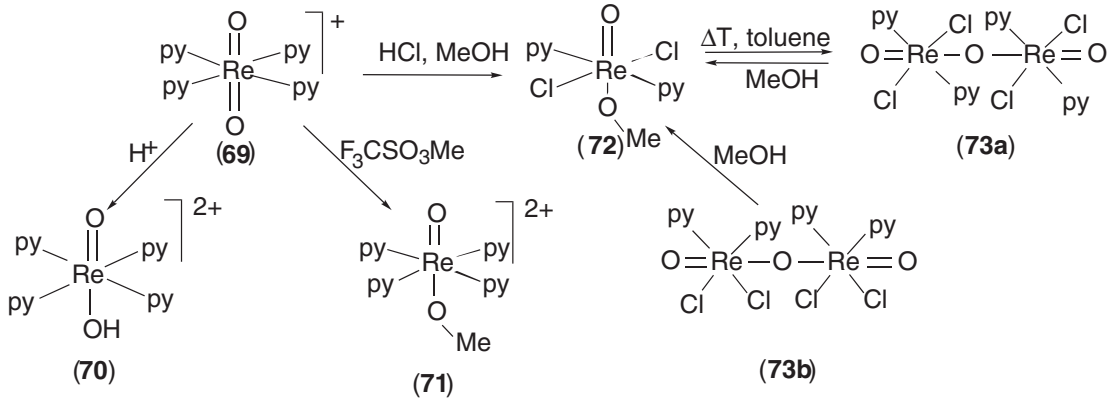
(d) Nitrogen donor ligands. The chemistry of *N*-donor ligands is dominated by complexes having the *trans*-$[ReO_2]^+$ core. This can be understood in terms of the poor π-donating properties of the neutral nitrogen donor ligands which are not able to compensate the positive charge on the $[ReO]^{3+}$ center and thus the metal center coordinates water with consecutive deprotonation as is outlined in (**58**). The *trans*-$[ReO(OH)]^{2+}$ or *trans*-$[ReO–(OR)]^{2+}$ units are subject to condensation and the formation of the linear $[O{=}Re–O–Re{=}O]^{4+}$ core. The Re=O double bond lengths are significantly longer (1.73–1.80 Å) than those in rhenium(V) monoxo compounds (1.65–1.71 Å). The bonds to the bridging oxo ligand in the binuclear compounds show partial double bond character.

The classical syntheses of *trans*-$[ReO_2(R\text{-}py)_4]^+$ complexes (R-py = substituted pyridine) start from rhenium(VII) materials or $[ReCl_6]^{2-}$ salts and give good yields when R is H or alkyl.[306,307] Improved procedures which also allow the isolation of complexes with ligands carrying electron-withdrawing substituents make use of rhenium (V) intermediates such as $[ReO_2I(PPh_3)_2]$[308] or the lability of the *cis*-$[ReO_2(R\text{-}py)_2I]$ species in preparative intermediates.[309]

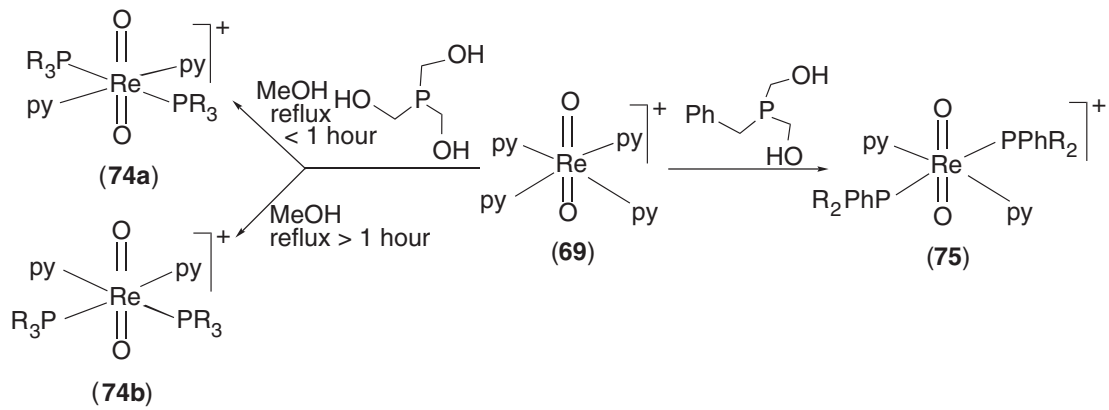
Cyclic voltammetry of *trans*-$[ReO_2(py)_4]^+$ in aqueous solutions shows that oxidation states Re^{VI} (d^1) and Re^{II} (d^5) are accessible. Reduction of the pyridine complex to Re^{II} at $0 < pH < 14$ leads to the release of H_2. Electrocatalytic water reduction can be suppressed at higher pH values by the addition of NO_2^- or SO_3^{2-} which leads to the formation of N_2O and NH_3 or H_2S and HS^-.[310–312] The Re^{VI} species $[ReO_2]^{2+}$ which can be generated photochemically or electrochemically is a powerful oxidant and is able to oxidize secondary alcohols and silanes very efficiently.[221] A kinetic study of the oxygen exchange in *trans*-$[ReO_2(py)_4]^+$ shows simple first-order kinetics and concludes that both oxygen atoms are equivalent. The half-life for isotopic oxygen-exchange is approximately 12 h at pH 5.0 (25 °C, $c_{py} = 0.1$ M) and increases with acidity.[313]

Protonation of *trans*-$[ReO_2(py)_4]^+$ (**69**) gives the monohydroxo species *trans*-$[ReO(OH)(py)_4]^{2+}$ (**70**) which has been characterized crystallographically as both ClO_4^- and PF_6^- salts (Scheme 5).[314] However, the reaction of *trans*-$[ReO_2(R\text{-}py)_4]^+$ cations with methyl trifluoromethanesulfonate leads to *trans*-$[ReO(OMe)(R\text{-}py)_4]^{2+}$ complexes (**71**) which show an almost identical electrochemical behavior to (**70**) with one remarkable exception: the formal substitution of the hydroxo hydrogen atom by a methyl group permits one of the two usual proton-transfer steps to be disconnected from the usual two-electron reductions of rhenium(V) species. As a result the normally inaccessible Re^{IV} state is stabilized relative to Re^{III} and Re^{V} and becomes electrochemically accessible at high pH.[315] Partial ligand exchange is observed when *trans*-$[ReO_2(py)_4]Cl$ is treated with methanol containing HCl. The deep-blue complex $[ReO(OMe)Cl_2(py)_2]$ (**72**) shows a *trans*,*trans* arrangement of the ligands and a bent Re–O–Me group (156°) as does the analogous ethoxo complex.[316,317] Thermolysis of this compound in boiling toluene gives the dark green oxo-bridged dimer *trans*,*trans*-$[\{ReOCl_2(py)_2\}_2O]$ (**73a**).[316] The stereochemistry of this compound is remarkable since its *cis*,*cis*-isomer (**73b**) is obtained when $[ReOCl_3(PPh_3)_2]$ is heated with excess of moist pyridine in benzene.[318] Isomerization of the *cis*-compound has also been observed during heating of *trans*,*trans*-$[\{ReOCl_2(py)_2\}_2O]$ in boiling THF.[319] Both dimeric complexes, however, form the *trans*-$[ReO(OR)Cl_2(py)_2]$ isomer when treated with boiling alcohols.[316] A similar observation has been made during the reaction of *cis*,*cis*-$[\{ReOCl_2(py)_2\}_2O]$ with $(TMS)_2SiNMe$ which gives $[ReO(OTMS)Cl_2(py)_2]$ with the pyridine ligands in *trans*-positions.[304] Obviously, the *cis*,*cis*-arrangement of two pyridine ligands appears to be thermodynamically less stable compared with the situation in (**73a**). Nevertheless, it is stable enough to undergo electrochemically induced redox processes. Four one-electron redox couples have been observed within the accessible potential range in CH_2Cl_2. The dimeric structure remains intact for the two oxidation and first reduction processes. The complex undergoes a reversible hydrolytic cleavage of the μ-oxo linkage following the second reduction step.[320]

Another situation is found for the stereochemistry of the products which are obtained from the reaction of $[ReO_2(py)_4]Cl$ with tris(hydroxymethyl)phosphine (THP) which yields both the *cis*- and *trans*-isomers of $[ReO(py)_2(THP)_2]$ (**74**) with a clear preference for the *cis*-compound (**74b**) at longer reaction times, whereas the *trans*-compound (**75**) could be isolated exclusively with the more bulky bis(hydroxymethyl)phenylphosphine ligand (Scheme 6).[321]



Scheme 5

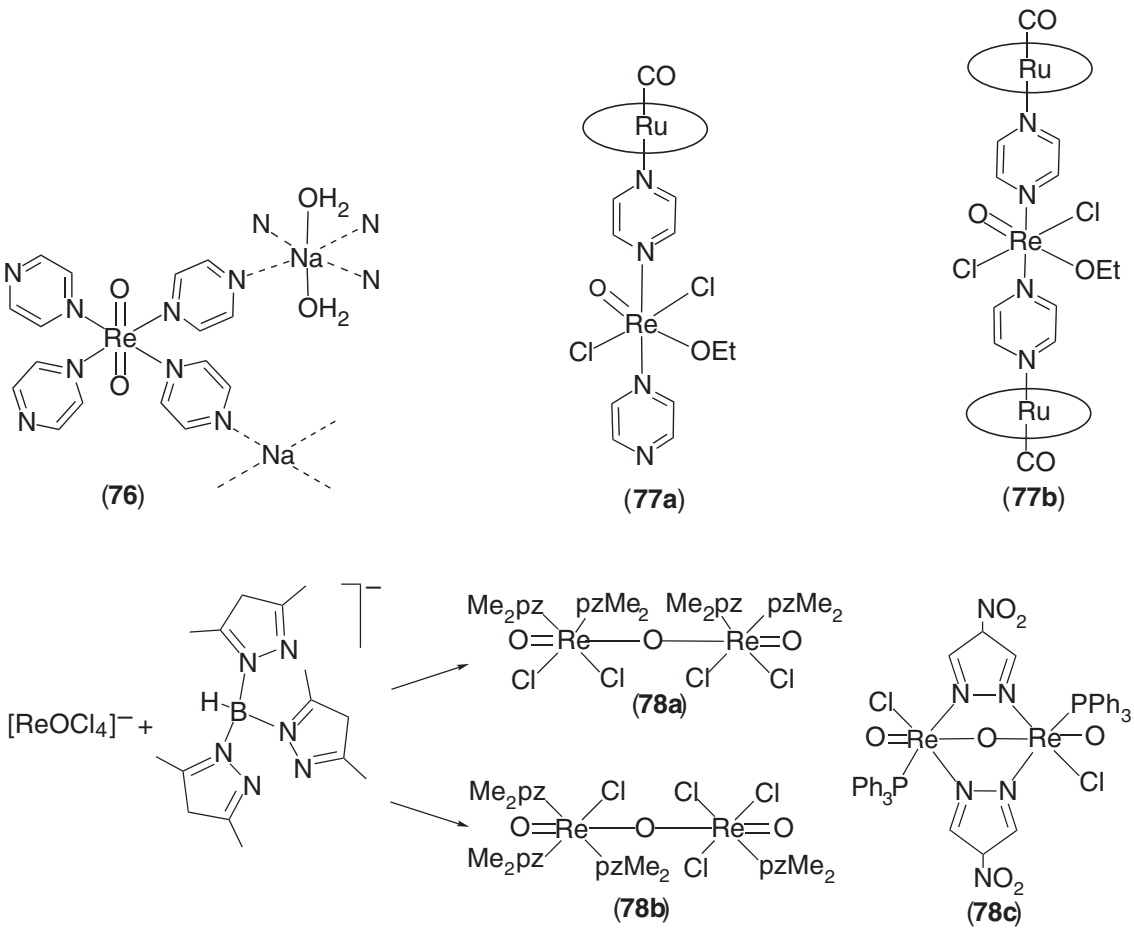


Scheme 6

A similar chemistry to that described for (substituted) pyridine rhenium(V) oxo complexes is also observed for other heterocyclic nitrogen donor ligands such as pyrimidine, pyrazine, substituted imidazoles, benzimidazoles, or benzotriazole.[322–325]

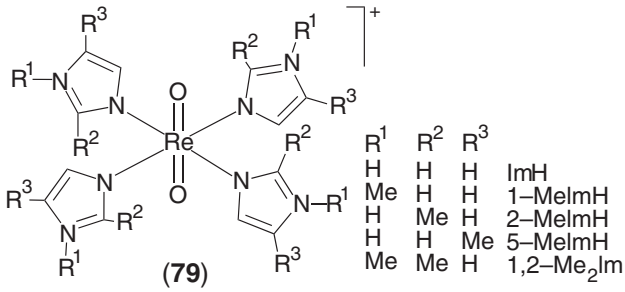
The disposition of the two nitrogen atoms in pyrazine (pyrz) and pyrimidine (pym) suggests that complexes of these ligands could be used as building blocks for the construction of polynuclear architectures. A range of pyrazine complexes has been prepared by ligand exchange procedures starting from $[ReOCl_3(SMe_2)(OPPh_3)]$.[326] Whereas reactions with a slight excess pyrazine in acetone at ambient temperature gives *cis*,*cis*-$[\{ReOCl_2(pyrz)_2\}O]$, the formation of *trans*-$[ReO(OEt)Cl_2(pyrz)_2]$ is observed when the same reaction is performed in boiling ethanol. A large excess of amine gives the dioxo compound $[ReO_2(pyrz)_4]^+$. The noncoordinated nitrogen atoms of the ligands are capable to further interactions with metals. This has been shown in the solid-state structure of *trans*-$[ReO_2(pyrz)_4](PF_6)$ which is co-crystallized with $NaPF_6$ and where the sodium atom interacts with the noncoordinating nitrogen of the pyrazine ligands at distances of about 2.5 Å (**76**). The difunctional pyrazine bases form slightly distorted square cavities of side lengths of about 7.4 Å with rhenium and sodium alternating at the corners and the pyrazine rings at the sides. The formation of di- and trinuclear compounds (**77**) have been concluded from a detailed NMR study of the reaction between *trans*-$[ReO(OEt)Cl_2(pyrz)_2]$ and [Ru(TPP)(CO)(EtOH)].[326] Symmetric (**78a**) and asymmetric (**78b**) isomers of the composition $[Re_2O_3Cl_2(L)_4]$ (L = 3,5-dimethylpyrazole, Me_2pz) have been isolated from the deboronation of the potentially tridentate ligand $\{HB(3,5\text{-}Me_2pz)_3\}^-$ by $[ReOCl_4]^-$ (Scheme 7).[327] The symmetric isomer has also been obtained from $[ReO_4]^-$, HCl, and $K\{HB(3,5\text{-}Me_2pz)_3\}$.[328] The binuclear nitropyrazole compound $[Re_2O_3(4\text{-}NO_2pz)_2(PPh_3)_2]$ (**78c**) was synthesized by heating $[ReOCl_2(OEt)(PPh_3)_2]$ and 4-nitropyrazole under reflux in ethanol.[329] The octahedral $[ReO_2N_2ClP]$ sites are linked by

two bridging nitropyrazole ligands and an oxo group with an Re–O–Re angle of 125°. The compound is electrochemically active and shows a reversible one-electron reduction at −0.55 V with respect to Ag/Ag^+.

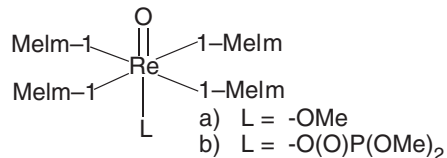


Scheme 7

With the potential use of rhenium compounds in nuclear medicine, the coordination chemistry of imidazole (Im), which is constituent of the natural amino acid histidine, and imidazole derivatives have attracted particular attention. A number of *trans*-$[ReO_2(R\text{-}Im)_4]^+$ complexes (**79**) with various methyl substituted imidazoles have been prepared in high yields from reactions with $[ReO_2I(PPh_3)_2]$. The complexes are formed more readily than the pyridine analogues even under stoichiometric conditions. The products are less sensitive to decomposition which can be attributed to the better σ-donor abilities of imidazoles (pK_a of $LH^+ \sim 7$) compared to pyridines ($pK_a = 5$–6). This makes the rhenium center more electron-rich and reduces its ability to act as π-acceptor for the oxo ligands.[322,330] Consequently, the Re=O double bond character is decreased and the oxo groups become more nucleophilic and a number of products of reactions at the oxo ligand have been isolated and characterized. In addition to simple protonation, a number of unexpected reactions have been observed.[331] Methylation of an oxo ligand is observed with excess methyl trifluoromethanesulfonate in CH_2Cl_2 under mild conditions (**80a**), whereas a phosphate ester complex (**80b**) was formed when the reaction is carried out in methanol in the presence of excess PF_6^-.[332] Finally, $[ReO(OBF_3)(1\text{-MeIm})_4]$ (**80c**) (1-MeIm = 1-methylimidazole) has been isolated by treatment of $[ReO_2(1\text{-MeIm})_4]^+$ with HBF_4 and characterized structurally.[332,333] These studies clearly indicate that the good σ-donor imidazole ligands are more resistant to ligand loss from the equatorial coordination sphere and show the synthetic potential which arises from electrophilic attack on terminal oxo ligands. The dimeric Re^V compound *trans*,*trans*-$[Re_2O_3Cl_4(1\text{-MeIm})_4]$ with a linear O=Re–O–Re=O backbone (for the structure of the pyridine analogue see (**73a**)) is formed by oxidation of the rhenium(III) complex $[ReCl_3(1\text{-MeIm})_2(PPh_3)]$ on air.[334]



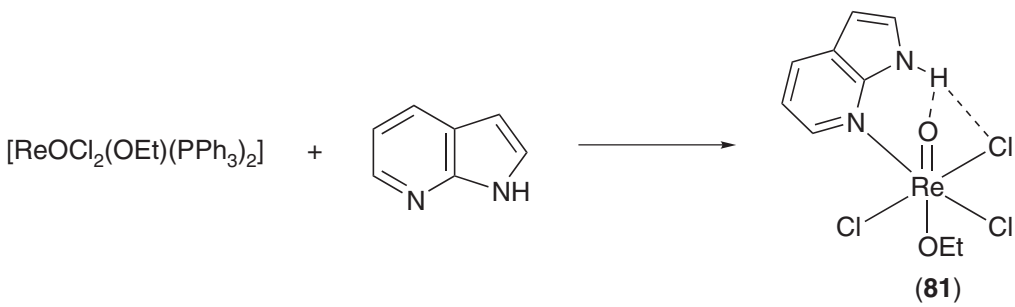
(**79**)



(**80**)

Monomeric $[ReOCl_3(L)(PPh_3)_2]$ and dimeric $[Re_2O_3Cl_4(L)_4]$ complexes with benzimidazole and 1,5,6-trimethylbenzimidazole ligands have been extensively studied structurally and by NMR spectroscopy,[324–337] whereas little information on triazole and benzotriazole derivatives is available.[338–340]

The formation rhenium(V) oxo complexes with azaindole (Haza) has been described as a result of ligand exchange reactions. Complexes of the structures *trans*-$[ReOCl_2(OEt)(Haza)(PPh_3)]$ and *trans*-$[ReOCl_2(OEt)(Haza)_2]$ have been studied crystallographically, both showing bifurcated intramolecular hydrogen bonds between the heterocyclic ligand and the oxo group and a Cl atom (**81**) (Scheme 8).[341,342]

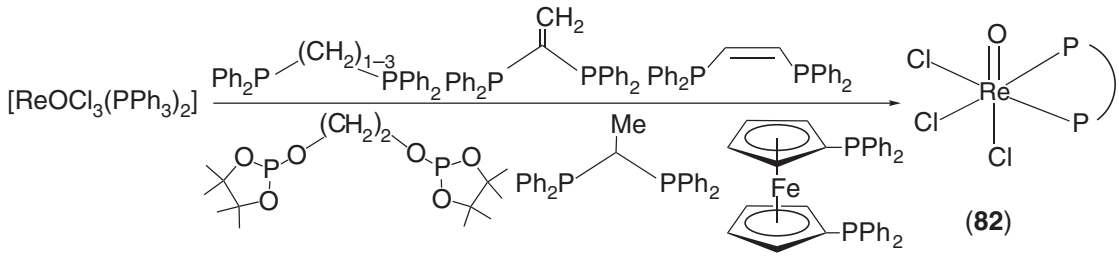


(**81**)

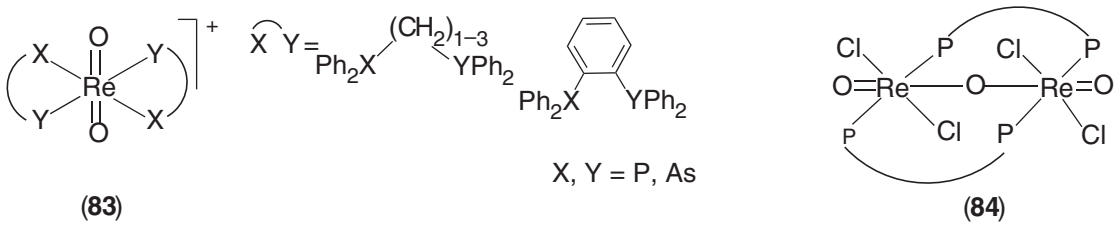
Scheme 8

(ii) Complexes with chelating ligands

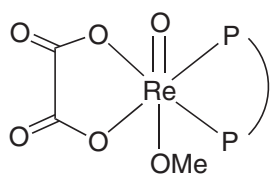
(a) Phosphorus and arsenic donor ligands. Oxorhenium(V) complexes with bis-phosphines are known with both $[Re{=}O]^{3+}$ and $[O{=}Re{=}O]^{+}$ cores. The monooxo unit is only stabilized when additional anionic ligands are present in the coordination sphere of the metal for charge compensation which cannot be achieved with neutral phosphines alone. Thus, ligand exchange reactions starting from $[ReOX_3(PPh_3)_2]$, $[ReOX_3(AsPh_3)_2]$, or $[Bu_4N][ReOX_4]$ (X = Cl, Br) with bis-phosphines (or phosphites) primarily result in neutral complexes of the type *fac*-$[ReOX_3(P^{\frown}P)]$ complexes ($P^{\frown}P$ = bidentate phosphine or phosphite) (**82**) (Scheme 9).[343–347] This is independent of the amount of phosphine added. Prolonged heating, however, leads to isomerization and reduction of the metal. This is induced by monodentate coordination of a second phosphine ligand which causes an intramolecular oxygen transfer from the rhenium to the (noncoordinated) phosphorous atom of that ligand. Intermedi-ates of the type $[Re^{III}Cl_3(P^{\frown}P)(P^{\frown}PO)]$ have been isolated and structurally characterized.[343,344] Oxidation with oxygen reforms $[ReOCl_3(P^{\frown}P)]$ and further reaction with excess phosphine yields the rhenium(III) cations *trans*-$[ReCl_2(P^{\frown}P)_2]^{+}$. The $[O{=}Re{=}O]^{+}$ core is able to stabilize bis-chelates with $P^{\frown}P$, $P^{\frown}As$ or $As^{\frown}As$ type ligands. A number of complexes of the general formula *trans*-$[ReO_2(L)_2]^{+}$ (**83**) have been described.[348–353] The main starting material for the synthesis of this group of complexes is $[ReO_2I(PPh_3)_2]$ which yields the cationic products in high yields. *trans*-$[ReO_2(L)_2]^{+}$ complexes are kinetically robust and exchange of the chelating ligands has only been observed in exceptional cases.[351] A binuclear compound containing the $[O{=}Re{-}O{-}Re{=}O]^{4+}$ core has been isolated in high yields as the final product of the oxidation of triply bonded $[Re_2X_4(\mu\text{-}P^{\frown}P)_2]$ (X = Cl, Br) complexes by air. The green, diamagnetic complex $[Re_2O_3Cl_4(\mu\text{-dppm})_2]$ (**84**) contains a linear $[Re_2O_3]$ backbone and is remarkably stable.[354]



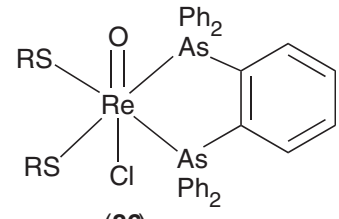
Scheme 9



Mixed-ligand bis-phosphine/oxalate complexes are accessible by an oxidative approach starting from $K_2[ReBr_6]$, oxalic acid, H_2ox, and a bis-phosphine in methanol. Dark orange products of the composition [ReO(OMe)(ox)(P∩P)] (**85**) have been isolated for P∩P = bis(diphenylphosphino)ethane (dppe) and bis(diphenylphosphino)ethene.[355] Mixtures of As∩As ligands (As∩As = bidentate arsine), thiolates and $[ReOCl_3(PPh_3)_2]$ or $[Bu_4N][ReOCl_4]$ yield rhenium(V) oxo complexes of composition $[ReOCl(SR)_2(As∩As)]$ (**86**) with two thiolato ligands in the equatorial coordination sphere of the metal.[350] Cationic oxo-fluoro complexes with the meridionally coordinated bis(dicyclohexylphosphinoethyl)diphenylphosphine (Cyttp) are formed by the reaction of the hydrido complex [ReOFH(Cyttp)] with $NaSbF_6$ and subsequent treatment with LiCl.[356]



(**85**)

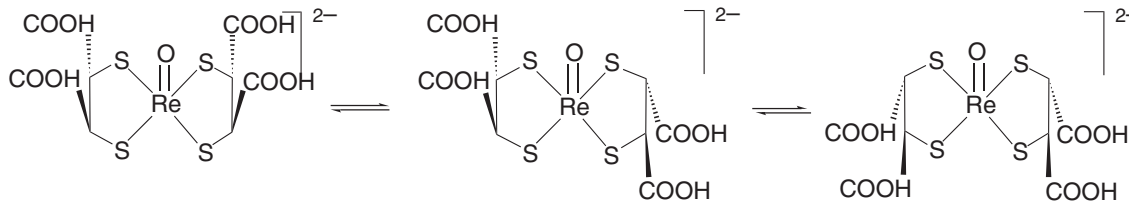


(**86**)

(b) Sulfur and oxygen donor ligands. The chemistry of rhenium(V) oxo complexes with chelating sulfur ligands was developed in the 1970s and 1980s and several examples with dithiolates and dithiolene-type ligands have been reviewed earlier.[21] Continuing this work, the structures and chemical behavior of $[ReO(S∩S)_2]^-$ complexes (S∩S = 1,2-ethanedithiolate,[357,358] 1,2-benzenedithiolate,[358,359] 2,3-dimercaptosuccinate,[360] 4,5-mercapto-1,3-dithiole-2-thionate,[361] tetrathiotungstenate,[362] 1,1′-mercaptoferrocene,[363] and S_4^{2-}[364]) have been studied. The compounds are five-coordinate with a square-pyramidal geometry.

An pH-dependent coordination isomerism has been observed for the tumor targeting rhenium(V) oxo complex $[ReO(DMSA)_2]^{2-}$ ($DMSA^{2-}$ = 2,3-mercaptosuccinate).[360] In solution the crystallographically characterized *syn*,*endo*-isomer (**87a**) slowly isomerizes into the anti- (**87b**) and the *syn*,*exo*-isomers (**87c**) which has consequences for the biodistribution of the potential pharmaceutical (Scheme 10). The conversion rate decreases with increasing pH suggesting an acid catalyzed reaction. The *syn*,*exo*-complex is favored in alkaline solutions (pH > 8.4) which can be understood in terms of the repulsions between the deprotonated carboxylic groups and the oxo ligand.

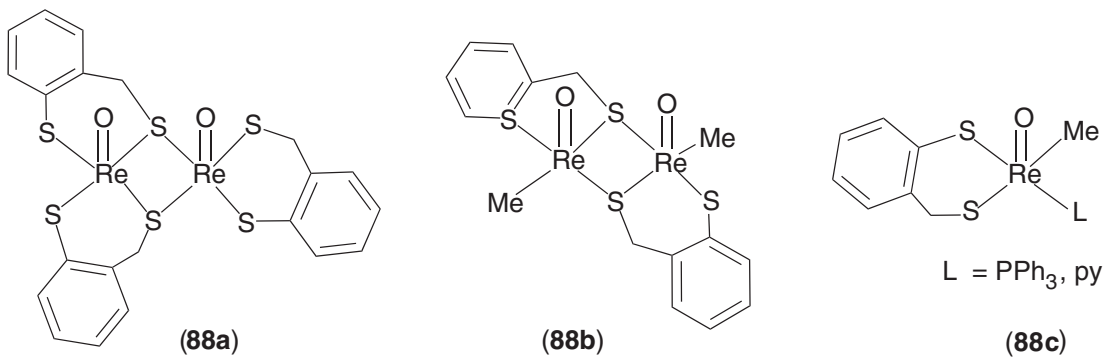
Interesting coordination behavior has been reported for the 2-thiomethylthiophenolate ligand which forms a number of binuclear oxorhenium(V), and methyloxorhenium(V) complexes (**88**).[365–367] The formation of (**88c**) is achieved by a monomerization of (**88b**) by interaction



(**87a**) (**87b**) (**87c**)

Scheme 10

with monodentate ligands such as pyridine or PPh_3. Compounds of the type (**88c**) react with the incoming phosphines in two stages, via a reaction scheme in which the stereoisomer of the final product can be detected as intermediate. Rearrangement then occurs, and turnstile and pentagonal mechanisms have been proposed for the stages.[368] Complex (**88a**) was found to be an efficient catalyst for oxygen transfer reactions. Strong Lewis bases such as phosphines coordinate to one of the rhenium atoms with cleavage of a Re—S bond, whereas no coordination was observed for alkylarylsulfides, diarylsulfides, triphenylarsine, or triphenylstibine. The complex catalysis mechanism involves the oxidation of phosphines, arsines, stibines, sulfides, and dienes by pyridine-*N*-oxide and the oxidation of phosphines by dimethylsulfoxide.[369]

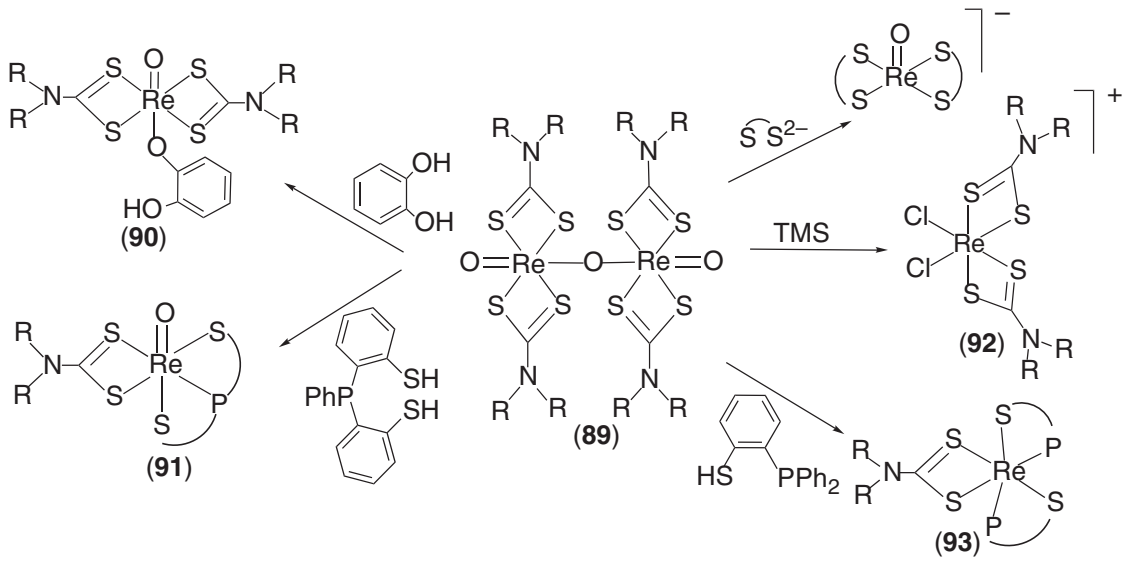


(**88a**) (**88b**) (**88c**)

Dimeric dialkyldithiocarbamato (dtc) complexes $[Re_2O_3(R_2dtc)_4]$ (**89**) (R = Me, Et, Pr^n, Bu^n, Ph) have been studied electrochemically showing that the redox potentials $E^{o\prime}$ of $[Re_2O_3(R_2dtc)_4]^0/[Re_2O_3(R_2dtc)_4]^-$ couples and the stability of the reaction product are dependent on the residue R. The E^o values are appreciably solvent-dependent which has been discussed in terms of solubility parameters. Ligand exchange reactions starting from (**89**) give access to a complex with monodentate-coordinated catechol (**90**) (Scheme 11). Reaction with dithiolates $S^{\cap}S^{2-}$ ($S^{\cap}S$ = 1,2-ethanedithiolate, 1,2-benzenedithiolate, 3,4-toluenedithiolate) lead to degradation of the dithiocarbamate and the formation of $[ReO(S^{\cap}S)_2]^-$ anions, whereas the mixed-chelate complex $[ReO(Et_2dtc)\{PhP(C_6H_4S)_2\}]$ (**91**) was obtained with the tridentate phosphinothiolate $PhP(C_6H_4SH)_2$ and a remarkable, oxygen-free rhenium complex of the composition $[ReCl_2(Et_2dtc)_2]^+$ (**92**) was formed upon treatment with TMSCl. Reduction of the metal center and the formation of the rhenium(III) compound $[Re(Et_2dtc)(Ph_2P(C_6H_4S)_2]$ (**93**) has been observed with the bidentate proligand $Ph_2P(C_6H_4SH)$.[370]

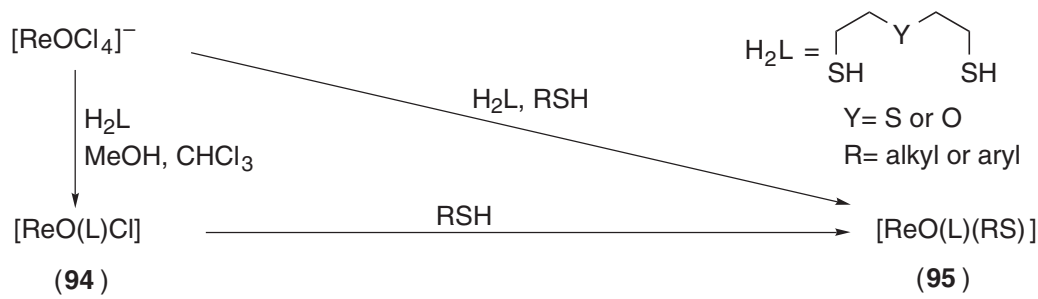
Rhenium(V) oxo complexes with bidentate thioether ligands of the composition $[ReOX_3(RSC_2H_4SR)]$ (X = Cl, Br; R = Bu^n, Et, benzyl) are formed during reduction of perrhenate with $SnCl_2$ in the presence of the thioether in glacial acid or by ligand exchange procedures starting from $[ReOCl_4]^-$. The products convert in methanol to the dimeric species $[\{ReO(RSC_2H_4SR)Cl_2\}O]$ via a $[ReOX_2(OMe)(RSC_2H_4SR)]$ intermediate.[371,372]

A number of neutral mixed-ligand oxorhenium(V) complexes containing tridentate $[SC_2H_4YC_2H_4S]^{2-}$ (Y = S, O) (**95**) and monodentate, monoanionic thiolate ligands have been prepared from $[ReOCl_4]^-$ and a mixture of the ligands (Scheme 12).[373,374] The intermediate $[ReO(SC_2H_4SC_2H_4S)Cl]$ (**94**) is accessible as dark-blue crystals whereas the complex $[ReO(SC_2H_4OC_2H_4S)Cl]$ could not be isolated. Its formation in solution, however, is strongly indicated by spectroscopic results.[375] The simultaneous reaction of tridentate and monodentate



Scheme 11

ligands with a rhenium precursor allows approach to rhenium complexes with functionalized receptor-binding molecules as has been demonstrated for 8α-amino-6-methyl-ergoline or a testosterone derivative.[376,377] The products undergo *trans*-chelation reactions with glutathione and other blood constituents carrying thiol functions.[378]

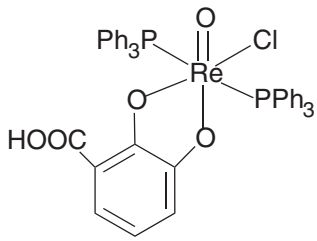


Scheme 12

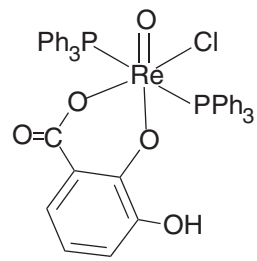
Rhenium chelates with carbon-free chelate-rings are known with derivatives of bis(diphenylphosphino)amine.[379] $[ReOCl_3(PPh_3)_2]$ and $[ReOCl_2(OEt)(PPh_3)_2]$ react with an excess of $NH(OPPh_2)_2$ to give $[ReOCl_2\{(OPPh_2)N\}(PPh_3)]$. When the donor atoms are changed by using $NH(SPPh_2)_2$ as incoming ligand the mono- and disubstituted complexes $[ReOCl_2\{(SPPh_2)N\}(PPh_3)]$ and $[ReOCl\{(SPPh_2)N\}_2]$ are obtained. The latter compound can also be prepared from $[ReOCl_4]^-$ and undergoes a further ligand exchange during recrystallization from CH_2Cl_2/EtOH to give $[ReO(OEt)\{(SPPh_2)_2N\}_2]$.[379]

Catecholato complexes of rhenium(V) are formed from reactions of $[ReOCl_3(PPh_3)_2]$ with two equivalents of the ligands and NEt_3 under anaerobic conditions, whereas similar reactions in air give the rhenium(VII) compound *cis*-$[ReO_2(cat)_2]^-$.[146] Structure determinations for $[NMe_4][ReO(O_2C_6H_4)_2]$ and $[NMe_4][ReO(O_2C_6H_4)_2(PPh_3)]$ show a square-pyramidal coordination sphere with the two catecholato ligands in basal sites for the former compound, whereas the geometry of the $[ReO(O_2C_6H_4)_2(PPh_3)]^-$ anion is a distorted octahedron with the PPh_3 ligand *cis* to the oxo oxygen.[380] Without addition of a supporting base $[ReO(L)(PPh_3)X]$ complexes (X = Cl, Br; H_2L = catechol, tetrachlorocatechol, tetrabromocatechol) are formed. Anionic compounds of the composition $[ReO(L)_2(OPPh_3)]$ (L = tetrachlorocatechol, tetrabromocatechol) result from reactions between $[ReOCl_3(PPh_3)_2]$ and tetrachlorobenzoquinone or tetrabromobenzoquinone.[381] The triphenylphosphine oxide ligand was found to be very labile and ligand exchange with methanol or pyridine was observed.

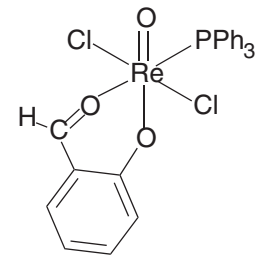
Two different coordination modes of dihydroxybenzoic acid have been observed in products from the reaction with $[ReOCl_3(PPh_3)_2]$.[382] The catecholato bonding mode (**96a**) is preferred rather than the salicylato mode (**96b**) in complexes of the composition $[ReOCl(L)(PPh_3)_2]$. The phenolato oxygen is bonded *trans* to the oxo ligand in the latter complex. A similar bonding situation is suggested from spectroscopic studies for a salicylaldehyde complex (**97**).[383]



(**96a**)



(**96b**)



(**97**)

An unusual approach to a rhenium(V) oxo complex has been reported by the oxidation of the metal in $[ReCl_4(PPh_3)_2]$ by decomposition products of the potentially tridentate ligand benzoylacetone benzoylhydrazone. The resulting benzoylacetonate ($benzac^-$) acts as ligand in the resulting rhenium(V) complex $[ReOCl_2(PPh_3)(benzac)]$.[384]

Anionic $[ReOBr_3(L)]^-$ and neutral $[ReOBr(L)_2]$ complexes are formed by reactions of $[NBu_4][ReOBr_4]$ with 2-methyl-3-oxy-4-pyrone or 1,2-dimethyl-3-oxy-4-pyridinone which act as monobasic ligands.[385] The monoligand complex can be regarded as an intermediate in the formation of the bis-chelate complex.

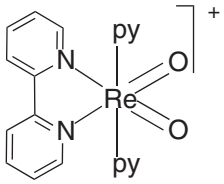
The potentially hexadentate ligand 1,3,5-trideoxy-1,3,5-tris(2-hydroxybenzyl)amino-*cis*-inositol (H_3thci) reacts with $[ReOCl_3(PPh_3)_2]$ in methanol under formation of the monomeric complex [ReO(thci)].[386] The amino and phenoxo groups of two (2-hydroxybenzyl)aminato entities are located in the equatorial positions of a distorted octahedron. The third (hydroxybenzyl)amino moiety does not interact with the rhenium atom at all. The axial positions of the Re coordination sphere are occupied by the oxo ligand and by a deprotonated hydroxy group of the cyclohexanetriol fragment.

Air-stable complexes with the Kläui-type ligand ($[cpCo\{PO(OR)_2\}_3)]^-$) (**19**) and derivatives thereof are formed by reduction of rhenium(VII) compounds with phosphines or by ligand exchange procedures starting from $[ReOX_3(PPh_3)_2]$ (X = Cl, Br) complexes. The compounds are stable as solids but undergo slow decomposition in aqueous media. This is most probably a consequence of oxidation processes in air which finally form the rhenium(VII) trioxo compound $[ReO_3L]$ which is sensitive against hydrolysis.[128]

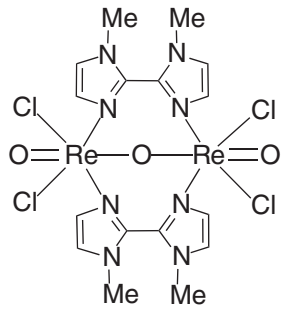
(c) Nitrogen donor ligands. Similarly to monodentate neutral nitrogen donor ligands, the $[ReO_2]^+$ core (**58d**) dominates in the coordination chemistry of rhenium(V) compounds with chelating amines. The most appropriate starting material for the synthesis of $[ReO_2(N^{\cap}N)_2]^+$ type cations ($N^{\cap}N$ = 1,2-diaminoethane (en), 1,3-diaminopropane (tn), 1,2-diaminocyclohexane (dach), *N*,*N*-diethyl-1,2-diaminoethane, and *N*,*N*,*N*′,*N*′-tetramethylaminoethane) is $[ReO_2I(PPh_3)_2]$.[308,387–391] An alternative approach to $[ReO_2(N^{\cap}N)_2]^+$ type complexes is from reactions of the rhenium(IV) precursor $[ReCl_6]^{2-}$ with $N^{\cap}N$ ligands.[392] The formation of $[ReO_2(N^{\cap}N)_2]^+$ type bis-chelates has also been observed with ligands such as diethylenetriamine or triethylenetetramine which potentially possess a higher denticity.[393] Comparative studies on the behavior of $[MO_2(N^{\cap}N)_2]^+$ complexes (M = Re, Tc) show similar behavior for the complexes of both metals in aqueous solutions and no significant difference in their *in vivo* behavior is expected.[394,395] Mixed-chelate complexes of the composition $[ReO(N^{\cap}N^{\cap}N)(N^{\cap}O)]^+$ containing diethylentriamine as tridentate and amino acids such as glycine, alanine, valine, leucine, or proline as bidentate $N^{\cap}O^-$ ligands are formed by the reaction of $[ReO_2I(PPh_3)_2]$ with each one equivalent of the ligands. The triamine ligand deprotonated singly and all *cis* positions to the oxo ligand are occupied by nitrogen atoms.[396]

The rare *cis*-dioxo configuration has been established for mixed-ligand complexes containing pyridine and bipyridine. $[ReO_2(R\text{-}py)_2(bipy)]^+$ cations (**98**) are formed by reactions of bipy with $[ReO_2(R\text{-}py)_4]^+$ and the yields can be optimized by the addition of HI which generates the labile *cis*-$[ReO_2(R\text{-}py)_2I]$ species as intermediates.[309,397] The same protocol allows the synthesis of *trans*-$[ReO_2(R\text{-}py)_2(Y\text{-}py)_2]^+$ complexes, where Y is an electron withdrawing substituent. The thermo-

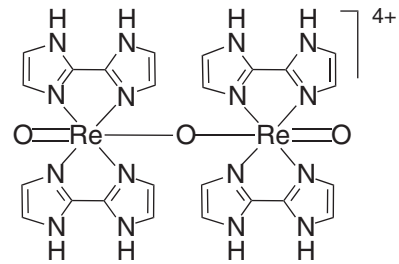
dynamically less favored *cis*-isomer of $[ReO_2(py)_2(bipy)]^+$ has Re=O distances of 1.73 Å which are slightly shorter than those found for *trans*-dioxo complexes with amine ligands. The angle between the oxo ligands is 121.4°.[398] Electrochemical studies show that substitutions on the bipy ligand exert large effects: the E^0 values for the one-electron oxidation step ($Re^{VI/V}$) increase by as much as several hundred millivolts upon replacement of electron-withdrawing by electron donating substituents.[399] Reduction is more complex: a two-electron process is followed by a one-electron step and a pH-dependence has been detected which indicates proton uptake and an oxo/hydroxo/aqua conversion. A neutral complex with two oxo ligands in a *cis*-arrangement is obtained when *trans*-$[ReO_2(py)_4]I$ reacts with 1,2-diaminobenzene (H_2dab).[400] The diamine loses one proton and NMR studies on the resulting purple *cis*-$[ReO_2(Hdap)(py)_2]$ complex show a convergence of the proton resonances of the aromatic rings as a consequence of the delocalization of π-electron density.



(**98**)



(**99**)

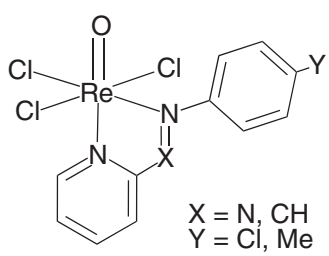


(**100**)

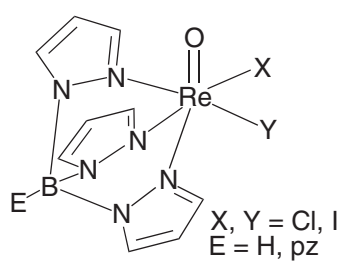
The complexes *trans*-$[ReO(OH)(N^{\frown}N)_2]^{2+}$ ($N^{\frown}N$ = bipy or 4,4′-dimethyl-bipy) and *trans*-$[ReO_2(N^{\frown}N)_2]^+$ ($N^{\frown}N$ = 1,10-phenanthroline) are synthesized by reacting Re_2O_7 with PPh_3 in the presence of the relevant ligands. Decomposition of the complexes occurs in aqueous media by slow oxidation of the coordinated bipyridine ligands to form the corresponding *N*-oxides.[401]

N,*N*′-Dimethylbiimidazole (Me_2biim) and bipyridine react with $[ReOCl_3(OPPh_3)(Me_2S)]$ to give *mer*-$[ReOCl_3(N^{\frown}N)]$ type compounds. Nonmethylated biimidazole (H_2biim) forms the *trans*-*O*,*O* $[ReOCl_2(OPh_3)(H_2biim)]^+$ cation, which is tightly associated with the Cl^- counterion via hydrogen bonds. Hydrolysis of $[ReOCl_3(Me_2biim)]$ in wet acetone leads to the bent oxo-bridged dinuclear species $[\{ReOCl_2\}_2(\mu\text{-}O)(\mu\text{-}Me_2biim)_2]$ (**99**), where each Re center retains the $[ReO_2Cl_2N_2]$ coordination but the Me_2biim ligands are bridging and the linear oxo-bridged dinuclear species $[\{ReOCl_2(Me_2biim)\}_2O]$ containing chelating Me_2biim.[402] The dimeric chelate $[Re_2O_3(H_2biim)_4]^{4+}$ (**100**) can be isolated from reaction mixtures containing $[ReOCl_3(PPh_3)_2]$ and H_2biim.[403] A mixed-ligand oxorhenium complex containing a terpy-ridine and two *S*-coordinated *p*-thiocresolato ligands is obtained as a black solid when $[ReO_2\text{-}(py)_4][CF_3SO_3]$ is mixed with a mixture of the ligands in ethanol. The central nitrogen atom of the terpyridine ligand is bonded *trans* to the oxo group.[404]

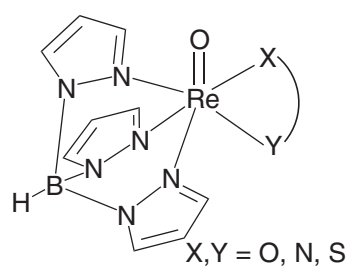
Compounds of the composition $[ReOCl_3(N^{\frown}N)]$ have also been isolated with pyridine-2-aldimine and π-acidic arylazopyridine and arylazoimidazole ligands.[405–407] The products (**101**) are readily reduced by oxygen atom transfer reactions from Re to phosphorus atoms of phosphines which results in the formation of rhenium(III) complexes. Depending on the reaction condition and the phosphines used either mononuclear or binuclear compounds are formed.[408,409] Azo splitting reactions with arylazopyridines give access to arylimido and binuclear oxo/imido complexes.[409,410]



(**101**)



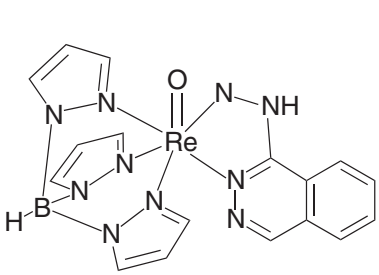
(**102**)



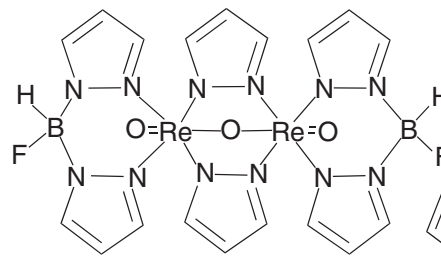
(**103**)

Rhenium(V) oxo complexes with hydrotris- or tetrakispyrazolylborato ligands, $\{HB(pz)_3\}^-$ (**17**) or $\{B(pz)_4\}^-$ (**18**), have attracted considerable interest due to their remarkable catalytical behavior and their synthetic potential owing to the easy replacement of the halide ligands in compounds of the type $[ReOCl_2(N^{\frown}N^{\frown}N)]$ ($N^{\frown}N^{\frown}N = HBpz_3^-$ or $HBpz_4^-$) (**102**).[411,412] Reactions of $[ReOCl_2\{HB(pz)_3\}]$ with monodentate thiols result in ligand exchange and products of the compositions $[ReOCl\{HB(pz)_3\}(L)]$ or $[ReO\{HB(pz)_3\}(L)_2]$ (HL = thiophenol) have been isolated depending on the amount of added thiol.[412,413] Chelating dithiols or diols give mixed-chelate complexes of the type $[ReO\{HB(pz)_3\}(X^{\frown}X)]$ ($X^{\frown}X$ = dithiolate, diolate, or diselenolate) (**103**).[123,124,412,414,415] The products undergo both electrochemical reduction and oxidation processes which are in many cases reversible. Diolato complexes of composition (**103**) form the complexes $[Re^{VII}(N^{\frown}N^{\frown}N)O_3]^+$ and alkenes at elevated temperatures in nonpolar solvents.[124,416] The opposite reaction, the addition of alkenes to trioxo complexes and the formation of diolato complexes has been observed for the homologous element technetium.[125] Oxygen transfer reactions of compounds of type (**102**) and their substitution products with alkoxides and triflate have been subject of detailed studies showing that these complexes can easily be oxidized to form aldehydes or ketones from the coordinated alkoxo ligands and trioxorhenium(VII) complexes.[417] Photolysis of $[ReOICl\{HB(pz)_3\}]$ or $[ReOI_2\{HB(pz)_3\}]$ in arenes gives the aryl complexes $[ReO(Ar)Cl\{HB(pz)_3\}]$ or $[ReO(Ar)_2\{HB(pz)_3\}$,[418] whereas the triflate derivative $[ReO(Ph)(OSO_2CF_3)\{HB(pz)_3\}]$ reacts with oxygen with oxidation of the phenyl group to give phenoxide products and the catecholate complex $[[Re\{HB(pz)_3\}(O_2C_6H_4)]$.[419] Reaction with DMSO gives the adduct $[ReO(Ph)(DMSO)\{HB(pz)_3\}][O_3SCF_3]$ which undergoes phenyl-to-oxo migration at 25 °C to give the phenoxide complex $[ReO(OPh)(DMSO)\{HB(pz)_3\}][O_3SCF_3]$ and SMe_2. The reaction proceeds via an intermediate rhenium(VII) dioxo complex which has been identified in an analogous reaction with pyridine *N*-oxide in which the formation of phenoxo and catecholato complexes has been observed at low temperatures. An unusual product, $[ReO\{HB(pz)_3\}(C_9HF_{12}NO_4)]$, where $(C_9HF_{12}NO_4)^{2-}$ is a bidentate $N^{\frown}O$ ligand which results from condensation of two molecules of hexafluoroacetone with one molecule of acetonitrile, has been obtained from the photolysis of $[ReO\{HB(pz)_3\}(oxalate)]$ in a mixture of these solvents in air.[420] The mixed-ligand starting material of this reaction and related compounds also containing other bidentate ligands such as glycolate or 9,10-phenanthrenediolate are obtained in excellent yields from $[ReOCl_2\{HB(pz)_3\}]$ and the corresponding diols.[421]

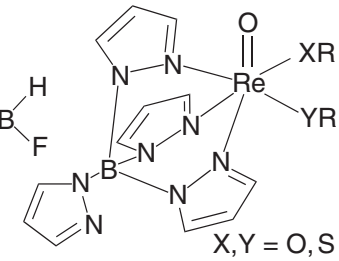
The reactions of $[ReOCl_2\{HB(pz)_3\}]$ with organic hydrazines show an interesting feature. In contrast to the common substitution pattern which occur through a condensation type reaction to displace the oxo group in forming a metal-hydrazido derivative, the reaction with hydrazinophthalazine gives $[ReO(HNNC_8H_5N_2)\{HB(pz)_3\}]$ (**104**) and a dinuclear, phthalazine-*N*,*N*′-bridged species is formed by reaction with bis(hydrazino)phthalazine.[413]



(**104**)



(**105**)

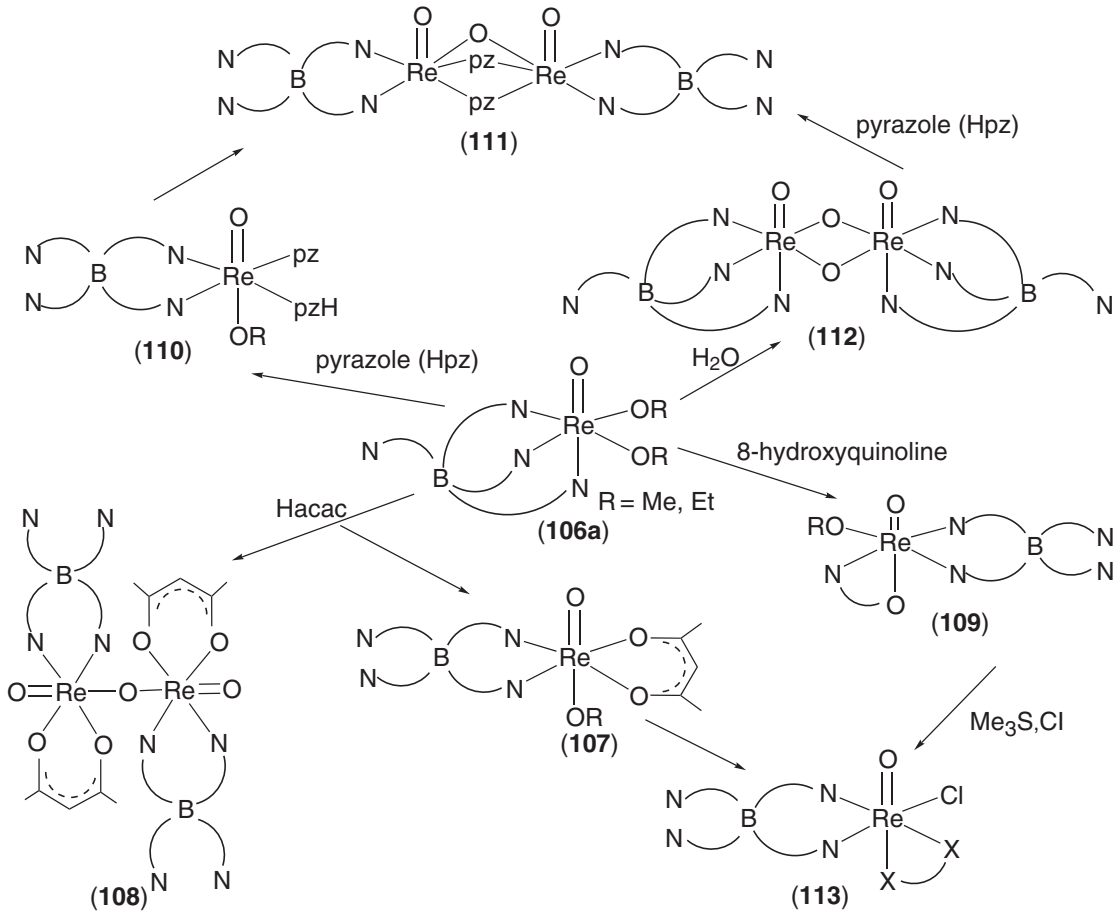


(**106**)

Attempts to prepare fluoro derivatives of (**102**) failed and resulted in the formation of the unusual μ-pyrazolyl μ-oxo dimer $[\{ReO\{HBF(pz)_2\text{-}N,N'\}\}_2(\mu\text{-}pz)_2(\mu\text{-}O)]$ (**105**).[422] An X-ray structural analysis shows that one pyrazolyl residue of each tridentate ligand has been substituted by fluoride. With the analogous complex containing hydridotris(3,5-dimethyl-1-pyrazolylborate), however, mixed Cl/F, I/F, or OSO_2CF_3/F derivatives of (**102**) are readily formed. The different reactivity of the hydridotris(pyrazolyl)borato rhenium complexes has been attributed to the greater steric protection of the boron atom afforded by the dimethyl-substituted ligand.

The analogous coordination behavior of hydridotris(pyrazolyl)borate and tetrakis(pyrazolyl)-borate has been demonstrated by numerous reactions. Reduction of the rhenium(VII) complex $[ReO_3\{B(pz)_4\}]$ with PPh_3 in THF gives a reactive dimeric intermediate which reacted with monodentate and bidentate protic substrates to yield products with tridentate $\{B(pz)_4\}^-$ ligands

of the general formulae (**102**), (**103**), or (**106**), all containing κ^3-coordinated $\{B(pz)_4\}^-$ ligands.[126,127,423,424] Key products of this reactions are alcoholato complexes ((**106**) with X = O and R = Me or Et) which can serve as versatile starting materials for further syntheses. Starting from $[ReO(OMe)_2\{B(pz)_4\}]$ and pyridine-2-thiolate ligands, a number of mixed-ligand products were isolated including a rhenium(V) complex with chelated pyridine-2-thiolate ligands.[425] During reactions of $[ReO(OR)_2\{B(pz)_4\}]$ (**106a**) (R = Me, Et) with potentially bidentate ligands several monomeric and dimeric oxorhenium compounds, in which the tetrakispyrazolylborate ligand exhibits different coordination modes, have been isolated: $[ReO(OMe)\{\kappa^2\text{-}B(pz)_4\}(acac)]$ (**107**) ($acac^-$ = acetylacetonate), $[\{ReO\{\kappa^2\text{-}B(pz)_4\}(acac)\}(\mu\text{-}O)]$ (**108**), $[ReO(OMe)\{\kappa^2\text{-}B(pz)_4\}(quinolin\text{-}8\text{-}olate)]$ (**109**), $[ReO(OMe)\{\kappa^2\text{-}B(pz)_4\}(pz)(Hpz)]$ (**110**), and $[\{ReO\{\kappa^2\text{-}B(pz)_4\}\}_2(\mu\text{-}pz)\}_2(\mu\text{-}O)]$ (**111**). The pyrazolyl-bridged dimer (**111**) is also formed when $[ReO\{\kappa^2\text{-}B(pz)_4\}(\mu\text{-}O)]_2$ (**112**) is treated with excess pyrazole. Reactions of the mixed ligand complexes with acetylacetonate (**107**) or 8-hydroxyquinolinolate (**109**) with trimethylsilylchloride provide monochlorides of type (**113**) (Scheme 13).[426]



Scheme 13

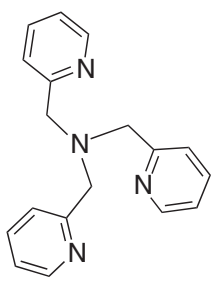
Dioxo compounds have been obtained during reactions of $[ReO_3\{\kappa^3\text{-}B(pz)_4\}]$ with strong σ-donor ligands such as pyridines, imidazoles or diphosphines.[427] The resulting neutral *trans*-dioxo complexes $[ReO_2\{\kappa^2\text{-}B(pz)_4\}(L_2)]$ (L = pyridine, 4-methylpyridine, 4-dimethylaminopyridine, 1-methylimidazole) and $[ReO_2\{\kappa^2\text{-}B(pz)_4\}(L)]$ (L = 1,2-dimethylphosphinoethane, dmpe) complexes can be obtained in good yields. Similar reactions also give access to compounds with κ^2-coordinated $\{HB(pz)_3\}^-$ ligands such as $[ReO_2\{\kappa^2\text{-}HB(pz)_3\}(py)_2]$ or $[ReO_2\{\kappa^2\text{-}HB(pz)_3\}(dmpe)]$. Cationic Re^V oxo complexes of the type $[ReO(OTMS)\{\kappa^2\text{-}HB(pz)_3\}(L)_2]Cl$ can be prepared by reacting appropriate $[ReO_2\{\kappa^2\text{-}HB(pz)_3\}(L)_2]$ complexes (L = pyridine, 1-methylimidazole, 4-dimethylaminopyridine, 1/2 dmpe) with trimethylchlorosilane. In solutions the cations with unidentate nitrogen donor ligands are unstable and rearrange into the neutral derivatives $[ReO(OTMS)Cl\{\kappa^2\text{-}HB(pz)_3\}(L)]$.[428]

Cyclic voltammograms of rhenium(V) oxo complexes with tetrakis(pyrazolyl)borato ligands generally display one anionic and cationic redox process, the potentials of which are dependent on the hapticity of the tetrakis(pyrazolyl)borate and the electronic properties of the co-ligands.[429]

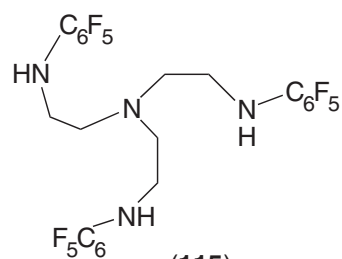
Neutral rhenium(V) oxo complexes with 1,4,7-triazacyclononane (tacn) and related ligands are formed by reduction of the rhenium(VII) compounds $[(tacn)ReO_3]Br$ with zinc amalgam: the initially obtained green, air-sensitive complex $[(tacn)ReO_2Br]$ is hydrolyzed in aqueous media to give the oxo-bridged, dimeric complex $[(tacn)ReO(\mu\text{-}O)_2ReOBr_2]$.[116] Surprisingly reduction of the Re^{VII} complex $[(Me_3tacn)ReO_3][BPh_4]$, which contains the *N*,*N*′,*N*″-trimethyl derivative of 1,4,7-triazacyclononane with zinc dust in methanol gives the pale green cis-dioxo rhenium(V) complex $[ReO_2(OH_2)(Me_3tacn)]^+$.[430] From a similar reduction of $[(tacn)ReO_3][ReO_4]$ the violet neutral $[(tacn)ReO(\mu\text{-}O)_2ReO(ReO_4)_2]$ was obtained, whereas monomeric complexes of the type $[(tacn)ReOX_2]X$ (X = Cl, Br, I) are obtained from reactions between $[ReOX_4]^-$ and the ligand in acetonitrile,[116] or starting from $[ReOCl_3(SMe_2)(OPPh_3)]$.[119]

The cationic mixed-ligand complex $[ReO(tacn)(OC_2H_4O)]^+$, which can easily be prepared from a mixture of $[ReOCl_3(PPh_3)_2]$, triazacyclononane, and ethyleneglycol, represents a useful starting material for further rhenium complexes with the tridentate amine.[117,118,250] The complex undergoes a series of disproportionation reactions in acidic solutions to give $[(tacn)ReO_3]^+$ and rhenium(IV) and rhenium(III) compounds which will be treated in Sections 5.3.2.4.2(i) and 5.3.2.5.2(ii). Re-oxidation of the dimeric rhenium(IV) complex $[(tacn)_2Re_2(OH)(H_2O)(\mu\text{-}O)_2]X_3$ (X = Br, I) in alkaline aqueous solution in air gives *anti*-$[(tacn)_2Re_2O_2(\mu\text{-}O)_2]^{2+}$ which contains a short rhenium-rhenium double bond of 2.4 Å as is expected for a metal–metal multiple bond between two d^2 systems. The terminal Re=O groups in $[(tacn)_2Re_2O_2(\mu\text{-}O)_2]^{2+}$ display nucleophilic character as shown by their reaction with $ZnCl_2$ and NaCl which gives $[(tacn)Re(OZnCl_3)(\mu\text{-}O)]_2$. The coordination of the $ZnCl_3^-$ -fragment to the Re=O group leads to a substantial lengthening of the Re—O bond by 0.295 Å and a shortening of the Re—Re bond by 0.047 Å.[117,118] Complexes with a very similar behavior to that of the tacn derivatives are obtained with tris(2-pyridyl)amine which reacts with $[ReOCl_3(PPh_3)_2]$ in the presence of ethyleneglycol to form $[ReO(OCH_2CH_2)(L)]Cl$ as a sparingly soluble light purple solid. The product converts upon prolonged heating into the rhenium(VII) cation $[ReO_3(L)^+]$.[121]

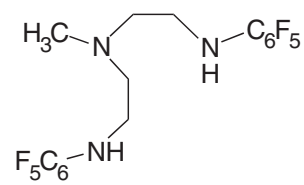
Tridentate coordination at rhenium(V) centers also occurs even with potentially tetradentate proligands as tris(2-pyridylmethyl)amine, (tpa) (**114**), or tris(pentafluorophenylaminoethyl)amine (**115**). Proligand (**114**) forms a cationic complex $[ReOL(tpa)]^+$ upon reaction with an rhenium(V) oxo precursor in the presence of dianionic bidentate co-ligands such as 1,2-amidophenolate or catecholate.[120,431] The third 2-pyridylmethyl arm of the ligands remains uncoordinated. An analogous structure is observed for the product of the reaction between $[Et_4N]_2$-$[ReOCl_5]$ and (**115**) in acetonitrile in the presence of Et_3N. The air-stable, emerald green, diamagnetic product, [ReO(L)Cl], contains doubly deprotonated, tridentate bis(pentafluorophenylamidoethyl)(pentafluorophenylaminoethyl)amine ligand. The protonated arm of the ligand is not coordinated to rhenium.[432] An analogous compound was prepared with bis(pentafluorophenylamidoethyl)-methylamine (**116**) and characterized crystallographically.[433] The complex has a trigonal bipyramidal coordination sphere with the oxo ligand in the equatorial plane.



(**114**)



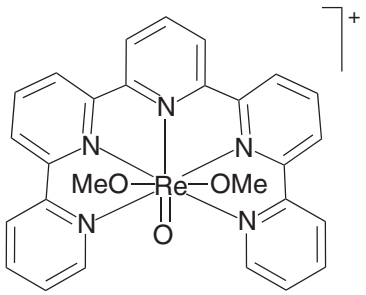
(**115**)



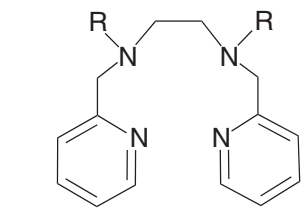
(**116**)

A rhenium(V) oxo complex with a unique structure has been obtained from a reaction of $[ReO_2(PPh_3)_2I]$ with 2,2′:6′,2″:6″,2‴-quarterpyridine.[434] The violet–red $[ReO(OMe)_2(L)]^+$ cation (**117a**) was isolated as a perchlorate salt and is a rare example of a seven-coordinate rhenium(V) oxo complex. The coordination environment of the metal is a pentagonal bipyramid with the oxo ligand being almost coplanar with the quarterpyridine ligand. This unusual coordination mode has also been observed for the rhenium(V) nitrido core with the same ligand (see Section 5.3.2.3.3(ii)(b))

and may be attributed to the unique co-ordination properties of the polypyridyl ligand. Other seven-coordinate complexes are formed with the tetra- or hexadentate ligands of type (**117b**). The cationic compounds of the formulae $[ReO(H_2pmen)Cl_2]^+$, $[ReO(bbpen)]^+$ and $ReO(bped)]^+$ (for ligand abbreviations see (117b)) have a pentagonal bipyramidal geometry with the oxo ligands being constituents of the pentagonal plane. The axial positions are occupied by the chloro ligands or the oxygen donor atoms of the organic ligands.[435]

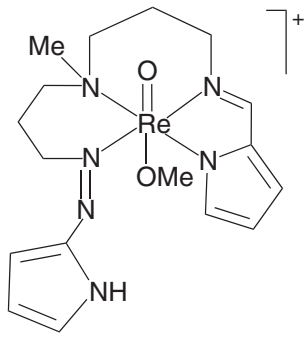


(**117a**)



R = H H_2pmen
R = -CH_2COOH H_2bped
R = -$CH_2(C_6H_4$-OH-2) H_2bbpen

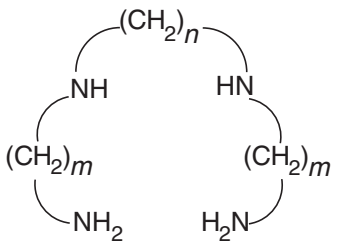
(**117b**)



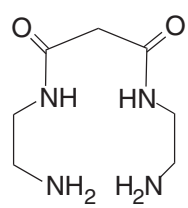
(**118**)

Attempts to bind potentially five-coordinate ligands such as $\{HNC_4H_3$-2CH=N$(CH_2)_3\}_2$NMe to a $[ReO]^{3+}$ core resulted in the formation of the cationic $[ReO(OMe)(L)]^+$ (**118**) where L is the monodeprotonated Schiff base and one terminal pyrrolyl group remains protonated und uncoordinated.[435]

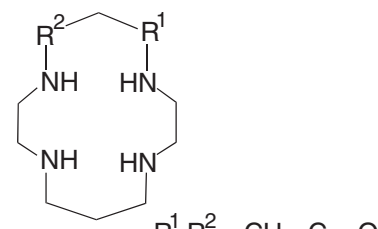
The poor donating properties of neutral nitrogen donors is also reflected in the coordination behavior of tetradentate open chain and cyclic amine ligands. Acyclic tetramines of type (**119**) form $[ReO_2(L)]^+$ cations which undergo no further ligand exchange reactions.[437] Protonation of an oxo ligand of the dioxo core has only been observed in highly acidic solutions such as 6 M HCl. The ability of an amido group to donate electron density to a Re^V center moderately better than a neutral amine is evident from experiments with 1,4,8,11-tetraazaundecane-5,7-dione (5,7-dioxo-tetH_6) (**120**). Reactions of the amide with $[ReOCl_3(SMe_2)(OPPh_3)]$ leads to oxorhenium compounds with doubly deprotonated amido ligands.[438] The dimeric, oxo-bridged species $[Re_2O_3$(5,7-dioxo-tet$H_4)_2]$ is formed when the reaction is performed under slightly basic conditions, whereas the cationic *trans*-$[ReO(OH_2)$(5,7-dioxo-tet$H_4)]^+$ cation is obtained when no supporting base is added. The cation has pK_a values of 4.1 and 8.7 and can also be prepared by acidification of aqueous solutions of the dimer.



(**119**)



(**120**)

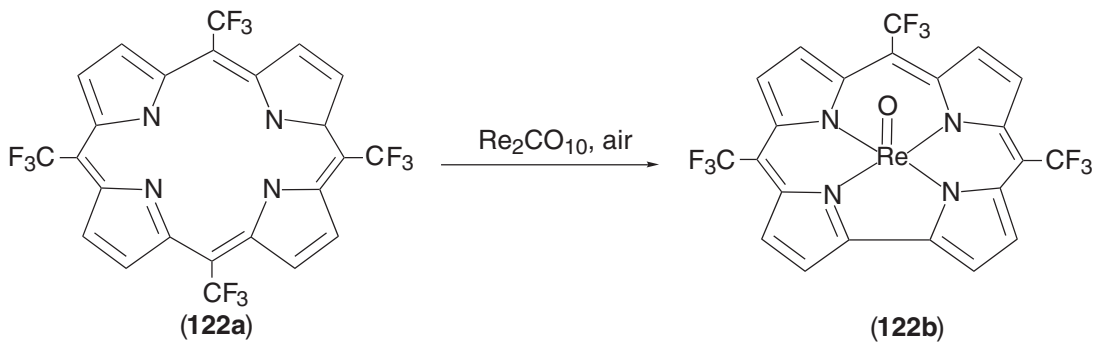


(**121**)

The general trend of the preferred formation of dioxo rhenium(V) complexes with neutral amines is confirmed by the coordination behavior of macrocyclic tetramine ligands of the cyclam type and its derivatives (**121**), whereas a five-coordinate monoxo compound of the composition $[ReO(L)]^+$ has been obtained when L is the tetramethyldibenzotetraaza[14]annulene dianion.[439] Monocationic $[ReO_2$(cyclam)$]^+$ type complexes (cyclam is ligand (**121**) with $R^1{=}R^2{=}CH_2$) have been prepared starting from various rhenium(V) precursors such as $[ReOCl_3(PPh_3)_2]$, $[ReO_2(en)_2]Cl$, $[ReO_2I(PPh_3)_2]$, $[ReNCl_2(PPh_3)_2]$, but also from the Re^{IV} and Re^{III} precursors $[ReCl_4(PPh_3)_2]$ and $[ReCl_3(PPh_3)_2(MeCN)]$.[440–443] Protonation of the oxo ligands occurs upon treatment of the complexes with perchloric acid to give the oxo/hydroxo species $[ReO(OH)$(cyclam)$]^{2+}$. Its ethoxo analogue $[ReO(OEt)$(cyclam)$]^{2+}$ is obtained when the ligand exchange reaction is performed in dry CH_2Cl_2 with subsequent recrystallization from absolute

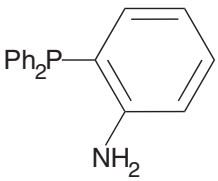
ethanol.[442] Re-dissolution in water, however, converts the complex into the species $[ReO(OH)(cyclam)]^{2+}$. The hydroxo group in $[ReO(OH)(cyclam)]^{2+}$ is a stronger acid than that in $[ReO(OH)(en)]^{2+}$ with a pK_a of 2.95 compared with 3.29 in the latter. Attempts to achieve a second protonation resulted in disproportionation of $[ReO(OH)(cyclam)]^{2+}$.

Phthalocyanine complexes of rhenium(V) are preferably made from $ReCl_5$ or Re_2O_7, since reactions between $[NH_4][ReO_4]$ and phthalodinitrile always yield the nitrido compound [ReN(pc)] (pc^{2-} = phthalocyanine dianion) in considerable amounts. Brown [ReO(pc)Cl] is obtained when $ReCl_5$ reacts with molten phthalodinitrile whereas the same reaction with Re_2O_7 yields $[ReO(pc)(OReO_3)]$. The latter complex can be converted into the neutral oxo-bridged dimer $[Re_2O_3(pc)_2]$ by re-precipitation from concentrated sulfuric acid or recrystallization from boiling pyridine.[444,445] Porphyrin derivatives such as tetraphenylporphyrin (H_2TPP) react in a similar fashion and the compounds $[ReO(TPP)(OReO_3)]$ and $[Re_2O_3(TPP)_2]$ have been studied crystallographically. The porphyrinato ligand in $[ReO(TPP)(OReO_3)]$ is saucer-shaped with the Re^V atom displaced out of the N_4-plane towards the oxo oxygen. The distorted porphyrinate ligand in the oxo-bridged dimer $[Re_2O_3(TPP)_2]$ are rotated by about 30°. $[ReO(TPP)(OReO_3)]$ reacts with OH^- with formation of the anionic dioxo species $[ReO_2(TPP)]^-$ which can be isolated as $[NR_4]^+$ salts (R = Et, Bu^n). The dioxo complex is stable in pyridine but converts to [ReO(OH)(TPP)] upon dilution with water.[444] The formation of an oxorhenium corrolate complex by ring contraction starting from the highly electron-deficient 5,10,15,20-tetrakis(trifluoromethyl)porphyrine (**122a**) has been observed during reactions with $Re_2(CO)_{10}$.[446] Red crystals of (**122b**) have been isolated when the reaction mixture is exposed to air (Scheme 14).

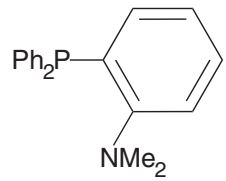


Scheme 14

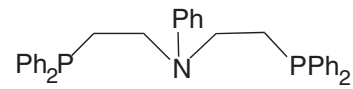
(d) Mixed-donor P/N-, P/O-, and P/S ligands. (*o*-Amidophenyl)diphenylphosphine (**123a**) acts as monodeprotonated chelating ligand in a number of $[ReO(NHC_6H_4PPh_2)_2(OR)]$ type Re(V) complexes (R = H, (substituted) alkyl, or phenyl) which can be prepared in good yields by reactions of $[Bu_4N][ReOCl_4]$ with (*o*-aminophenyl)diphenylphosphine in alcohols using a supporting base[447] or by an oxidation–substitution reaction of $[Re^{III}(NHC_6H_4PPh_2)_2(NH_2C_6H_4PPh_2)]Cl$ with Et_3N in ROH in air.[448] The chelating ligands are co-planar with a *cis*-phosphorus configuration, whereas the position *trans* to the oxo ligand is occupied by the oxygen-containing monodentate ligands. Reactions of the $[ReO(NHC_6H_4PPh_2)_2(OR)]$ complexes with HX (X = halide) give $[ReO(NHC_6H_4PPh_2)_2X]$ species in which two orthogonal $NHC_6H_4PPh_2^-$ ligands coordinate the metal while still preserving the *cis*-positions of the P atoms. The coordination spheres are completed with the oxo and halide ligands. Reactions of various rhenium(V) oxo precursors with the *N*-dimethyl-substituted ligand 2-$Me_2NC_6H_4PPh_2$ (**123b**) give neutral monoxo complexes of the general composition $[ReOX_2Y(2\text{-}Me_2NC_6H_4PPh_2)]$ (X = Cl, Br, I; Y = X, OEt, OMe), while reactions in basic media or treatment of $[ReOCl_2(OMe)(2\text{-}Me_2NC_6H_4PPh_2)]$ with the weakly coordinating trifluoromethanesulfonic acid give the cationic bis-chelates $[ReO_2(Me_2NC_6H_4PPh_2)_2]^+$ and $[Re^{III}Cl_2(Me_2NC_6H_4PPh_2)_2]^+$, respectively.[449] The formation of a neutral $[ReOCl_3(L)]$ complex from reactions of $[ReOCl_3(AsPh_3)_2]$ with $PhN(CH_2CH_2PPh_2)_2$ (**124**) has been reported. Spectroscopic and analytical data of the compound are consistent with an octahedral structure in which the three chloro ligands occupy three facial positions and L acts as a bidentate ligand with one phosphorus donor atom unbound.[450] Products with the same basic structure are obtained from $[ReOCl_4]^-$ and diphenylpyridylphosphine ($pyPPh_2$).[451] The nitrogen atom in this compound is *trans* to the oxo ligand.



(**123a**)

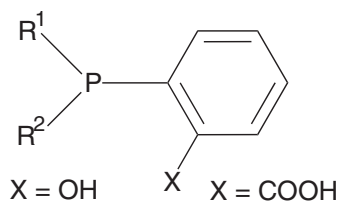


(**123b**)

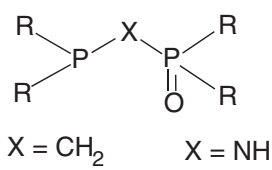


(**124**)

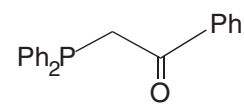
Ligands of the type $R_2P(C_6H_4\text{-}2\text{-}O)^-$ (**125a**) which contain both "hard" and "soft" donor sites have been shown to be excellent for the stabilization of rhenium(V) oxo cores. Depending on the starting materials used monosubstituted complexes of the compositions $[ReOCl_3(L)]^-$ or $[ReOCl_2(L)(PPh_3)]$ have been isolated which can be used for further ligand substitution reactions to give a range of novel rhenium(V) chelates involving anionic dioxo $[ReO_2(L)]^-$, neutral monoxo $[ReOX(P^{\frown}O)_2]$ (X = Cl, Br, I) and neutral monoxo mixed-ligand $[ReOX(L)(P^{\frown}NH)]$ complexes, where $P^{\frown}NH$ represents (*o*-amidophenyl)diphenylphosphine.[452–456] In all of the bis-substituted monoxo compounds, the second chelating ligand binds almost orthogonal to the first one, with the two phosphorus atoms in *cis*-positions. Replacement of one residue R in $R_2P(C_6H_4\text{-}2\text{-}O)^-$ by another C_6H_4-2-O unit gives a potentially tridentate, dianionic ligand which forms stable rhenium(V) oxo compounds. Mixed-chelate complexes containing this novel tridentate ligand and a bidentate $R_2P(C_6H_4\text{-}2\text{-}O)^-$ ligand have been isolated with several cores including ReO^{3+}.[457,458]



(**125a**) (**125b**)



(**126a**) (**126b**)



(**127**)

The tridentate ligand 2-$\{Ph_2P(CH_2)_3N{=}CH\}C_6H_4OH$ reacts with $[Bu_4N][ReOCl_4]$ to form a $[ReOCl_2(L)]$ complex in which the trimethylene chain is folded to bring the phosphorus atom into a position which allows the ligand to bind facially to the $[Re{=}O]^{3+}$ core. The bonding site trans to the Re=O oxygen is occupied by the phenolic oxygen.[459]

An unusual oxo-bridged tetrameric compound of the composition $[ReO(\mu\text{-}O)\{P(CH_2OH)_3\}\{\mu\text{-}\eta^2\text{-}P(CH_2OH)(CH_2O)\}]_4$ has been isolated in low yields from the reaction between $[ReO_2I(PPh_3)_2]$ and $P(CH_2OH)_3$. It represents a unique structural pattern with an eight-membered ring through four Re–O–Re′ bridges.[321]

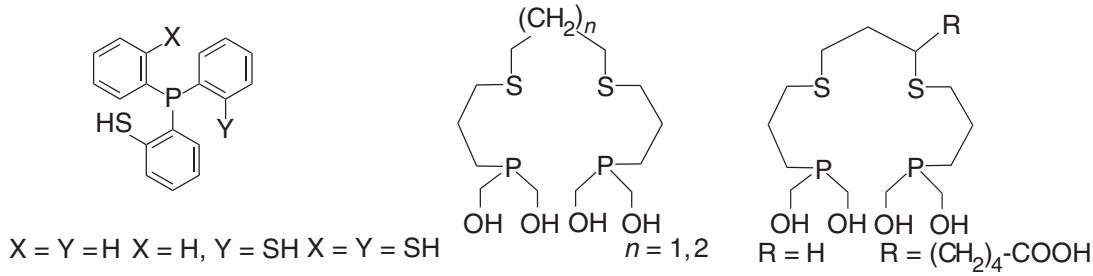
$[Bu_4N][ReOCl_4]$ or $[ReOCl_2(OEt)(PPh_3)_2]$ react with 2-(diphenylphosphino)benzoic acid (HL) (**125b**) in different stoichiometries leading to the mono-substituted complexes $[ReOCl_3(L)]$ and $[ReOCl_2(L)(PPh_3)]$, respectively. The mixed-ligand species $[ReO(OCH_2CH_2O)(L)(MeO)]$ is obtained by reacting $[ReOCl_4]^-$, HL, and ethylene glycol in methanol.[460]

Monooxides of potentially chelating phosphines or mixed phosphines/arsines (**126a**) form stable rhenium(V) oxo complexes of the compositions $[ReOCl_3(L)]$ or $[ReOCl_2(OEt)(L)]$ upon reactions with common oxorhenium(V) precursors[461] or the oxidation of triply bonded dirhenium(II) complexes with dioxygen,[462] whereas the analogous ligand bis(diphenylphosphino)amine (**126b**) reduces the metal and rhenium(III) and rhenium(IV) species have been isolated.[463]

1-Phenyl-2-(diphenylphosphino)ethanone (**127**) acts as a monoanionic ligand in rhenium(V) complexes via deprotonation of its enolic form. Green crystals of $[ReOCl(L)_2]$ are produced from reactions between $[Bu_4N][ReOCl_4]$ and HL.[464] Comparative near-IR luminescence studies between the analogous oxo and analogous nitrido compounds show that the emitting state energy of the oxo complexes is less than that for the nitrido compounds by a factor of about two.[465]

Thioanalogues of the ligands of the type (**125**) have been the subject of several studies. These includes the potentially bi-, tri-, and tetradentate ligands of the formulae (**128**) and their phosphine oxides which are partially formed during reactions with rhenium oxo precursors.[88,466] Most of the isolated products can simply be obtained by direct reduction of perrhenate in the presence of the ligands. The rhenium phosphanethiolate chemistry is characterized by a variety of structural types, reflecting the multiple oxidation states available to rhenium, the denticity of the

ligand, and the presence of steric constraints. The versatility of phosphinothiolate chelates is illustrated by the oxo/chloro species $[ReOCl\{OP(C_6H_5)_2(C_6H_4S\text{-}2)\}\{P(C_6H_5)_2(C_6H_4S\text{-}2)\}]$ and the binuclear $[ReO(OReO_3)\{P(C_6H_5)_2(C_6H_4S\text{-}2)\}_2]$ which originate from the same reaction mixture. Employing the potentially tetradentate proligand $P(C_6H_4SH\text{-}2)_3$ (**128c**), the seven-coordinate neutral compound $[Re\{P(C_6H_4S)_3\}\{P(C_6H_4S\text{-}2)_2(C_6H_4SH\text{-}2)\}]$ and the eight-coordinate anionic complex $[HNEt_3][Re\{P(C_6H_4S\text{-}2)_3\}_2]$ were isolated. These compounds demonstrate the preference for the Re^V oxidation state and illustrate that the oxo group can be removed from a rhenium(V) center when an appropriate ligand system is provided and when steric congestion is minimized. The importance of steric factors has been studied by means of trimethylsilyl-substituted ligands.[88]

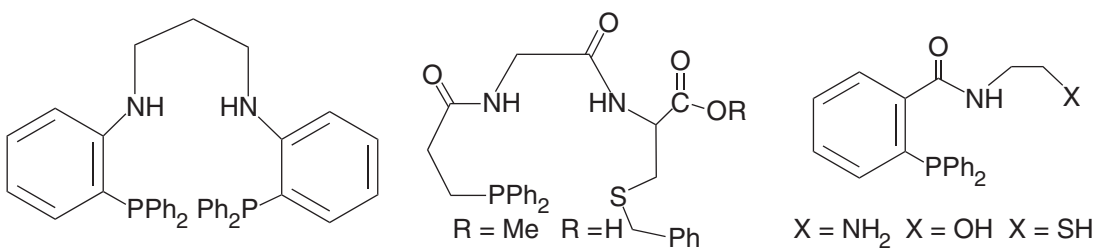


(**128a**) (**128b**) (**128c**) (**129**) (**130a**) (**130b**)

$[ReOCl\{N(PPh_2Se)_2\}_2]$ can be obtained from the reaction of $[ReOCl_3(PPh_3)_2]$ or $[AsPh_4][ReOCl_4]$ with $K[N(PPh_2Se)_2]$ in low boiling solvents. This disubstituted complex is formed irrespective of the molar ratio used. Attempts to recrystallize the green complex from CH_2Cl_2/EtOH mixtures resulted in the loss of one selenium atom from each ligand and brown crystals of $[ReO(OEt)(PPh_2NPPh_2Se)_2]$ have been isolated.[467]

The high tendency of rhenium(V) centers to form stable bonds to phosphorus, nitrogen, and sulfur donor ligands lead to the development of numerous multidentate ligand systems in order to profit from both the effective π-back bonding capabilities of phosphorus and sulfur and the chelate effect. Water-soluble ligands such as P^1,P^1,P^2,P^2-tetrakis(*o*-hydroxyphenyl)diphosphinoethane or the thioether/phosphine derivatives (**129**) and (**130**) form cationic dioxo rhenium(V) complexes.[468–470] Whereas compound (**130**) coordinates one rhenium atom as a P_2S_2 chelating ligand, dimeric $[Re_2O_2(L)_2]^{2+}$ units with η^2-bonded ligands are formed with compounds of type (**129**). Complexes of both types show a high *in vivo* stability.

Neutral [ReOX(L)] complexes (X = Cl, OH, OMe, OEt, $OOCCF_3$) are formed with the potentially tetradentate aminophosphine (**131**).[471] The compound deprotonates twice upon reaction with $[ReOCl_4]^-$ or $[ReO_4]^-$ under reducing conditions and coordinates as a P_2N_2 donor ligand in a plane orthogonal to the Re=O linkage. The central "$[ReO(L)]^+$" core shows a remarkable acid–base stability which enables the exchange of the labile monodentate ligand *trans* to the oxo group over a wide pH range.



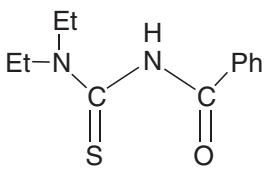
(**131**) (**132a**) (**132b**) (**133a**) (**133b**) (**133c**)

The search for stable complexes with bioactive molecules has led to the development of dipeptide ligands modified by a phosphine group (**132**).[472,473] *N*-{*N*-[3-Diphenylphosphino)propionyl]glycyl}-L-S-benzylcysteine and its methyl ester derivative represent potentially dianionic (**132a**) or trianionic (**132b**) tetradentate ligand systems for the preparation of six-coordinate rhenium(V) oxo complexes. Neutral [ReO(X)(L)] complexes are formed for both ligands; charge balance is achieved by the ligands X (Cl^- or OH^- for the dianionic ester ligand or OH_2 for the

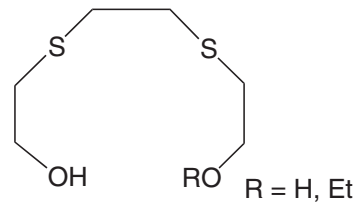
trianionic carboxylate derivative). The amide nitrogen functions are deprotonated in both complexes. When the cysteine carboxylic group is unbound, in organic solvents, it can replace the thioether sulfur.

Potentially tridentate ligands can be derived from 2-(diphenylphosphino)benzamide by the substitution with aminoethyl, thioethyl, or hydroxyethyl substituents (**133**). Various complexes have been isolated and structurally characterized. Ligands (**133a**) and (**133b**) can act as nondeprotonated, bidentate ligands as in $[ReOCl_3(L)]$[474] using the phosphorus and amido oxygen atoms for coordination, or as mono- or dianionic tridentate ligands with deprotonated amido NH and OH or SH sites. The individual bonding mode depends on the reaction conditions applied and the formation of mixed-chelate complexes combining the tridentate ligands (**133**) and bidentate P$^\frown$O ligands (P$^\frown$O = (**125b**) or nondeprotonated (**133b**)) has been demonstrated.[475] Mixed-ligand complexes containing tridentate, dianionic P$^\frown$N$^\frown$S (**133c**) or P$^\frown$N$^\frown$O (**133b**) ligands together with a monodentate thiolato ligand in the equatorial plane of five-coordinate ReO complexes can be prepared by simultaneous reaction of both ligands with $[ReOCl_4]^-$.[476] This introduces the possibility of coordinating ligands with receptor-binding groups such as 1-(2-methoxyphenyl)piperazine to rhenium centers.

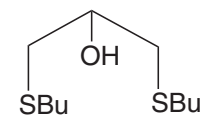
(e) Mixed-donor O/S and O/N ligands. The rhenium(V) oxo anion $[ReO(2\text{-}SC_6H_4COO)_2(py)]^-$ is formed when $[ReO_2py_4]Cl$ reacts with thiosalicylic acid. The chelating thiosalicylato ligands are almost perpendicular to each other with an oxygen atom *trans* to Re=O bond in the complex anion as has been proved by crystallography.[477] A distorted octahedron has also been found for the coordination geometry of rhenium in the neutral complex $[ReOCl(PhCONCSNEt_2)_2]$ which is formed during the reaction of $[Bu_4N][ReOCl_4]$ with *N*,*N*-diethyl-*N*′-benzoylthiourea (**134**). The oxo and the chloro ligands are in *cis* positions in this compound. The oxo complex reacts with substituted anilines, $ArNH_2$, to give imido compounds (see Section 5.3.2.3.4(ii)(c)) and with PPh_3 to form the rhenium(III) complex $[Re(PhCONCSNEt_2)_2(PPh_3)_2]^+$.[478]



(**134**)



(**135a**)

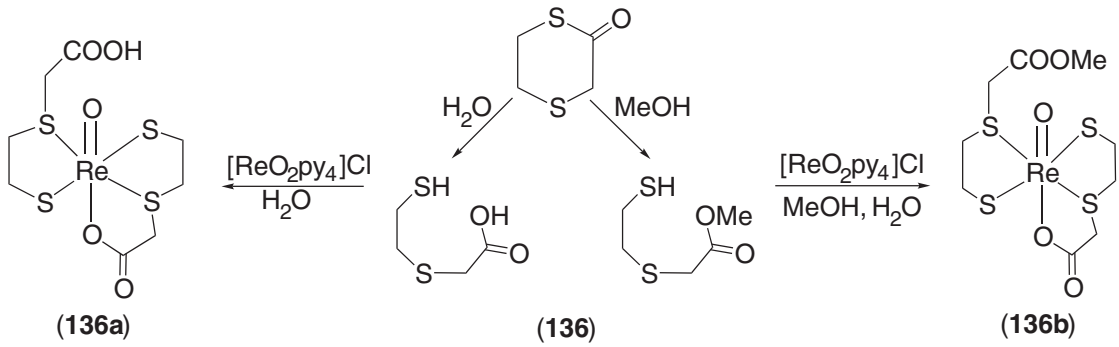


(**135b**)

Neutral oxorhenium(V) complexes of the general formula $[ReO(L)Cl_2]$ are obtained by reactions of $[ReO_4]^-$ or $[ReOCl_4]^-$ with functionalized dithiaalcohols containing the donor atom sequences S$^\frown$S$^\frown$O$^-$ or S$^\frown$O$^{-\frown}$S (**135**). The products show distorted octahedral geometry with the chlorine and sulfur atoms in the equatorial plane. The oxygen of the hydroxy group is coordinated in *trans* position with respect to the Re=O core.[479] $[ReOCl_2\{O(CH_2)_2S(CH_2)_2S(CH_2)_2OH\}]$ reacts with an excess of acetyl chloride with cleavage of the *trans* Re—O bond and acylation of both of the hydroxy groups to form the μ-oxo bridged complex $[ReOCl_2\{MeOCO(CH_2)_2S(CH_2)_2S(CH_2)_2OCOMe\}]_2O$. The combination of tridentate mixed donor atom ligands of the types $^-$S$^\frown$O$^\frown$S$^-$ or $^-$O$^\frown$S$^\frown$O$^-$ with other mono- or bidentate ligands allows the synthesis of a large number of mixed-ligand complexes with the rhenium(V) oxo core and has been demonstrated for thiolates and selenolates,[480] thiaalcoholates,[481] thiopyridine, and thiopyrimidine.[482]

Functionalized thioether ligands are produced by the solvolysis of the cyclic compound 2-oxo-1,4-dithiacyclohexane (**136**). Two different rhenium oxo complexes have been isolated from mixtures of $[ReO_2(py)_4]Cl$, ligand (**136**) and sodium acetate depending on the conditions applied. The reaction in water resulted in the formation of the carboxylato/carboxylate complex $[ReO\{S(CH_2)_2S(CH_2)COO\}\{S(CH_2)_2S(CH_2)CO_2H\}]$ (**136a**), whereas in methanol the mixed carboxylato/ester species $[ReO\{S(CH_2)_2S(CH_2)COO\}\{S(CH_2)_2S(CH_2)COOMe\}]$ (**136b**) is obtained (Scheme 15).[483]

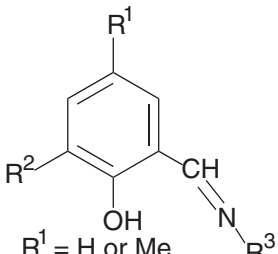
A class of ligands which is very flexible in terms of its denticity, donor atom geometry, and steric demands are Schiff bases derived from salicyladehyde or related carbonyl compounds carrying additional hydroxo groups. The use of bi- and tridentate ligands of this type allows the synthesis of mixed-chelate complexes with a number of O$^\frown$N, N$^\frown$N or N$^\frown$S bidentate ligands. The products are of considerable interest for nuclear medical applications as well as for homogeneous catalysis.[484]



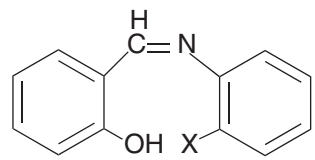
(**136a**) (**136**) (**136b**)

Scheme 15

Simple six-coordinate bis-chelates of the composition $[ReOCl(L)_2]$ where HL is a *N*-aryl- or *N*-alkylsalicylideneimine (compound (**137**) with $R^1 = R^2 = H$ or Cl; $R^3 =$ Ph or Me) have been isolated as green crystals from reactions of $[ReOCl_4]^-$ with an excess of the ligands.[485–488] Crystallographic studies confirm an asymmetric arrangement of the chelating ligands in the complexes with each having a hydroxo group *trans* to the Re=O core.[487] The same type of ligands react with $[ReOX_3(PPh_3)_2]$ (X = Cl, Br) complexes to give Schiff base/phosphine mixed-ligand compounds of the composition $[ReOX_2(L)(PPh_3)]$ with the two halide ligands *cis* to the oxo oxygen atom.[489] The red complex $[ReOCl_3(L)]$ is obtained when a ligand of type (**137**) with $R^1 = Me$; $R^2 = CH{=}N{-}R^3$; $R^3 =$ (substituted) aryl) is used. Only one of the two Schiff base arms is used for coordination.[490]

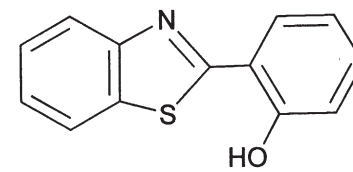


(**137**)



X = OH H_2OPhsal (**138a**)

X = SH H_2SPhsal (**138b**)



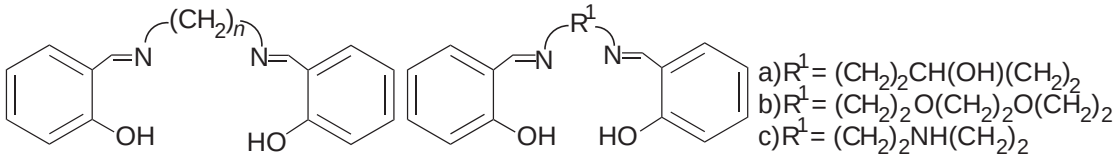
Hhbt (**139**)

Mixed-chelate complexes containing ligands of the type (**138a**), H_2Ophsal, are known with bidentate ligands such as 8-quinolinolate,[486] bipy, 2,2′-phenanthroline, or 2,2′-dipyridylamine.[491] Appropriate starting materials for the syntheses of these compounds are [ReOCl(MeOH)(Ophsal)][486] or $[ReOCl(PPh_3)(Ophsal)]$.[491] The thioanalogous Schiff base H_2Sphsal (**138b**) shows a more complicated behavior since the compound readily converts into its cyclic oxidized form 2-(2-hydroxyphenyl)benzothiazole Hhbt (**139**). This reaction proceeds very rapidly at room temperature under the influence of metal complexes such as $[ReOCl_4]^-$. When the conversion is conducted in acetone, the formation of isopropanol is detected within a few minutes after mixing the reagents[492] and the mixed-ligand complex [ReO(Sphsal)(hbt)] has been isolated from such mixtures.[492,493] More rhenium(V) oxo complexes with 2-(2-hydroxyphenyl)benzothiazole ligands have been obtained from similar reactions and the product of the compositions $[ReOCl_3(hbt)]^-$ and $[ReOX(hbt)_2]$ (X = Cl, Br) contain the ligand as a singly deprotonated N∩O donor.[492] Careful control of the reaction conditions between $[ReOCl_3(PPh_3)_2]$ or $[ReOBr_4(OPPh_3)]^-$ and H_2Sphsal in methanol allows the isolation of [ReO-(MeO)(PPh_3)(Sphsal) or [ReOBr(Sphsal)].[493,494] The latter compound is an excellent starting material for the synthesis of neutral mixed-ligand complexes of the type [ReO(Sphsal)(SR)] which have been isolated with a number of monodentate benzenethiols and benzylmercaptans, whereas reactions with thiols derived from heterocyclic amines such as 2-mercaptopyridine yield complex cations of the composition $[ReO(Sphsal)(HSR)]^+$.[494] Similar mixed-ligand complexes which combine tridentate Schiff bases and bidentate N∩O or N∩N ligands can be obtained from $[ReOCl_2(L)(PPh_3)]$ complexes, where L

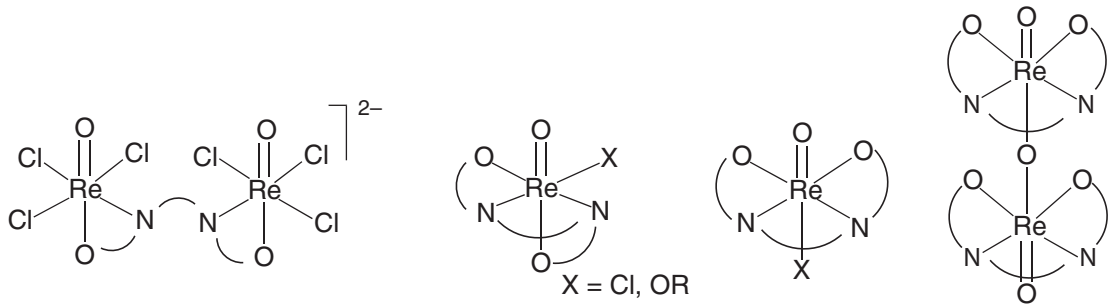
is 2-(2-hydroxyphenyl)benzoxazole or (2′-hydroxyphenyl)2-thiazoline and tridentate Schiff base ligands[495] or related reactions with 8-hydroxy-5-nitroquinoline as bidentate ligand.[496] An unexpected formation of an imino species has been observed during the reaction of $[ReOCl_3(PPh_3)_2]$ with salicylaldoxime in $CHCl_3$. In addition to a small amount of the pink rhenium(IV) complex trans-$[ReCl_4(OPPh_3)_2]$, green crystals of $[ReOCl_2(PPh_3)[\eta^2\text{-}OC_6H_4\text{-}2\text{-}CH{=}NH)]$ have been isolated as major product formation of which involves the cleavage of the N—O bond of the oxime.[497]

The structural flexibility of the Schiff bases of type (**137**) allows the synthesis of ligand systems with specific properties in terms of donor capabilities and steric requirements. Their ability to control the structures of complexes is illustrated by two different O∩N∩O Schiff base ligands coordinating rhenium in two distinct ways.[498,499] Complexes of the type $[ReOCl_2(O{\cap}N{\cap}N)]$ containing monoanionic tridentate ligands of the type (**137**) with R^3 = naphthyl[500] or pyridinyl,[501] have been isolated and structurally characterized. The pyridyl complex contains the almost planar tridentate ligand coplanar with the oxo oxygen atom. A similar product, but with the ligand binding facially to the Re=O core, has been isolated with a ligand in which R^3 is $-(CH_2)_3PPh_2$.[459]

Schiff base building blocks have widely applied to design ligand systems of potentially high denticity ((**140**) and (**141**)). Most of them are based on the bis(salicylidene)amine, H_2salen, skeleton (**140**). The tetradentate ligands form [ReOX(salen)] complexes (R = X, OR, ½ O) of various structures (**142a–d**). This behavior has been the subject of several studies and the formation of the distinct structures has been attributed to various factors such as the length of the alkyl bridge, the nature of the second ligand X and the temperature of the reaction. Monomeric rhenium complexes are preferably formed with ligands which contain alkyl bridges with at least three carbon atoms between the imine functions. The isolation of the trimeric cationic complex $[\{ORe(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2\text{-})_2(\mu\text{-}O)\}_2Re(OC_6H_4\text{-}2\text{-}CMe{=}NCH_2\text{-})_2]^+$,[502] suggests that electronic effects are also important. It illustrates the tendency for oxygen donor atom *trans* to Re=O groups to allow a better delocalization of electron density by the formation of Re—O bonds with partial double bond character. This is confirmed by the relatively short Re—(*trans*)O bond lengths and the tendency to form μ-oxo dimers.[503,504] This results in the formation of dimeric complexes with ethylene-bridged ligands (**142a**) and isomeric mononuclear compounds with larger bridges. The nonsymmetric form (**142b**) is preferred for many ligands, but symmetric complexes (**142c**) have been prepared with a propylene-bridged salen ligand and alkoxo co-ligands. These compounds can be converted by heating to give the nonsymmetric isomers.[504] The formation of dimeric, μ-oxo bridged structures (**142d**) has been observed during recrystallization from various solvents by traces of water.[505,506] Electrochemical studies of complexes of the types (**142c**) and (**142d**) suggest the existence of an equilibrium between the neutral [ReOCl(L)] compounds and $[ReOL]^+$ cations. A one-electron reduction and one-electron oxidation are observed, followed by a fast chemical reaction, resulting in decomposition of the complex. The μ-oxo dimeric complexes underwent a two-electron reduction followed by decomposition. Successive one-electron oxidations of each rhenium in $[Re_2O_3(L)_2]$ are observed. Each electron-transfer step is coupled to a chemical reaction, the generation of $[Re_2O_3(L)_2]^+$ was followed by the cleavage of the μ-oxo bond and the formation of mono-oxo species. This reaction is much slower than the decomposition which follows the generation of $[Re_2O_3(L)_2]^{2+}$.[507–509]



Attempts to prepare rhenium oxo complexes with penta- and hexadentate Schiff base ligands containing additional oxygen donor groups (**141a**) and (**141b**) resulted in products of type (**142b**) and the additional hydroxo or ether functions do not contribute to the coordination of the metal.[510,511] From reactions of $[ReOCl_4]^-$ with ligand (**141c**), however, brown crystals of the composition [ReO(L)] (L = triply deprotonated ligand (**141c**)) have been isolated in moderate yields.[512] One oxygen atom of the N_3O_2 pentadentate ligand is located *trans* to the Re=O bond, while the four remaining coordinating atoms lie *cis* to the oxo group giving a distorted octahedral



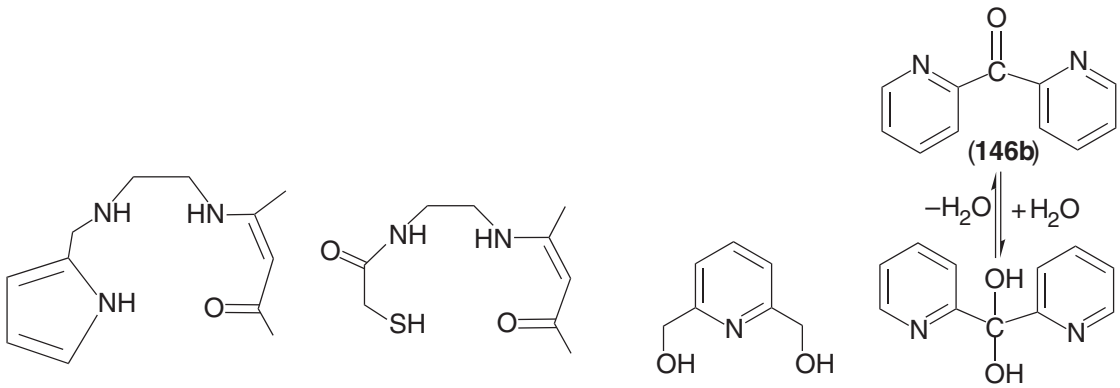
(**142a**) (**142b**) (**142c**) (**142d**)

geometry around the metal. Similar products have been obtained for the related ligand *N*,*N*′-3-azapentane-1,5-diylbis(3-(iminoethyl)-6-methyl-2H-pyran-2,4(3H)-dione.[513]

Tetradentate, potentially triacidic Schiff base ligands with N_2OS donor sets (type (**134**) with $R^1 = R^2 = H$; $R^3 = -(CH_2)_nNHC(O)CH_2SH$; $n = 2–4$)) react with $[ReO_2(py)_4]Cl$ or $[ReOCl_3(PPh_3)_2]$ under complete deprotonation and the formation of five-coordinate [ReO(L)] complexes when $n = 2$ or six-coordinate products of the compositions [ReO(L)(py)] or $[ReO(L)(PPh_3)]$ when $n = 3$ or 4.[514]

The coordinating properties of Schiff bases have been regarded concerning potential applications in nuclear medicine and promising results have been obtained by the coupling of cholesterol to complexes of type (**142c**) and the use of their coordinating capacity for the synthesis of functionalized tetradentate calix[4]arene ligands and rhenium(V) oxo complexes thereof.[515]

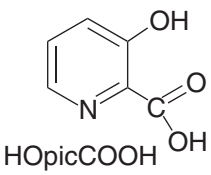
Aminophenolate ligands which result from the reduction of the tetradentate Schiff bases of type (**140**) possess a low capacity to transfer electron density to the metal and, consequently, complexes containing the $[O{=}Re{-}O{-}Re{=}O]^{4-}$ core are formed.[516,517] The products can be obtained in low yields only when $[ReOCl_4]^-$ or $[ReOCl_5]^{2-}$ are used as precursors since side-reactions which give oligomeric products and ReO_2 play a considerable role.[516] This problem has been solved by the intermediate production of an ethylene glycolato complex of the tentative composition $[ReO(eg)_2]^-$. The less reactive compound decreases the rate of the ligand exchange and the chelate formation is preferred.[517] Similar findings have been reported for the synthesis of five-coordinate rhenium(V) complexes with the trianionic $N^{\cap}N^{\cap}N^{\cap}O^{3-}$ ligand derived from (**143**),[518] whereas no supporting ligand is required for the formation of the neutral compound [ReO(L)] with the triply deprotonated compound (**144**). This complex can be prepared directly from the triphenylmethyl-protected $S^{\cap}N^{\cap}N^{\cap}O$ ligand and $[ReOBr_4]^-$ or $[ReOCl_3(PPh_3)_2]$.[519]



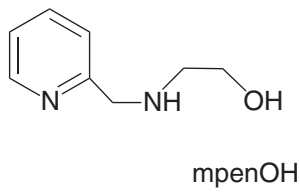
(**143**) (**144**) (**145**) (**146b**) (**146a**)

Some unusual reactions have been observed with hydroxypyridine ligands such as 8-hydroxyquinoline (Hoxine), *N*-phenylsalicylideneimine (Hphsal), 2,6-bis(hydroxymethyl)pyridine ($py(CH_2OH)_2$) (**146**), or dihydroxydi(2-pyridyl)methane (**147a**) which is formed by hydrolysis of di(2-pyridyl)ketone (**147b**). The nitrido complex $[ReNCl_2(PPh_3)_2]$ reacts with formation of the complexes $[ReOCl(quin)_2]$, $[ReOCl_2(phsal)(PPh_3)]$, *cis*-$[ReOCl_2\{py(CH_2OH)(CH_2O)\}(PPh_3)]$, and $[ReOCl_2\{(py)_2CO(OH)\}]$, respectively.[520] The formation of the oxo ligand is surprising in view of the fact that the rhenium–nitrogen triple bond is very stable and examples of Re≡N bond

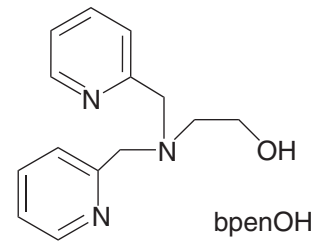
cleavages are rare. But three of the products observed are identical to those isolated earlier from reactions of $[ReOCl_3(PPh_3)_2]$ with these ligands,[521,522] while in *cis*-$[ReOCl_2\{py(CH_2OH)(CH_2O)\}(PPh_3)]$ ligand (**146**) acts as a bidentate $N^{\frown}O^{-}$ donor, spanning one axial and one equatorial coordination site with the pyridine nitrogen *cis* to the PPh_3 ligand.[523] This is unexpected bearing in mind the *trans* positions of the PPh_3 ligands in the starting complexes $[ReNCl_2(PPh_3)_2]$ or $[ReOCl_3(PPh_3)_2]$.



(**147**)

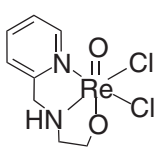


(**148**)

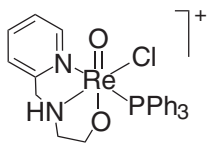


(**149**)

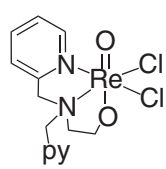
The compositions and structures of oxorhenium(V) complexes with substituted pyridines can be controlled over a wide range by the precursors and the reaction conditions (particularly the solvents) applied. This has been demonstrated for (2-pyridyl)diphenylphosphine (PPh_2py), where the formation of $[ReOCl_3(PPh_2py\text{-}P,N)]$ vs. $[ReOCl_3(OPPh_2py\text{-}P,O)]$ has been controlled by the reaction temperature,[451] 3-hydroxypicolinic acid (HOpy-3-CO_2H) (**147**), (*N*-(2-pyridylmethyl)-2-aminoethanol (mpenOH) (**148**) and *N*,*N*-bis(2-pyridylmethyl)2-aminoethanol (bpenOH) (**149**). The reaction of ligand (**147**) with $[Bu_4N][ReOCl_4]$ in a 2:1 molar ratio in boiling benzene gives the green anionic complex $[ReOCl_3(HOpy\text{-}3\text{-}COO)]$ in good yields. When the same reaction is performed in boiling ethanol, the blue neutral bis-complex $[ReOCl(HOpy\text{-}3\text{-}COO)_2]$ is obtained.[524] The *trans* positions to the Re═O core is occupied by oxygen atoms of the carboxylic groups in both complexes. Reactions starting from $[ReO_2I(PPh_3)_2]$ give the complexes $[ReOI_2(PPh_3)(HOpy\text{-}3\text{-}COO)]$ and $[ReO(PPh_3)(HOpy\text{-}3\text{-}COO)_2]I$ in moderate yields.[525]



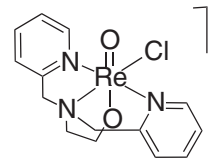
(**148a**)



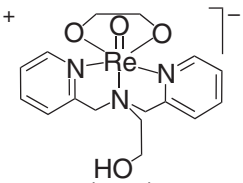
(**148b**)



(**149a**)



(**149b**)

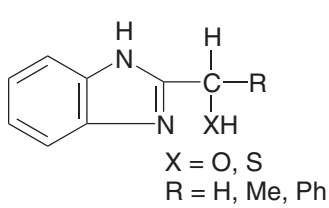


(**149c**)

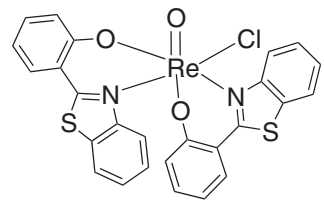
A mixture of rhenium(V) oxo complexes, from which the dichloro complex $[ReOCl_2(mpenO\text{-}N,N',O)]$ (**148a**) and the chlorotriphenylphosphine complex $[ReOCl(PPh_3)(mpenO\text{-}N,N',O)]^+$ (**148b**) were isolated, is afforded during the reaction of $[ReO(OEt)Cl(PPh_3)_2]$ with the potentially tridentate $N^{\frown}N^{\frown}O$ ligand mpenOH (**148**).[526] Similar reactions with bpenOH (**149**) gives the complexes $[ReOCl_2(bpenO\text{-}N,N',O)]$ (**149a**) and $[ReOCl(bpenO\text{-}N,N',N'',O)]^+$ (**149b**) with two different bonding modes for the potentially tetradentate ligand. The addition of ethyleneglycol (H_2eg) to the reaction mixture results in the isolation of the mixed-chelate complex $[ReO(eg)(bpenOH\text{-}N,N',N'')]^+$ (**149c**). It is suggested that the reduction of the metal by liberated PPh_3 is avoided by the formation of the O═Re—O core which is present in all the formed complexes since considerable amounts of rhenium(V) are reduced during comparable reactions with PPh_2py[451] or tris(2-pyridylmethyl)amine.[526]

The coordination capacity of heterocyclic amines has already been outlined in Sections 5.3.2.3.1(i)(d) and 5.3.2.3.1(ii)(c). Substitutions of benzimidazole, benzothiazole, oxazoline, or thiazoline rings with aliphatic alcohols or phenols results in chelating ligands which mimic naturally occurring coordination sites. Neutral rhenium(V) complexes of the compositions $[ReOCl_2(L)(PPh_3)]$, $[ReOCl(OEt)(L)(PPh_3)]$ or $[ReOCl(L)_2]$ where HL is a benzimidazolylalcohol or benzimidazolylthiol of type (**150**) have been isolated during reactions between $[ReOCl_3(PPh_3)_2]$ and the ligands in ethanol depending on the reaction conditions applied. The products have been isolated as solids and characterized by elemental analysis and spectroscopic methods.[527,528] A structurally related product, $[ReOCl(hbt)_2]$, (**151**) (Hhbt = 2-(2-hydroxyphenyl)benzothiazol (**139**)) has been studied by X-ray crystallography and shown to have an asymmetric coordination of the

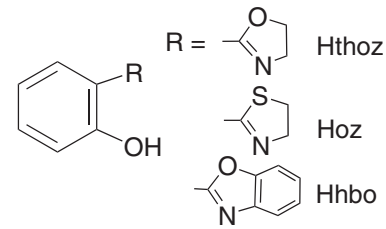
chelating ligands with one phenolato donor *trans* to the oxo oxygen.[529] Compounds of the type (**152**) readily deprotonate and can then also act as mononegative chelating N^O ligands in rhenium(V) oxo complexes. A series of $[ReOBr(L)_2]$ complexes with HL = Hoz, Hthoz, or Hhbo has been isolated from ligand exchange reactions starting from $[ReOBr_4]^-$ and structurally characterized.[530] The structures follow the general feature discussed for $[ReOCl(hbt)_2]$. The chloro analogues are formed when $[ReOCl_3(OPPh_3)(Me_2S)]$ is used as precursor. The chloro ligand in $[ReOCl(oz)_2]$ can readily be removed by treatment with silver triflate giving the cationic complex $[ReO(oz)_2(OH_2)]^+$.[531] $[ReOCl(oz)_2]$ as well as $[ReO(oz)_2(OH_2)]^+$ catalyze oxygen atom transfer reactions from aryl sulfoxides to alkyl sulfides and oxygen scrambling between sulfoxides to yield sulfone and sulfide. Superior catalytic activity has been observed for $[ReO(oz)_2(OH_2)]^+$ due to the availability of a coordination site at the rhenium atom. The active form of the catalyst is a dioxorhenium(VII) intermediate, $[ReO_2(oz)_2]^+$, which is rapidly reduced in the presence of sulfide to $[ReO(oz)_2]^+$ with sulfoxide as the sole organic product.[531]



(**150**)

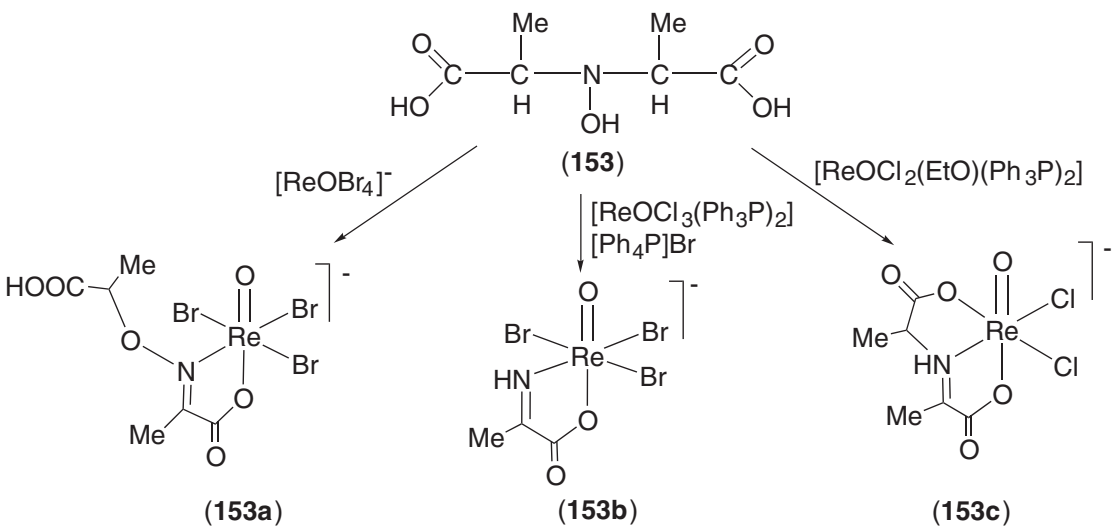


(**151**)



(**152**)

A study with bioinorganic background examined reactions of common rhenium(V) precursors with *N*-hydroxyiminodipropionic acid (H_3hidpa) (**153**) which is constituent of amavadin. During the reactions of $[Bu_4N][ReOBr_4]$, $[ReOCl_3(PPh_3)_2]$ or $[ReOCl_2(OEt)(PPh_3)_2]$ with H_3hidpa only complexes with N^O ligand fragments involving 2-[(1-carboxyethoxy)imino]propionic acid have been isolated and structurally characterized (**153a**–**c**) (Scheme 16).[532]



Scheme 16

Mixed-chelate complexes containing the monoanionic P^O ligand 2-diphenylphosphinophenolate (L^-) and a number of model peptide fragments such as tiopronin, GlyGly, GlycL–Phe, or gluthathione show the radiopharmaceutical potential of this class of compounds. Reacting equimolar amounts of the peptides with the $[ReOCl_3(L)]^-$ precursor in refluxing aqueous MeCN/MeOH mixtures, the following complexes were obtained: $[ReO(L)\{SC(Me)CONCH_2COO\}]^-$, $[ReO(H_2NCH_2CONCH_2COO)(L)]$, $[ReO\{H_2NCH_2CONCH(CH_2C_6H_5)COO\}(L)]$, and $[ReO\{SCH_2CH(NHCOCH_2CH_2CHNH_2CO_2H)CONCH_2COO\}(L)]^-$. By a comparative study of the first three complexes against excess gluthathione it was shown that

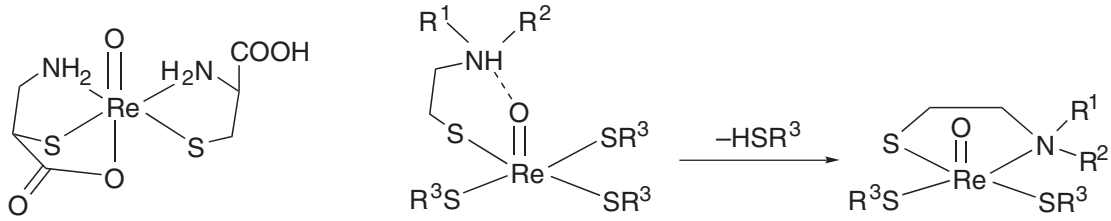
the complex with the bulky $C_6H_5CH_2$ substituent adjacent to the coordinated carboxylate group is the most stable.[533] A similar coordination mode has been found for mixed-chelate complexes containing bidentate phosphinophenolato or phosphinocarboxylato and tridentate, dianionic O^N^S or O^N^O Schiff bases. The coordination environment around rhenium is distorted octahedral with the donor atoms of the tridentate ligand and the phosphorus atom of the P^O$^-$ ligand in *cis* positions to the oxo oxygen.[534,535]

(f) Mixed-donor N/S ligands. Native and synthetic sulfur-containing amino acids and their derivatives are of great interest because of their considerable potential to provide access to novel compounds for medical applications. This type of ligands combines the perfect donating abilities of N^N or O^N chelating ligands with amine or amido donor functions with a "soft" sulfur atom which perfectly meets the electronic requirements of the ReO^{3+}, ReN^{2+}, or $ReNR^{3+}$ cores (see also Sections 5.3.2.3.3(ii)(b) and 5.3.2.3.4(ii)(b)). This may explain the large number of rhenium compounds containing bi-, tri-, and tetradentate N^S mixed-donor ligands.

Nevertheless, reports on well-characterized rhenium(V) oxo complexes with native amino acids such as cysteine or methionine or small peptides containing these building blocks are rare. Reactions of common ReO precursors such as $[ReOCl_4]^-$, $[ReOCl_3(PPh_3)_2]$, or $[ReO_2I(PPh_3)_2]$ result in the formation of products which are contaminated with undefined polymeric species. This is mainly due to the high reactivity of these starting materials with the thiolates and has been studied more in detail for analogous technetium compounds.[536,537] Well-defined complexes could however be isolated by a ligand-exchange procedure starting from a less reactive gluconato oxorhenium(V) precursor. This approach yields monomeric complexes with cysteine and cysteine methyl ester.[538] The ester ligand is partially hydrolyzed during this procedure and octahedral complexes with one doubly deprotonated cysteinato ligand ($^-OOCCH(NH_2)CH_2S^-$) having the carboxylato group in *trans* position to the oxo ligand and one singly deprotonated cysteinato or cysteine methylester ligand ($ROOCCH(NH_2)CH_2S^-$, R = H (**154a**) or Me) are obtained. A facile procedure to obtain [ReO(OOCCH(NH$_2$)CH$_2$-S)(HOOCCH(NH$_2$)CH$_2$S)] is given using the disulfide of cysteine, cystine. This reaction starts from perrhenate which has been reduced in the presence of cystine with sodium dithionite in alkaline solutions to give a brown powder of complex (**154**) in moderate yields. The noncoordinated carboxylic group of the product can readily be deprotonated to give a complex anion.[539] This procedure does not influence the first coordination sphere of the metal significantly. A conversion of the rhenium center into a *trans*-$OReO^+$ core, however, has been observed in aqueous solutions at pH 12 by means of EXAFS.[538] A coordination behavior similar to that of cysteine has been found for penicillamine (H_4pen) and its methyl ester.[540–543] A neutral oxo complex of the type (**154**) is formed in neutral media. Differences in solution chemistry has been observed for the species [ReO(D-penH$_3$)(D-penH$_2$)] and [ReO(D-penH$_3$)(L-penH$_2$)]. [ReO(D-penH$_3$)(L-penH$_2$)] shows unique solution behavior due to its mixed DL ligand stereochemistry. Unlike [ReO(D-penH$_3$)(D-penH$_2$)], the DL compound exists as a pair of enantiomers that undergo base-catalyzed interconversion and does not form a COO-ligated *N*-deprotonated species and prefers methoxy over hydroxy coordination in its COO-delegated form in MeOH/water mixtures. Ester hydrolysis as discussed for cysteine methyl ester has also been observed for D-penicillamine methylester. Spectroscopic studies suggest that in aprotic, noncoordinating solvents one amine group in the 1:2 oxorhenium(V) complex is deprotonated. In presence of coordinating solvents such as water the *trans* position to the oxo ligand is occupied with water without any change in the NH/NH$_2$ coordination mode. In water, however, hydrolysis of the ester is observed and the formed carboxylic group binds *trans* to Re=O.[543]

The simultaneous action of potentially bidentate aminothiols of the type $R^1R^2NCH_2CH_2SH$ ($R^1 = R^2 =$ Et or $R^1R^2 = C_5H_{10}$) and monodentate thiols on $[ReOCl_3(PPh_3)_2]$ results in the formation of neutral products of the formula $[ReO(R^1R^2NHCH_2CH_2S)(SR^3)_3]$ (**155a**) where the aminothiol acts as a monodentate ligand with a protonated nitrogen atom. In solution the brown complexes gradually transform to green compounds of the type $[ReO(R^1R^2NCH_2CH_2S)(SR)_2]$ (**155b**) (Scheme 17).[544] This transformation has also been observed for technetium analogues and is much slower for the rhenium compounds.

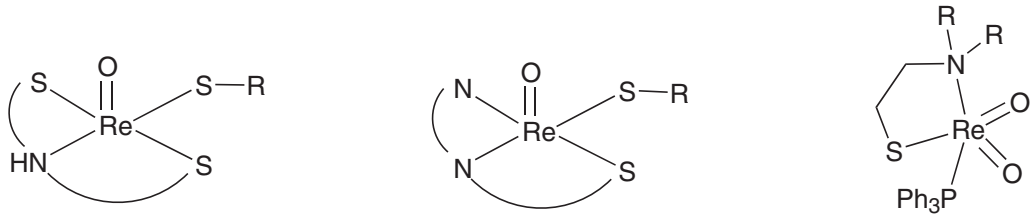
The general procedure described above, the simultaneous action of two different ligands on a rhenium precursor, has been applied for numerous types of bi- and tridentate aminothiol ligands with monodentate ligands such as thiols,[375,545–555] halides,[556] or alkyls.[557] The properties of the resulting complexes of the types (**155b**) or (**156**) can be controlled over a wide range by variations in the backbone of the chelating ligand and/or substitutions at one or both of the ligands and has caused considerable interest with regard to potential pharmaceutical applications. Functionalization of the ligands allows the development of molecules that possess specific pharmacological



(**154**) (**155a**) (**155b**)

Scheme 17

profiles. This has been demonstrated with a rhenium complex of type (**156b**) where $^{-}$SR is an *N*-ethanethiol derivative of tropane which binds to the dopamine transporter.[558]

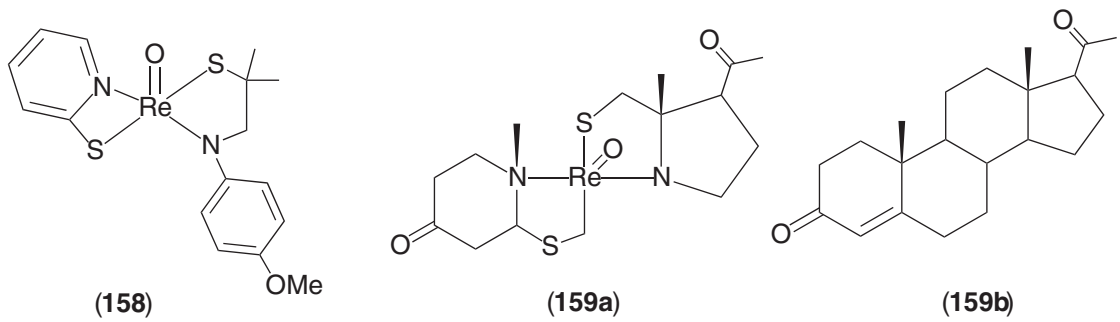


(**156a**) (**156b**) (**157**)

Rare examples of *cis*-dioxorhenium(V) complexes of the composition (**157**) are formed when $[ReOCl_3PPh_3)_2]$ is exposed to $R_2NCH_2CH_2SH$ ligands where R_2N is NEt_2, $N(C_2H_4)_2C(OC_2H_4O)$, or $N(C_2H_4)_2C_6H_4$-2-OMe.[559,560] The complexes have trigonal bipyramidal structure with both oxo ligands and the sulfur atom of the aminothiolate forming the trigonal plane. Water is the origin of the second oxo ligand as has been shown with an ^{18}O labeling experiment.

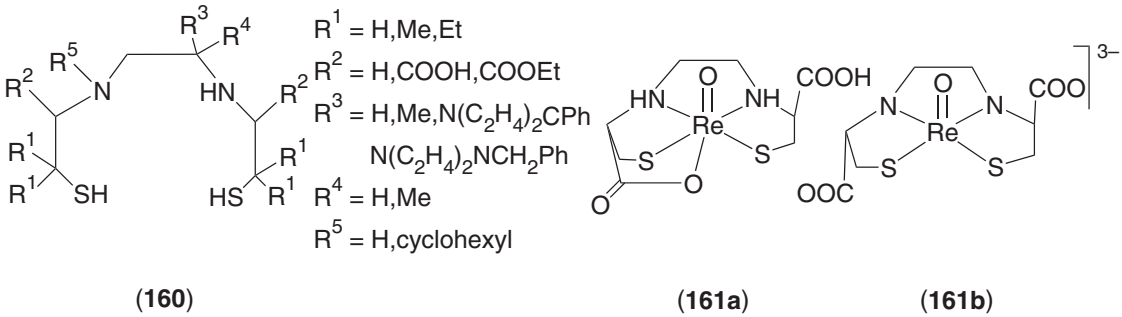
The monodentate thiolato ligands in complexes of the type (**156**) are readily replaced by competing thiols. This has been demonstrated by ligand-exchange experiments with various thiols including gluthathione and other blood constituents containing thio groups.[378,561,562]

A completely different approach to potential rhenium-containing pharmaceuticals is given with attempts to mimic native steroid receptor ligands by a metal-containing framework. This requires the synthesis of heterodimeric bis-chelates, that means oxo complexes containing two different chelating ligands, in preference to the homodimeric compounds. The high versatility of N^S chelating ligands recommends this class of ligands for such experiments. An example of the selective formation of heterodimeric bis-chelates is provided by the reaction of $[ReOCl_3(PPh_3)_2]$ with equimolar amounts of 1-(4′-methoxyphenyl)amino-2-methylpropane-2-thiol and pyridine-2-methanethiol which gives the mixed-chelate complex (**158**) in essentially quantitative yields.[563] This has been used for the preparation of rhenium complexes whose shape resembles that of molecules that bound to steroid receptors. *Trans*-geometry is required for the N^S ligands and that this is the case for the rhenium complexes has been demonstrated by the crystal structure of a complex (**159a**) which resembles the shape of progesterone (**159b**).[564] Neutral Re=O mixed-chelate complexes are also known containing 2,6-dithiomethylpyridinato and 2-diphenylphosphinophenolato,[552] or *N*-(2-hydroxybenzyl)-2-thioaniline and 2-thiopyridine ligands.[565]



(**158**) (**159a**) (**159b**)

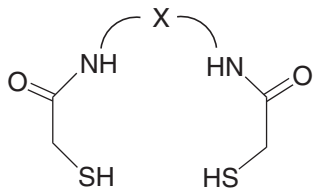
Tetradentate S∩N∩N∩S aminothiolato ligands found considerable interest since their complexes represent structural analogues of the neutral technetium(V) complex [TcO(ECD)] ($H_3ECD = N,N'$-1,2-ethylenediylbis-L-cysteine diethylester, (**160**) with $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = COOEt$) which is used as a brain imaging agent in diagnostic nuclear medicine.[566] The ligands (**160**) can easily be substituted in several positions and, thus, their chemical and biological properties can be optimized. They normally coordinate as tetradentate ligands in their *S*,*S*,*N* triply deprotonated form and neutral rhenium oxo complexes are obtained from ligand exchange reactions with common ReO starting complexes such as $[ReOCl_3(PPh_3)_2]$ or $[ReOCl_4]^-$ or by reduction of ReO_4^- in the presence of the ligand.[567–572] The formation of anionic $[ReOL]^-$ complexes is the exception for tetradentate diaminodithiolato ligands, but has been observed for a ligand with an aromatic backbone: ethylenebis(*N*,*N*′-2-thioaniline).[573] A more complicated complex formation pattern has been observed for 2,7-dicarboxy-3,6-diaza-1,8-octanedithiol (ligand (**160**) with $R^1 = R^3 = R^4 = R^5 = H$, $R^2 = CO_2H$), H_6EC.[574] Two different products have been isolated with this ligand, the purple neutral complex $[ReO(H_3EC)]$ and the anionic species $[ReO(EC)]^{3-}$. Both compounds show unexpected features in their solid state structures. One of the carboxylate groups is coordinated to the metal *trans* to the oxo ligand (**161a**) in the neutral compound, whereas the coordination geometry of the anionic complex is distorted square pyramidal and both nitrogen donor atoms are deprotonated (**161b**). NMR studies imply the co-existence of several complex species in aqueous solutions at physiological pH and a complicated equilibrium between them. This is supported by the isolation of an isomeric form of (**161a**) with the oxygen atom of the carboxylic group coordinating in the equatorial plane and an axial nitrogen atom. This species dominates at high pH values.[575]

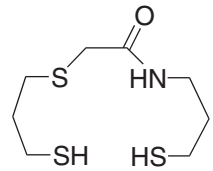


(**160**) (**161a**) (**161b**)

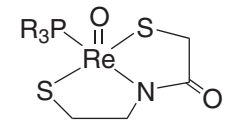
Deprotonation of the nitrogen atoms is facilitated in amide donor groups and consequently a number of N∩S∩S∩N ligands have been designed which contain one or two amido groups. This represents an important step towards the coordination chemistry of rhenium with peptide ligands. Whereas common diamido–dithiolato ligands of type (**162**) readily deprotonate at the nitrogen and sulfur atoms with formation of anionic complexes of the composition $[ReO(L)]^-$,[576–579] the introduction of thioether units into the framework of the ligands (**163**) allows the synthesis of stable neutral ReO complexes. This has been demonstrated for amido ligands of the type (**163a**) which are available with various ring sizes and substitutions as well as with their reduced form (**163b**).[580] The resulting [ReO(L)] complexes react with tertiary phosphines under cleavage of a carbon–sulfur bond, the loss of a SCH_2CH_2 group and the formation of five-coordinate mixed-ligand complexes of the type (**164a**). The decomposition of the ligand can be avoided by introduction of methyl groups in the framework of the ligand which results in the formation of six-coordinate species of the composition (**164b**).[581] The strong bond between the ReO core and amido/thiols has been used to prepare small, lipophilic chelates which form inclusion complexes with native β-cyclodextrin and β-cyclodextrine dimers.[582] The stability of the obtained complexes may suggest potential for a novel method for radiolabeling biomolecules.

Ligands with mixed amine/amide/thiol donor groups have a complex formation behavior intermediate between that of the amine/thiol and the amide/thiol ligands. The extent of the deprotonation of H_4L ligands of this type can be controlled by the reaction conditions and consequently neutral or anionic compounds with a central ReO unit can be isolated.[583–586] As explained for mixed-chelate compounds of type (**159**), complexes of tetradentate N_2S_2 ligands have been proposed as mimics for estrogen receptor ligands. The metal containing unit effectively replaces the C and D rings of estradiol. The resulting neutral rhenium complexes showed a higher stability than the compounds which were prepared following the bis-bidentate approach, but demonstrated an only weak binding to the estrogen receptor.[587,588]

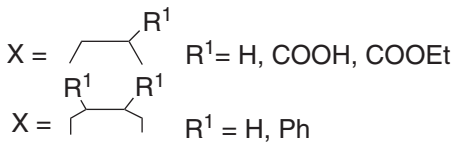




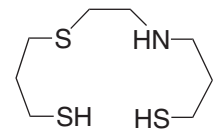
(**163a**)



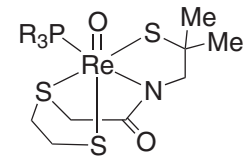
(**164a**)



(**162**)

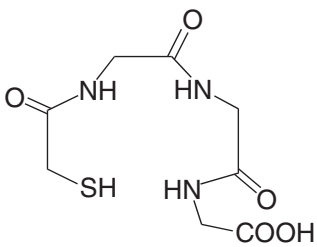


(**163b**)

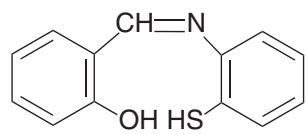


(**164b**)

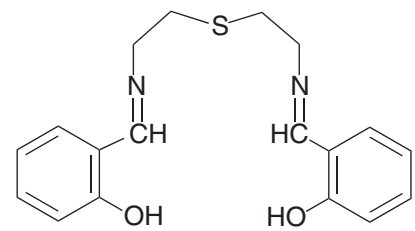
The use of a technetium complex containing the pentaanionic form of mercaptoacetyltriglycine (**165**), H_5MAG_3, also stimulated the coordination chemistry of rhenium with small peptides. The analogous complex $[ReO(MAG_3)]^{2-}$ as well as its monoanionic form and several derivatives have been isolated and characterized spectroscopically and by X-ray diffraction.[589–594] As a result of these studies new peptides and peptide derivatives such as dimethylglycyl-L-seryl-L-cysteinylglycin-amid,[595] mercaptoacetyl-L-histidinyl-S-benzyl-cysteine methylester,[596] and new peptide-based 2,3,5,6-tetrafluorophenyl esters[597] with distinct properties have been synthesized and applied as chelators for rhenium(V) oxo centers.



(**165**)



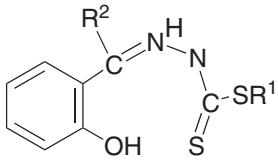
(**166**)



(**167**)

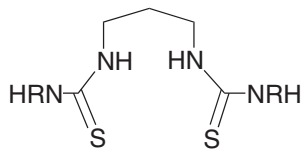
The Schiff base ligand derived from salicylaldehyde and 2-aminothiophenol H_2L (**166**) reacts with $[Bu_4N][ReOCl_4]$ with formation of the yellow–brown complex [ReOCl(L)] when higher alcohols are used as solvents, whereas red crystals of $[Bu_4N][ReOCl_2(L)]$ were isolated from acetone.[598] [ReOCl(L)] reacts with various bidentate, monanionic N∩O or N∩S ligands HL′ to give mixed-chelate compounds of the composition [ReO(L)(L′)]. A different complex formation pattern has been observed with the potentially pentadentate Schiff base ligand (**167**), H_2salthim, which afford the mononuclear complex [ReO(OEt)(salthim)] when it is reacted with $[Bu_4N][ReOCl_4]$ in methanol. The thioether sulfur remains uncoordinated giving rise to an eight-membered chelate ring.[599] The reduced form of the Schiff base which can be obtained by reduction with $NaBH_4$, affords a binuclear complex and the pentadentate ligand binds to both metal ions forming an amine complex with one metal center and an amide complex with the other. The two rhenium atoms are components of a 10-membered dimetallocyclic $\{–ReSCH_2CH_2N–\}_2$ ring. Other $Re^{V}O$ complexes with Schiff base ligands are known with *N*,*N*′-ethylenebis(thioacetylacetonylideneimine),[600] derivatives of dithiocarboxylic acid[601] or dithiocarbazic acid esters.[602] Tridentate ligands O∩N∩S of the type (**168**) readily deprotonate twice and form complexes of the composition [ReOX(L)] (X = Cl, I, Saryl) having a square pyramidal structure.[603,604] *N*-Protected amino acids conjugated with *S*-methyl-2-methyldithiocarbazate give the same type of complexes and underline the viability of this ligand system for the synthesis of modified peptides.[605] The halide complexes of the composition [ReOX(L)] (X = Cl, I) as well as their analogues derived from S-methyl-*β*-*N*-(2-hydroxynaphtylmethylidene)dithiocarbazate react with PPh_3 to give the complexes $[ReOCl(L)(PPh_3)]$ which can easily be converted in air to the phosphine oxide complexes

$[ReOCl(L)(OPPh_3)]$.[606] The *trans* positions to the oxo ligands are occupied by Cl^- in the phosphine complexes and by the oxygen atom of the phosphine oxide in the latter compounds. Complexes containing derivatives of dithiocarboxylic acid bind these ligands singly deprotonated in an N⌒S chelating mode giving $[ReOCl(L)_2]$ or $[ReOCl_2(L)(PPh_3)]$ complexes depending on the starting materials used,[607] whereas 2-benzimidazole-2′-ylethanethiol gives the $[ReO(L)_2]^+$ cation when perrhenate is reduced in the presence of this ligand.[608]



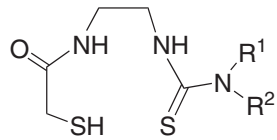
R^1 = Me, Benzyl
R^2 = H, Me

(**168**)



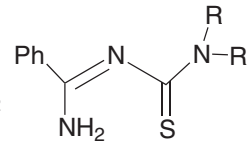
R = Me, Ph, C_6H_4-4-OMe

(**169a**)



R^1 = H, Me
R^2 = Me, Ph, C_6H_4-4-OMe

(**169b**)



(**170**)

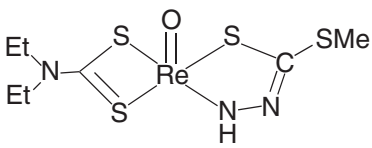
Bulky thiourea ligands such as Me_4tu form stable complexes with the rhenium(V) oxo core as has been described in Section 5.3.2.3.1(ii)(b).[303] The thiourea ligands in the $[ReO(Me_4tu)_4]^{3+}$ cation, however, coordinate monodentately via the sp^2 hybridized sulfur atom. Chelate formation under deprotonation of nitrogen atoms is obtained in the thiourea units of dithiourea ligands of the type $RHNC(=S)NH(CH_2)_3NHC(=S)NHR$ (R = Me, Ph, 4-$MeOC_6H_4$) (**169a**) or their thiol/amide derivatives (**169b**). The ligands of type (**169a**) deprotonate at the two binding and at one nonbinding nitrogen during reactions with common Re^VO precursors and form neutral complexes with two four-membered chelate rings. Chelate formation is only observed with ligands having a propylene backbone. Attempts with ethylene-bridged ligands failed since the resulting central five-membered ring is too small to accommodate bidentate coordination of both thiourea units. The neutral form of the complex is favored in neutral and basic solutions. Under acidic conditions, however, a cationic form with both uncoordinated nitrogen atoms protonated is favored.[609] The chelating thiourea unit can be used as building block for the development of multifunctional ligand systems as has been demonstrated with compounds (**169b**) which form stable neutral [ReO(L)] chelates with rhenium atoms in a square pyramidal geometry.[610] Ligands which also contain thiourea units are *N*-(*N*,*N*-dialkylthiocarbamoyl)benzamidines (**170**). However, they coordinate via the sulfur atom of the thiourea unit and the terminal amino group under single deprotonation and the formation of bis-chelates containing six-membered chelate rings.[478,611]

Although *N*-heterocyclic thiols favorably occur in the tautomeric thione form as has been discussed in Section 5.3.2.3.1(i)(c), deprotonation and chelate formation can be observed when the thiol is located in the two-position to nitrogen in a six-membered heterocycle.[482] This behavior has been observed for 2-mercaptopyridine (HSpy) and 2-mercaptopyrimidine (HSpym). Reactions of HSpy or HSpym with $(Bu_4N)[ReOBr_4(OH_2)]$ in THF lead to the neutral complexes $[ReO(\eta^2\text{-Spy})_2(\eta^1\text{-Spy})]$ or $[ReO(\eta^2\text{-Spy})_2(\eta^1\text{-Spy})]$ with nitrogen atoms of one of the heterocyclic rings *trans* to the oxo ligands. The same type of compound is obtained with 3-(trimethylsilyl)pyridine-2-thiol, whereas increasing the sterical constraints by the introduction of two *t*-butyldimethylsilyl substituents in the three- and six-position of HSpy results in a new structural type, the six-coordinate complex $[ReO(OH)(SC_5H_2N\text{-}3,6\text{-}SiMe_2Bu^t)_2]$ with the two pyridinethiolato ligands are in *cis* positions to the oxo group.[253] μ-Oxo-bridged dimeric complexes are formed with 4,6-dimethylpyrimidine-2-thiol or 6-purinethiol.[297,612] Stepwise ligand exchange and reduction to rhenium(III) compounds has been observed during reactions of $[ReOCl_2(OEt)(PPh_3)_2]$ with HSpy or HSpym and derivatives.[613–615] Intermediates of the composition $[ReOCl_2(SpymR_2)(PPh_3)]$ have only been obtained when sterically hindered pyrimidinethiols have been used.[613,614]

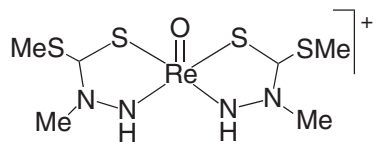
Nitrido ligands are often formed from oxo precursors by reactions with hydrazine derivatives. More details of the formation of hydrazido and diazenido species will be given in Section 5.3.2.10. Here, only those complexes which still contain oxo ligands and, thus may be regarded as intermediates of this conversion are regarded. The dithiocarbamato complex $[ReO(Et_2dtc)(NHNCSSMe)]$ (**171**) is formed in good yields by reacting $[Re_2O_3(Et_2dtc)_4]$ (**89**) with excess $NH_2NHC(S)SMe$. *S*-Methyldithiocarbazate is singly deprotonated at both nitrogen atoms and acts therefore like a hydrazido ligand with an extensive delocalization of the negative

charge over the ligand framework.[616] A similar bis-complex, [ReO(NHNC(S)Ph)-(NHNHC(S)Ph)], has been obtained from reactions of thiobenzoylhydrazine with $[ReO_2I(PPh_3)_2]$ or $[Re_2O_3(Et_2dtc)_4]$.[617] This compound may be regarded as an analogue for intermediates in the synthesis of nitrido complexes such as the oxo compound $[ReO(HNNMeCS_2Me)_2]^+$ (**172**). The latter complex is also suggested as an intermediate in the synthesis of rhenium nitrido species under radiopharmaceutically relevant conditions.[618,619]

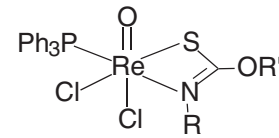
The formal insertion of RNCS (R = Ph, 4-Me-C_6H_4) into the Re—OR^2 bonds of $[ReO-Cl_2(OR^2)(PPh_3)_2]$ complexes and the formation of the complexes $[ReOCl_2(PPh_3)\{R^1N{=}C-(OR^1)S\}]$ (**173**) has been observed. The thiazetidine ligand is formally monoanionic and is coordinated with an almost planar four-membered ring.[620]



(171)



(172)



(173)

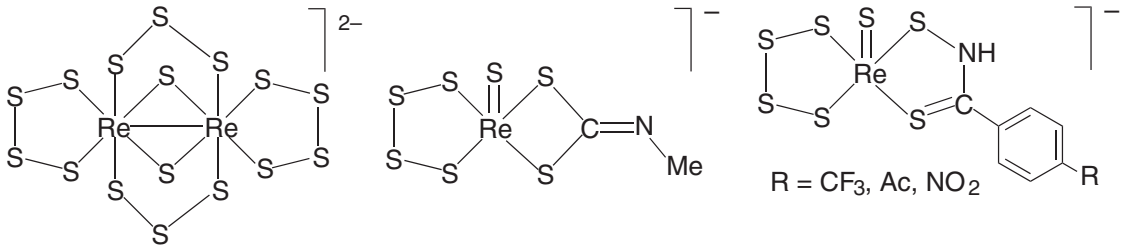
An unusual approach to rhenium(V) oxo compounds is provided by the reaction of the rhenium(IV) complex $[ReCl_4(PPh_3)_2]$ with benzoylacetone thiobenzoylhydrazone or salicylaldehyde thiobenzoylhydrazone. The ligands do not stabilize rhenium(IV) complexes, and rapid oxidation in air gives $Re^{V}O$ chelates with one of the potentially tridentate ligands coordinating as a tridentate dianion and the other as a bidentate monoanion. The position *trans* to the oxo ligand is occupied by the oxygen donor atom of the tridentate ligand in both products.[384]

5.3.2.3.2 *Sulfido complexes*

Compared with the huge number of oxo complexes only a few rhenium(V) compound with terminal sulfido complexes are known. The square-pyramidal complex anion $[ReS(S_4)_2]^-$ was first isolated in pure form in 1986 by a reaction of Re_2O_7 with $(Ph_4P)Br$ and ammonium polysulfide in acetonitrile and the structure of the Ph_4P^+ salt has been elucidated.[151] Later, the same complex anion was prepared from starting materials such as $[Re_2Cl_8]^{2-}$,[621] perrhenate,[622] or $ReCl_5$.[364] When the reactions with the polysulfides are performed in acetone, the derivative $[ReS(S_4)(S_3CMe_2)]$ in which formally one of the sulfur atoms of one S_4^{2-} ligand is substituted by the carbon skeleton of the solvent acetone is obtained.[622] The use of polysulfides with a high sulfur content yields sulfur-rich complex anions, such as the $[Re_2S_{16}]^{2-}$ ion in which two rhenium atoms are linked by each two μ_2-S^{2-} and μ_2-S_3^{2-} ligands (**174**).[153] The anion is characterized by strongly covalent Re—S bonds and represents a new type of a molecular metal sulfide.

Several approaches have been reported for the synthesis of rhenium complexes with terminal sulfido ligands which avoid the use of polysulfides and give access to compound with organic co-ligands. The square-pyramidal complex $[ReS(SCH_2CH_2S)_2]$ with the sulfido ligand in apical position is formed during a reaction of $K_2[ReCl_6]$ with 1,2-ethanedithiol in methanol. The source of the sulfido ligand is partial decomposition of the dithiol.[357] Oxo ligands can be replaced by S^{2-} by reactions of the corresponding ReO complexes with B_2S_3 or P_4S_{10} as has been demonstrated for $[ReSCl_2[HB(pz)_3\}]$,[414,623] $[ReS(Me)(PPh_3)(SCH_2C_6H_4S)]$,[366] or the sulfido-bridged, mixed oxo/sulfido species $[ReO(Me)(\mu_2\text{-}SCH_2C_6H_4S)_2Re(\mu_2\text{-}S)(\ Me)]$.[366]

The tetrathiorhenate(VII) anion is a very useful synthon for the synthesis of sulfur-rich rhenium complexes. Thus, it reacts with a number of unsaturated organic compounds to give complexes with dithiolene-type ligands.[165–167] Isocyanides undergo [3+1] cycloadditions with $[ReS_4]^-$ to give the dithiocarboimidate derivatives $[ReS(S_4)(S_2CNR)]^-$ (**175**) and $[Re_2S_5(S_2CNR)_2]^{2-}$, which undergo S-atom transfer and, in the case of the monometallic species, *N*-alkylation.[164] Addition of S_8 and F_3CCN to ReS_4^- in acetonitrile in air results in the formation of *cis*- and *trans*-$[ReO(S_2NCCF_3)_2]^-$ complexes. A similar reaction has been observed with 4-RC_6H_4CN which yields the mixed-chelate sulfido complex $[ReS(S_4)(S_2NCC_6H_4R)]^-$ (**176**). A rhenium(VII) precursor appears essential for the formation of the adducts, since the rhenium(V) complex $[ReS(S_4)_2]^-$ does not react with nitriles.[624]



(174) (175) (176)

5.3.2.3.3 *Nitrido complexes*

The "N^{3-}" ligand is one of the strongest π-donor ligands known. It stabilizes metal ions in high oxidation states and, thus, numerous stable representatives are known for the d^2 electronic configuration of rhenium (V). "Classical" reactions for the formation of terminal nitrido ligands start from metal halides and nitrogen trichloride or chlorine azide.[224,625] The resulting nitride chlorides $ReNCl_3$ and $ReNCl_4$ can readily be converted into the complex anion $[Re^{VI}NCl_4]^-$ or reduced to rhenium(V) complexes containing organic ligands.[626] For large-scale syntheses, however, this approach seems to be less appropriate in view of the hazardous reagents. Thus, frequently the neutral rhenium(V) complex $[ReNCl_2(PPh_3)_2]$ or its less reactive analogue $[ReNCl_2(PMe_2Ph)_3]$ are used as precursors for the synthesis of nitridorhenium(V) compounds.[174] A renaissance in the use of the $[ReNCl_4]^-$ anion occurred with the report of its facile synthesis by the reaction of perrhenate with sodium azide in HCl as described in Section 5.3.2.2.2.[225] The formation of terminal nitrido ligands has also been reported for reactions of rhenium oxo or halide complexes with dithiocarbazates, [627,628] diphenylsulfur imine,[629] triphenylphosphoraneiminates,[630] or from thionitrosyls,[631] isocyanate,[632] or hydrazines.[176] A summary is given in Figure 4.

(i) Complexes containing exclusively monodentate ligands

Ligand exchange reactions with halides and pseudohalides starting from $[ReNCl_4]^-$ or $[ReNBr_4]^-$ result in rhenium(VI) compounds $[ReNX_4]^-$ ($X = F^-$, N_3^-, or NCS^-).[631] Reduction of the metal is often observed when cyanide is used. However, EPR evidence for rhenium(VI) species with a maximum number of two coordinated CN^- ligands was found when solutions of $[Bu_4N][ReNCl_4]$ were treated with KCN.[629] Ultimately the rhenium(V) complex $[ReN(CN)_4(OH_2)]^{2-}$ is formed and this has previously been prepared from reactions of cyanide with $[ReNCl_2(PPh_3)_2]$ and the tetraphenylarsonium salt structurally characterized.[633,634] The kinetics of the reaction between $[ReN(CN)_4(OH_2)]^{2-}$ and cyanide have been studied in the pH range 8–14 and show that the aqua ligand is replaced by both CN^- and HCN by a dissociative mechanism.[635] The ready replacement of the aqua ligand which is labilized by the strong *trans* influence of the nitrido ligand is confirmed by the reaction of $K_2[ReN(CN)_4(OH_2)]$ with sodium azide which yields after addition of CsCl yellow–orange crystals of $Cs_2K[ReN(CN)_4(N_3)]$ in good yields.[636] The complex is isostructural with its molybdenum and tungsten analogues.

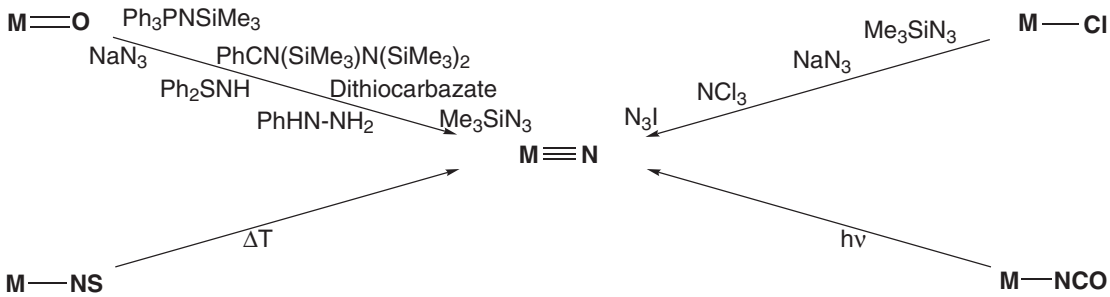


Figure 4 Synthetic approaches to the Re≡N core.

High-yield syntheses for $[ReNCl_2(PPh_3)_2]$ have been reported with the reactions of $[ReOCl_3(PPh_3)_2]$ with PPh_3 and phenylhydrazinium chloride,[278] or by the reduction of perrhenate in HCl in the presence of PPh_3 and sodium azide.[225] The corresponding dimethylphenylphosphine complex $[ReNCl_2(PMe_2Ph)_3]$ has been prepared from the rhenium(III) compound $[ReCl_2(NCO)(PMe_2Ph)_3]$.[632] A photochemical decomposition of the isocyanato ligand has been used to produce the nitrido ligand and carbon monoxide. A similar reaction has also been observed for *mer*-$[Re(NCO)_3(PMe_2Ph)_3]$ which gives *mer*-$[ReN(NCO)_2(PMe_2Ph)_3]$. Only one isocyanate ligand is decomposed in accord with the proposed mechanism.[632] The analogous iodo complex *mer*-$[ReNI_2(PMe_2Ph)_3]$ can be obtained from a reaction of *mer*-$[ReO_2I(PMe_2Ph)_3]$ with TMSN(Me)TMS in moderate yields in the form of green crystals.[280] *mer*-$[ReNBr_2(PMe_2Ph)_3]$ has been isolated from reactions of *mer*-$[ReNCl_2(PMe_2Ph)_3]$ with TMSBr in CH_2Cl_2,[637] whereas an analogous reaction with TMSI results in reduction of the metal and protonation of the nitrido ligand.[638]

Isothiocyanato complexes are produced by exchange of the chloro ligands in $[ReNCl_2(PPh_3)_2]$ or $[ReNCl_2(PMe_2Ph)_3]$ using KSCN. The five-coordinate complex $[ReN(NCS)_2(PPh_3)_2]$ precipitates from CH_2Cl_2/MeOH as a yellow microcrystalline solid. Recrystallization from acetonitrile gives the six-coordinate complex $[ReN(NCS)_2(PPh_3)_2(NCMe)]$ with the acetonitrile ligand *trans* to the nitride.[639] The reaction of $[ReNCl_2(PMe_2Ph)_3]$ with KSCN yields the corresponding nitrido complex $[ReN(NCS)_2(PMe_2Ph)_3]$. The use of TMSNCS, however, causes a four-electron reduction of the metal and the formation of the rhenium(I) thionitrosyl compound $[Re(NS)(NCS)_2(PMe_2Ph)_3]$.[640] This unexpected reaction can be explained by the reactivity of terminal nitrido ligands towards sulfur which has been observed previously for other metals such as molybdenum.[641] The relationship between thionitrosyl and nitrido ligands will be treated more in detail in Section 5.3.2.9.

As observed for $[ReN(CN)_4(OH_2)]^{2-}$, the position *trans* to the nitrido ligand is labilized by the *trans*-effect. This can be used for selective ligand exchange reactions as has been demonstrated for $[ReNCl_2(CF_3SO_3)(PMe_2Ph)_3]$ with the triflate ligand *trans* to "nitride".[642]

The five-coordinate nitridorhenium(V) complexes $[ReNCl_2(Pcyc_3)_2]$, $[ReNBr_2(Pcyc_3)_2]$, $[ReNCl_2(PPh_3)_2]$ and $[ReNBr_2(PPh_3)_2]$ ($Pcyc_3$ = tricyclohexylphosphine) are luminescent and produce structured emission spectra upon excitation at low temperatures. The spectra contain resolved vibronic structure. Vibrational spectroscopy was used to assign the ReN stretching frequencies and to verify that the vibronic progression in the emission is attributable to the ReN stretch. Angular overlap model calculations account for the emission energy changes and are consistent with the assignment of the emissions as d_{xy} to d_{yz} transitions. The changes in the ReN bond lengths in the excited states are about 0.09 Å and are consistent with a decrease in the ReN bond order.[643]

Ligand exchange reactions of $[ReNCl_2(PPh_3)_2]$ with the bulky thiol 2,4,6-tri-isopropylbenzenethiol (Htipt) gave the yellow compound $[ReN(tipt)_2(PPh_3)_2]$ and the pale orange dianionic complex $[ReN(tipt)_4]^{2-}$, which is readily oxidized by air to the green rhenium(VI) compound $[ReN(tipt)_4]^{-}$.[232] $[ReN(tipt)_2(PMe_2Ph)_2]$ has also been isolated starting from $[ReNCl_2(PMe_2Ph)_3]$.

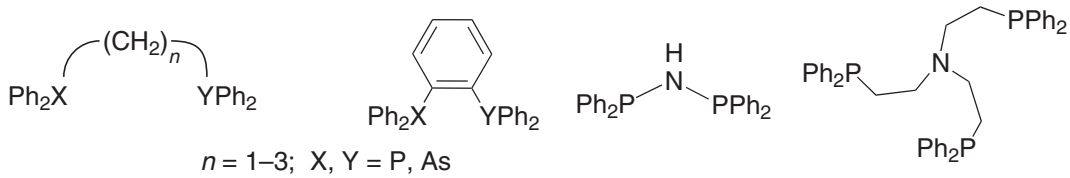
The nitrido complex $[ReNCl(Me_2CNNCOPh)(PPh_3)_2]$ is formed in the reaction of $[ReOCl_3(PPh_3)_2]$ with $Me_2C{=}NNHCOPh$ in ethanol in the presence of HCl. The complex has a pseudo-octahedral geometry with the nitrido ligand *trans* to the oxygen atom of the N^O-chelated hydrazonato ligand.[176] A similar reaction with $Ph_2NNH_2{\cdot}HCl$ gives a mixture of $[ReNCl_2(NNPh_2)(PPh_3)]$ and $[ReCl_3(NNPh_2)(PPh_3)_2]$ containing diphenylhydrazido ligands, whereas in the presence of base the cation $[ReCl_2(NNPh_2)(PPh_3)_2]^+$ is formed.[176]

(ii) Complexes containing chelating ligands

(a) Phosphorus and arsenic donor ligands. Cationic complexes of the composition $[ReNCl(P^{\frown}P)_2]^+$ or $[ReNCl(P^{\frown}As)_2]^+$ are formed when $[ReNCl_2(PPh_3)_2]$ reacts with bidentate phosphines or arsines of the types (**177**) or bis(diphenylphosphino)amine (**178**).[344,348,644] An intermediate of this ligand exchange has been observed with dppm: $[ReNCl_2(dppm)(PPh_3)]$ contains a monodentately coordinated dppm ligand located *trans* to PPh_3. Analogous compounds are formed with alkyl-substituted ligands. They are luminescent and protonation of both their ground and excited states occurs in HCl which gives imido species of the composition $[Re(NH)Cl(R_2PCH_2CH_2PR_2)_2]^{2+}$ which has been extensively studied for the compound with R = Me.[645,646] Titration of the ground and excited states of this compound yields apparent

pK values of about −1.0 and 4.5, respectively, demonstrating a profound increase in basicity in the excited state. This change is due to an increase in electron density at the nitrido ligand in the excited state. The luminescence quantum yield can be increased by a factor of $>10^3$ when the chloro ligand is removed from the metal as has been demonstrated for $[ReN(dppe)_2(MeCN)]^{2+}$.[647] This complex can be prepared by the reaction of $[ReNCl(dppe)_2]ClO_4$ with $Ag(CF_3SO_3)$ in acetonitrile.

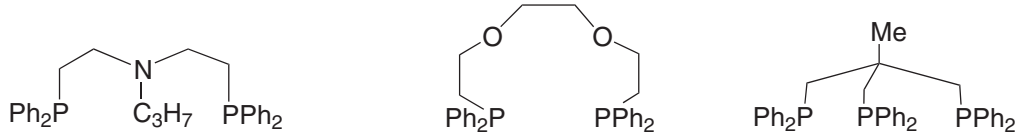
The reaction of $[ReNCl_2(PPh_3)_2]$ with tris(2-diphenylphosphinoethyl)amine, NP_3 (**179**), in THF gives $[ReNCl_2(\eta^3\text{-P,P-NP}_3)]$, in which NP_3 acts as tridentate ligand using the nitrogen and two of the phosphorus donor atoms for coordination. Heating this product under reflux in polar solvents such as ethanol produces the cationic complex $[ReNCl(\eta^4\text{-NP}_3)]Cl$. The oxidation state of the rhenium atom is maintained during the reaction of NP_3 with the nitrido complex $[ReNCl_2(PPh_3)_2]$, whereas during the reaction with $[ReOCl_3(PPh_3)_2]$ reduction and the formation of a rhenium(III) compound is observed.[648]



(**177a**) (**177b**) (**178**) (**179**)

A pair of structurally related octahedral oxo and nitrido complexes has been prepared with 1-phenyl-2-(diphenylphosphino)ethanone, HP⌒O (**127**). $[ReOCl(P⌒O)_2]$ and $[ReN(PPh_3)(P⌒O)_2]$ with singly deprotonated organic ligands are formed during reactions of $[Bu_4N][ReOCl_4]$ or $[ReNCl_2(PPh_3)_2]$ with the ligand in ethanol.[464] Both complexes show a *cis* arrangement of the phosphorus atoms and the coordination of one of the oxygen atoms *trans* to the oxo group. A comparative visible and near-IR luminescence study shows that the emitting state energy of the nitrido complex is higher by a factor of about two.[465]

Chelating mixed-donor P/N and P/O ligands of the types (**181**) or (**182**) do not act as three- or tetradentate ligands in rhenium nitrido complexes. Reactions with $[ReNCl_2(PPh_3)_2]$ give neutral $[ReNCl_2L]$ complexes in which the phosphinoamine or phosphinoether ligands are coordinated as bidentate phosphines.[628,649,650] A tridentate binding mode has been observed for the phosphine (**182**). Reactions of these complexes with an excess of potassium *O*-ethyl dithiocarbonate yields neutral dithiocarbonate compounds $[ReN(S_2COEt)L]$, while the cationic and neutral complexes $[ReN(S_2CNEt_2)L]^+$ and $[ReN(S_2CNEt_2)_2]$ were obtained upon reaction with $K(S_2CNEt_2)$.



(**180**) (**181**) (**182**)

(b) Nitrogen donor ligands and mixed-donor N/S or P/S ligands. Nitridophthalocyaninatorhenium(V) is prepared by the reaction of Re_2O_7, $[NH_4][ReO_4]$ or $[ReOCl_3(PPh_3)_2]$ with molten 1,2-dicyanobenzene.[651,652] The diamagnetic complex is chemically and thermically extremely stable. In the UV–vIS spectra the typical π-π^* transitions of the phthalocyaninato ligand are observed. Extra bands in the solid-state spectrum are due to the strong excitonic coupling of about 2.8 kK. In the resonance Raman spectra the intensity of the Re≡N stretching vibration at 969 cm^{-1} is selectively enhanced by laser excitations above 19.0 kK. Soluble phthalocyaninato derivatives have been prepared starting from 4-*t*-butylphthalodinitrile in a similar reaction as described above. The resulting green nitrido complex was characterized by spectroscopic methods which suggest the occurrence of a monomeric compound in solution which aggregates to dimers and polynuclear units in the solid state.[445,653] The presence of different constitutional isomers has been concluded from the NMR spectra. Analogous compounds are obtained when other 4,5-di-*n*-alkylphthalodinitriles are used.[654]

Oxorhenium(V) porphyrins or trichlororhenium(V) porphyrins are transformed into nitridorhenium(V) porphyrins with hydrazine hydrate in the presence of ethanol in good yields. The

diamagnetic complexes are stable towards hydrolysis and contain five-coordinate rhenium atoms in a square-pyramidal geometry. Their structure is deduced spectroscopically and the octaethyl-derivative has been studied crystallographically and shows a short Re≡N bond length of 1.633 Å.[655]

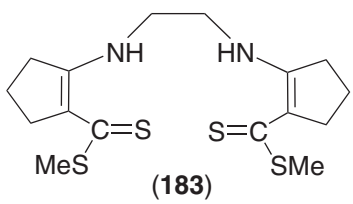
An unusual nitrido complex of rhenium(V) has been isolated from the reaction between $[ReNCl_2(PPh_3)_2]$ and 2,2′:6′,2″:6″,2‴-quarterpyridine in methanol. The rhenium atom in the $[ReNCl(PPh_3)(L)]^+$ cation, which represents the first seven-coordinate d^2 nitrido metal complex, has a distorted pentagonal bipyramidal geometry with the nitride ligand being almost coplanar with the nitrogen atoms of the chelating ligand.[434]

An unusual cleavage of the Re≡N bond during the reaction of $[ReNCl_2(PPh_3)_2]$ with cylam-type ligands (**121**) suggested further studies in order to explore the driving force of this type of reaction and the nature of the nitrogen-containing products. Cleavage of the C—N bonds of diethylenetriamine has been promoted by the reaction of the amine with $[ReNCl_2(PPh_3)_2]$ and the formation of β-alanine has been reported.[656] The conversion of $H_2NCH_2CH_2CH_2NH_2$ to $H_2NCH_2CH_2CO_2H$ requires the presence of atmospheric oxygen and CO_2.

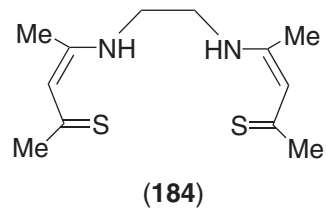
Reaction of $[ReOCl_3(PPh_3)_2]$ with *S*-methyl-2-methyldithiocarbazate under mild conditions gives the N⁀S-chelated complex $[ReO\{NHNMeC(SMe)S\}_2]Cl$ (**172**) which produced $[ReNCl_2(PPh_3)_2]$ when it is heated in the presence of HCl and PPh_3.[618]

The dianionic tetradentate N_2S_2 ligand *N*,*N*′-ethylenebis(methyl-2-aminocyclopentene-1-dithiocarboxylate (**183**) reacts with $[ReNCl_2(PPh_3)_2]$ to give an orange–red complex of the composition [ReN(L)]. It is interesting to note that deprotonation of the ligand is much slower than a similar reaction with *N*,*N*′-ethylenebis(thioacetonylideneimine) (**184**).[601]

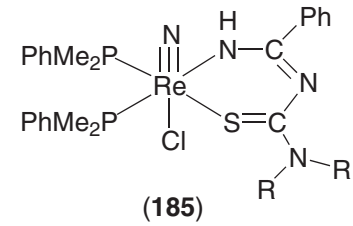
Different products have been isolated during ligand exchange reactions of dialkylthiocarbamoylbenzamidinates, HR_2tcb (**170**), with $[ReNCl_4]^-$ or $[ReNCl_2(PMe_2Ph)_3]$. Whereas the chloro complex gives red crystals of the composition $[ReN(R_2tcb)_2]$ in good yields,[225] the phosphine precursor yields $[ReNCl(PMe_2Ph)_2(R_2tcb)]$ with the chloro ligand *trans* to the nitrido nitrogen (**185**).[657] The compound undergoes stepwise ligand exchange reactions. Halides or pseudohalides preferentially replace the chloro ligand as has been demonstrated for Br^-, I^-, N_3^-, SCN^-, or CN^-.[658] Complexes with the coordination number five are obtained when sulfur-containing ligands are used: the reaction with 2,6-dimethylthiophenol substitutes one of the PMe_2Ph ligands and gives complexes of the type $[ReN(PMe_2Ph)(SC_6H_3\text{-}2,6\text{-}Me_2)(R_2tcb)]$ and $[ReN(PMe_2Ph)(mnt)]$ is obtained when the chelating ligand 1,2-dicyanoethene-1,2-dithiolate, mnt^{2-}, is used.[659]



(**183**)



(**184**)



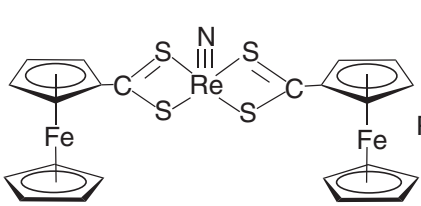
(**185**)

(c) Sulfur, oxygen, and mixed-donor S/O ligands. Nitrido complexes of rhenium(V) with chelating sulfur ligands have been known for a long time and a dithiocarbamato complex was the first ReN compound to have been characterized structurally.[660,661] In the light of the search for new rhenium chelates with promising nuclear medical properties the interest in this class of compounds has been renewed. This resulted in the development of TcN and ReN dithiocarbamato complexes of the general formula $[MN(L)_2]$ which accumulate in brain.[662] Structurally related, five-coordinate rhenium(V) nitrido complexes are obtained with thio-β-diketones[663] or ferrocenyldithiocarboxylato ligands. The blue bis-chelate (**186**) is formed in good yields when $[ReNCl_2(PPh_3)_2]$ reacts with piperidinium ferrocenyldithiocarboxylate.[664] Cyclic voltammetry of a CH_2Cl_2 solution of the complex showed that a quasi-reversible oxidation process occurring at 0.306 V relative to the ferrocene/ferrocenium couple was established to involve a two-electron transfer by controlled electrolysis at 0.960 V (vs. Ag^0/Ag^+). This electron transfer was assigned to the oxidation of the two Fe^{II} atoms in the ligands and has also been observed for the analogous technetium complex.

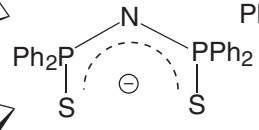
As discussed for dialkylthiocarbamoylbenzamidinates in Section 5.3.2.3.3(ii)(b), ligand exchange reactions starting from $[ReNCl_2(PMe_2Ph)_3]$ occur stepwise and stable mixed-ligand complexes can be isolated during such procedures. This has also been observed for reactions with

dialkyldithiocarbamates, R_2dtc^-, or 1,2-dicyanoethene-1,2-dithiolate, mnt^{2-}, where complexes of the compositions $[ReN(Cl)(R_2dtc)(PMe_2Ph)_2]$[665] and $[ReN(R_2dtc)_2(PMe_2Ph)]$[665] or $[ReN(mnt)(PMe_2Ph)_2]$[659] are formed intermediately. The final products of the reactions are the five-coordinate bis-chelates $[ReN(R_2dtc)_2]$[665] and $[ReN(mnt)_2]^{2-}$.[225] A similar ligand exchange behavior has been observed for bis(diphenylthiophosphoryl)amide, $\{N(SPPh_2)_2\}^-$ (**187**). The mononegative ligand reacts with $[ReNCl_2(PMe_2Ph)_3]$ with formation of the mixed-ligand complex $[ReNCl\{N(SPPh_2)_2\}(PMe_2Ph)_2]$ independent of the $[ReNCl_2(PMe_2Ph)_3]$/ligand ratio and the reaction conditions applied, whereas with $[ReNCl_2(PPh_3)_2]$ the bis-chelate $[ReN\{N(SPPh_2)\}_2]$ is obtained.[666,667] The nitrido ligand in the latter compound is nucleophilic and reacts readily with Lewis acids.[666,668]

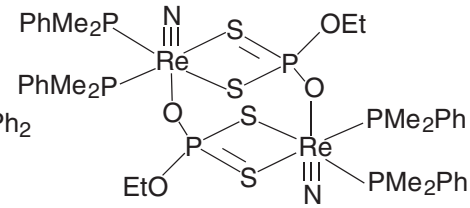
A more complicated reaction pattern has been reported for the reaction of $[ReNCl_2(PMe_2Ph)_3]$ with *O*,*O*′-diethyldithiophosphate. Each one of the ethyl groups of the ligands is removed during the reaction and the resulting fragments act as tridentate, dianionic ligands which connect two rhenium atoms giving the dimeric complex $[ReN(PMe_2Ph)_2\{S_2PO(OEt)\}]_2$ (**188**).[665]



(**186**)



(**187**)

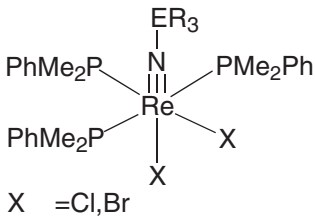


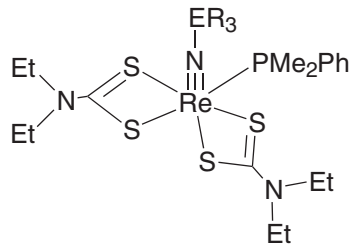
(**188**)

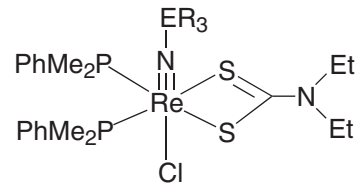
A remarkable rhenium(V) nitrido complex has been isolated with Kläui's tripod ligand $[Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3]^-$ (**19**) which is known to stabilize metal ions in high oxidation states due to its excellent π-donating capabilities. The neutral rhenium(V) chelate $[ReNCl(PPh_3)\{Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3\}]$ is obtained from a reaction of the sodium salt of the tripodal ligand with $[ReNCl_2(PPh_3)_2]$ in form of yellow crystals in moderate yields.[229] The compound can readily be oxidized with $AgBF_4$ to the corresponding rhenium(VI) cation. Its nitrido ligand is nucleophilic and reacts with carbonium salts or Lewis acidic metal complexes under formation of imido complexes and heterometallic, nitrido-bridged compounds, respectively.

(iii) Complexes with Bridging Nitrido Ligands

The first reports of adduct formation between rhenium nitrido compounds and boron halides were published by Chatt[669,670] and Dehnicke.[671] The first crystallographically characterized compound of this type was $[Re(NBCl_3)Cl_2(PMe_2Ph)_3]$, prepared from the reaction of $[ReNCl_2(PMe_2Ph)_3]$ with boron trichloride.[672] Following this general procedure a number of new compounds with Re≡N—B and Re≡N—Ga bonds have been prepared. Nitrido ligands of complexes with six-coordinate rhenium atoms (particularly $[ReNX_2(PMe_2Ph)_3]$ (X = Cl, Br, NCS) or $[ReN(Et_2dtc)_2(PMe_2Ph)]$) readily react with boron halides, $GaCl_3$ or boranes to form stable adducts $[Re(NER_3)X_2(PMe_2Ph)_3]$ (**189**) or $[Re(NER_3)(Et_2dtc)_2(PMe_2Ph)]$ (**190**).[251,637,673–677] A similar reactivity has been observed towards carbonium cations which yield imido compounds (see Section 5.3.2.3.4). Rearrangements in the equatorial coordination sphere of the metal have been observed during reactions of $[ReN(Cl)(Et_2dtc)(PMe_2Ph)_2]$ or $[ReN(Cl)(Et_2tcb)(PMe_2Ph)_2]$ with boron halides,[676,678] whereas $B(C_6F_5)_3$ and BCl_2Ph form simple adducts of the type (**191**).[676,677] The formation of the nitrido bridge has little effect on the Re—N multiple bond, whereas the bond in *trans* position to the nitrogen atom is significantly shortened. This suggests a marked decrease of the structural *trans* influence of the nitrido ligand as a consequence of the formation of a nitrido bridge.[679] Another interesting feature is the mean bond angle between the nitrido nitrogen and the equatorial coordination sphere of the metal atom which remains almost unchanged despite the decrease of *trans* bond lengths. This strongly suggests that the reason for the *trans* influence is mainly of electronic nature as has also been suggested by density functional theory calculations for five- and six-coordinate osmium nitrido complexes.[680] The experimentally obtained bond distances and angles of the nitrido-bridged boron and gallium adducts are well reproduced by quantum chemical calculations using gradient-corrected density functional theory (B3LYP) and *ab initio* methods at the MP2 level.[681]



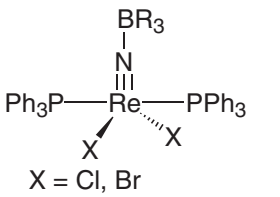


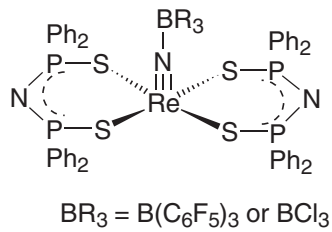


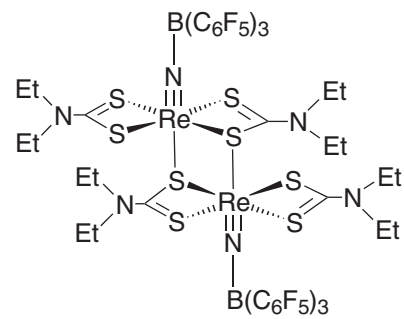
$ER_3 = BCl_3, BBr_3, BCl_2Ph, B(C_6F_5)_3, BEt_3, BPh_3, BH_3, GaCl_3$

(**189**) (**190**) (**191**)

Nitrido bridges with five-coordinate rhenium complexes are only formed with the most reactive Lewis acids such as BCl_2Ph, BCl_3, and $B(C_6F_5)_3$. This has been shown for the complexes $[ReNCl_2(PPh_3)_2]$, $[ReN\{N(SPPh_2)_2\}_2]$ and $[ReN(Et_2dtc)_2]$ and compounds of the types (**192**)–(**194**) have been isolated and structurally characterized.[666,677,679] Similar behavior has been proposed for nitrido(phthalocyaninato)rhenium(V) complexes based on spectroscopic data.[654] As previously observed for complexes with coordination number 6, only a moderate increase of the rhenium–nitrogen multiple bond was observed and the N—Re—L angles remain almost uninfluenced even when bulky Lewis acids such as $B(C_6F_5)_3$ are used. A remarkable feature of this chemistry is the increase in the coordination number of $[ReN(Et_2dtc)_2]$ as a consequence of the formation of a nitrido bridge.[682] The five-coordinate starting complex dimerizes during the reaction with $B(C_6F_5)_3$ with formation of two Re—S bonds (2.835 Å and 2.856 Å) with sulfur atoms of the neighboring molecules (**194**). This strongly suggests that five-coordination in nitrido (and probably also oxo) complexes is a consequence of the strong *trans*-influence of the multiple bond.



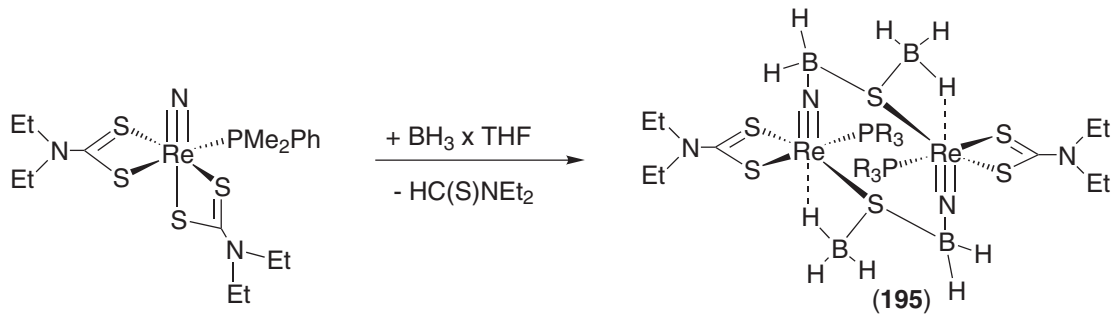




(**192**) (**193**) (**194**)

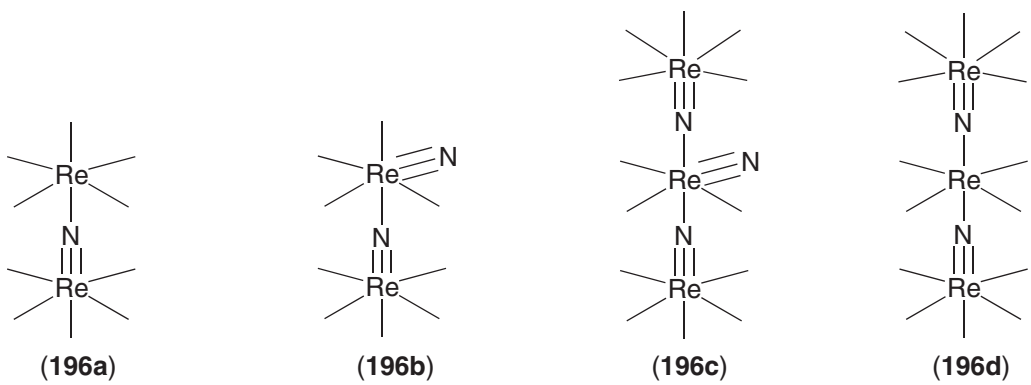
Whereas reactions of $[ReN(Et_2dtc)_2(PMe_2Ph)]$ with boron halides, alkyl boranes, or aryl boranes produce Lewis acid adducts at the nitrido group, the electrophilic attack of BH_3 (as THF adduct) is directed to a sulfur atom of a dithiocarbamate ligand.[683] This results in the release of thioformic acid diethylamide and the formation of the $[H_2B—S—BH_3]^-$ anion which then attacks the nitrido ligand to form a nitrido bridge. The final product is an orange–red, dimeric rhenium(V) complex with two bridging $(NBH_2SBH_3)^{4-}$ ligands (**195**) (Scheme 18). Two Re≡N—B bridges are contained in a carbon-free, eight-membered metallacycle. The position *trans* to the nitrido group is occupied by a hydrido hydrogen atom of the —S—BH_3 unit.

The neutral nitride chloride $[ReNCl_4]$ is the first compound in which an asymmetric nitrido bridge between two rhenium atoms has been found. Its structure is built of indefinite one-dimensional chains containing alternating short (1.58 Å) and long (2.48 Å) rhenium–nitrogen bonds.[224] This structural pattern is also found in bi-, tri-, or tetranuclear compounds which result from reactions of rhenium nitrido complexes with Lewis acids when their electrophilic attack is not directed towards the nitrido ligand but results in cleavage of rhenium-ligand bonds. The coordinating capabilities of the attacking Lewis acid and the conditions applied control the extent of the ligand release and the structure of the products. This general approach is not restricted to reactions with halides of main group elements, but has also been observed for Lewis-acidic halides



Scheme 18

of some transition metals.[684,685] The individual compositions of the nitrido-bridged chains, cages, or rings depend on the acceptor properties of the Lewis base. This has been demonstrated for the starting complexes $[ReNCl_2(Me_2PhP)_3]$ and $[ReN(Et_2dtc)(Me_2PhP)]$ which give compounds of the types (**196a**) to (**196g**) when exposed to Lewis acidic compounds such as Al_2Cl_6, TlCl, $GeCl_4$, $SbCl_3$, $SbCl_5$, Pr(tosylate)$_3$, $ZrCl_4$, or $NbCl_5$.[231,686–690] All these arrangements contain almost linear, asymmetric nitrido bridges with one rhenium–nitrogen bond of about 1.7 Å which can be assigned to a triple bond and one longer bond which corresponds to a single bond. A similar result has been observed for the reaction of the neutral rhenium(V) chelate $[ReNCl(PPh_3)\{Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3\}]$ (**53**) with $[ReO_3Me]$ which gives the red adduct complex $[Re(NReO_3Me)Cl(PPh_3)(Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3)]$ in moderate yields.[229] The compound is unstable and decomposes in solution with re-formation of the starting materials.

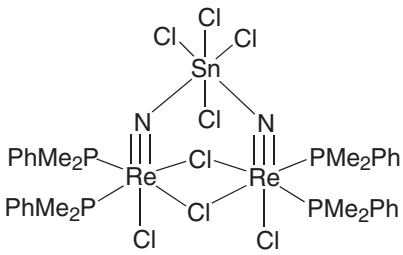


Two more examples of rhenium complexes with nitrido bridges contain additional thionitrosyl and/or dinitridosulfato ligands. The dianionic $[Cl_2Re(N_3S_2)(\mu\text{-}NSN)(\mu\text{-}N{\equiv}ReCl_3)]_2^{2-}$ is formed during the reaction of $[ReCl_4(NSCl)_2]^-$ with N(TMS)$_3$ in dichloromethane.[173] The complex anion consists of a planar ReN_3S_2-heterocycle which is connected with a second rhenium atom by a μ-nitrido bridge as well as by a μ-dinitridosulfato ligand. Two of these $[Cl_2Re(N_3S_2)(\mu\text{-}NSN)(\mu\text{-}N{\equiv}ReCl_3)]$ units dimerize via one of the *N*-atoms of the $(NSN)^{4-}$ ligand to give a centrosymmetric Re_2N_2 four-membered ring. A similar reaction with an excess of N(TMS)$_3$ gives the

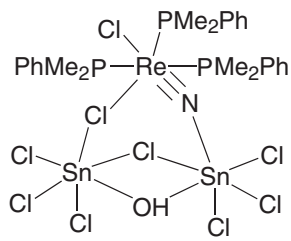
dimeric complex anion $[(SN)ReCl_3)(\mu\text{-}N)(\mu\text{-}NSN)ReCl_3(THF)]^{2-}$. The rhenium atoms are connected by an asymmetric nitrido bridge (ReN bond lengths of 1.883 Å and 2.244 Å) as well as by a $(NSN)^{4-}$ bridge to form a planar $Re_2N(NSN)$ six-membered heterocycle. Both rhenium atoms are coordinated by three chlorine atoms, one of them by a thionitrosyl ligand, the other by a THF molecule.[691]

A number of Lewis-acidic fragments of transition metal complexes have been found to coordinate at terminal nitrido ligands of rhenium complexes and, thus, represent building blocks for multinuclear complexes. A number of binuclear compounds with asymmetric nitrido bridges between rhenium and another metal are known derived from $[ReNCl_2(PMe_2Ph)_3]$ and Lewis acidic metal halides or their derivatives. This involves gold,[692] zinc,[693] titanium,[694] zirconium,[695] tin,[695] molybdenum,[696] and ruthenium compounds.[229,697,698] The formation of nitrido-bridged compounds is supported by the presence of coordinating solvents such as acetonitrile or THF. A binuclear compound, $[Re(NAuPPh_3)Cl(PPh_3)\{Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3\}]$, can also be isolated as greenish yellow crystals from a reaction of the rhenium(V) nitrido complex $[ReNCl(PPh_3)(Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3)]$ (**53**) with $[Au(PPh_3)(CF_3SO_3)]$ in diethylether.[229]

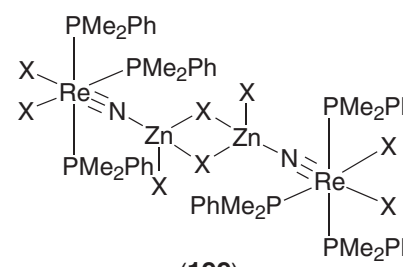
Trinuclear compounds with Re≡N—M—N≡Re units have been synthesized with central $NbCl_4$,[685] $MoCl_4$,[696] $TiCl_4$,[694] and $VOCl_2$ units.[699] More complicated structures have been found for bridging zinc or tin halides. In the brown, air-sensitive complex $[\{ReNCl(PMe_2Ph)_2(\mu\text{-}Cl)\}SnCl_4]$ two rhenium fragments, which are connected by two chloro bridges, coordinate one $SnCl_4$ molecule via their nitrido ligands (**197**). The two resulting nitrido bridges complete the distorted octahedral coordination sphere of the Sn atom with a *cis*-arrangement of the nitrogen atoms.[700] The bent nitrido bridges with a Re–N–Sn angle of 155° are asymmetrical. An incomplete exclusion of water leads to the formation of red–violet, air-stable crystals of $[\{ReNCl(PMe_2Ph)_3\}Sn_2(OH)Cl_7]$ (**198**).[700] In the diamagnetic complex one molecule of $[ReNCl_2(PMe_2Ph)_3]$ is coordinated by the nitrido ligand and one Cl bridge to the tin atoms of a $[Sn_2(OH)Cl_7]$ unit. In this unit the two Sn atoms are connected by one Cl and one OH bridge. The reaction of $[ReNCl_2(PMe_2Ph)_3]$ with $ZnCl_2$ or $ZnBr_2$ yields the tetranuclear complexes $[X_2(PMe_2Ph)_3Re{\equiv}NZnX_2]_2$ (X = Cl, Br) (**199**).[693] In the case of the reaction with $ZnBr_2$, halogen exchange is observed. The centrosymmetric complexes have central $[XZn(\mu\text{-}X)_2ZnX]$ units and the tetrahedral coordination sphere of zinc is completed by the nitrido ligands of the $[ReNCl_2(PMe_2Ph)_3]$ units. Trinuclear compounds with Re≡NPt bridges have been obtained by the reaction of $[ReNCl_4]^-$ with various platinum starting materials. The nitrido bridges are linear and asymmetric with platinum–nitrogen distances between 1.88 Å and 1.94 Å.[701]



(**197**)



(**198**)



(**199**)

5.3.2.3.4 *Imido complexes*

The formally dianionic imido ligands "NR^{2-}" are isoelectronic with the oxo ligand and stabilize metals in their high oxidation states. Numerous synthetic approaches to organoimido complexes have been described involving reactions of oxorhenium complexes with appropriate precursors of the NR fragment such as $ArNH_2$, ArNCO, ArNHNHCOPh, ArNSO, $Ph_3PNCOPh$, or RNHNHR·2HCl (R = alkyl).[702] The driving force in all these reactions is the oxygen transfer from the rhenium atom to an appropriate acceptor to form species such as H_2O, CO_2, SO_2, or $OPPh_3$. For reactions with RNHNHR·2HCl, an excess of PPh_3 is employed as oxygen acceptor. The potential of the imido core for future nuclear medical applications is obvious since the organic substituent can readily be varied which allows a fine-tuning of the biological properties of the potential radiopharmaceutical or the introduction of functional groups which allow the coupling with biomolecules.

(i) Complexes containing exclusively monodentate ligands

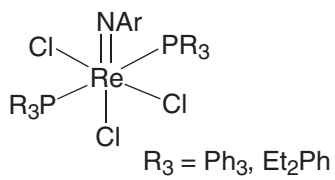
Phosphine complexes of the general composition $[Re(NAr)X_3(PR_3)_2]$ (Ar = (substituted) aryl; X = Cl, Br, I; $PR_3 = PPh_3$, PEt_2Ph) can be regarded as key compounds for the synthesis of arylimido complexes with chelating ligands and, thus, their synthesis and characterization was subject of special interest. $[Re(NPh)Cl_3(PPh_3)_2]$ is obtained from reactions of $[ReOCl_3(PPh_3)_2]$ with phenylformamidine in boiling THF,[703] *N*-trimethylsilylaniline,[704,705] heptamethyldisilazan,[304] PhNHCH=NPh,[706] substituted anilines,[707,708] or by thermal decomposition of the rhenium(III) triazenido complex $[ReCl_2(PhNNNPh)(PPh_3)_2]$.[706] These routes are also appropriate for other precursors such as $[ReOCl_3(PEt_2Ph)_2]$,[704] or substituted anilines[706] which allows access to compounds which are interesting for nuclear medical research. Thus, reactions of $[ReOCl_3(PPh_3)_2]$ with *N*-substituted acetylarylhydrazines have been applied to prepare rhenium-containing derivatives of glycine and the cytotoxic compound chlorambucil.[709] The same approach can be used for labeling estradiol ligands with rhenium.[710] The imidorhenium(V) complex $[Re\{NC_6H_4CO_2N(COCH_2)_2\}Cl_3(PPh_3)_2]$ containing an *N*-succinimidyl ester function has been prepared starting from a functionalized phosphoraneiminate and is able to couple in aqueous dimethylformamide solutions with a series of primary and secondary amines, amino acids and biotin derivatives.[711]

The formation of arylimido ligands is often accompanied with ongoing ligand exchange in the equatorial coordination sphere of the metal. Depending on the starting materials and the conditions applied, phosphine and/or halide ligands can be replaced by amines which are formed from the nitrogen containing starting materials by solvolysis.[90,705,712]

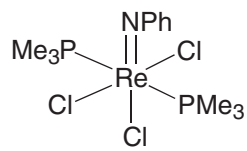
The reaction of 4-phenylenebis(triphenylphosphoraneimine), $Ph_3P{=}NC_6H_4N{=}PPh_3$, with two equivalents of $[ReOCl_3(PPh_3)_2]$ produces $OPPh_3$ and the 4-phenylendiimido-bridged dirhenium species $[(PPh_3)_2Cl_3Re{=}NC_6H_4N{=}ReCl_3(PPh_3)_2]$.[713] Ligand exchange products of this complex with dithiocarbamates can be used as building block for the synthesis of oxo-bridged, multi-metallic chains.

The formation of arylimido complexes starting from phosphine-free precursors has been demonstrated for $[ReOCl_4]$ and the dimeric, oxo-bridged pyridine complex *cis*-$[Re_2O_3Cl_4(py)_4]$. $[ReOCl_4]$ reacts with PhCNO to give the polymeric $[Re(NPh)Cl_4]_n$ which is an excellent precursor for ligand exchange reactions.[235] Dissolution in THF or acetonitrile gives the rhenium(VI) adducts $[Re(NPh)Cl_4(THF)]$ or $[Re(NPh)Cl_4(MeCN)]$, whereas the reactions with $[Me_4N]Cl$, PPh_3 or $TMSNHCMe_3$ yield $[Me_4N][Re(NPh)Cl_5]$, $[Re(NPh)Cl_3(PPh_3)_2]$, and $[Re(NPh)Cl_3(NH_2CMe_3)_2]$, respectively. The reaction of *cis*-$[Re_2O_3Cl_4(py)_4]$ with *N*-trimethylsilylaniline yields the cationic complex $[Re(NPh)(OTMS)Cl(NH_2Ph)(py)_2]^+$ with two pyridine ligands in *cis*-arrangement to each other.[319]

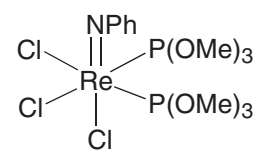
$[Re(NPh)Cl_3(PPh_3)_2]$ (**200**) is a useful material for ligand exchange reactions as has been demonstrated for the synthesis of numerous complexes with chelating ligands. Replacement of PPh_3 ligands by trimethylphosphine, PMe_3, or trimethylphosphite, $P(OMe)_3$, leads to *mer*,*trans*-$[Re(NPh)Cl_3(PPh_3)(PMe_3)]$ (**201a**) and *fac*-$[Re(NPh)Cl_3(PPh_3)\{P(OMe)_3\}]$ (**201b**), respectively. The different arrangements of the phosphorus ligands in both products have been attributed to differences in the coordinating abilities between trimethylphosphine and trimethylphosphite to the five-coordinate fluxional intermediate.[714] *fac*-Arrangement of the chloro ligands is also observed in $[Re(NPh)Cl_3(PPh_3)(CO)]$ which was obtained in good yields from a reaction of $[Re(NPh)Cl_3(PPh_3)_2]$ with 5 atm of CO at room temperature.[715] Anionic aryimido complexes of the composition $[Re(NAr)(SR)_4]^-$ (Ar = Ph, 4-C_6H_4OMe, 4-C_6H_4Me; R = 2,4,6-triisopropylphenyl) can be isolated by the reaction of $[Re(NAr)Cl_3(PPh_3)_2]$ complexes with the bulky thiol and triethylamine, whereas N_2 loss and the isolation of an oxo complex was observed during a similar reaction with unsubstituted thiophenol.[232]



(**200**)



(**201a**)



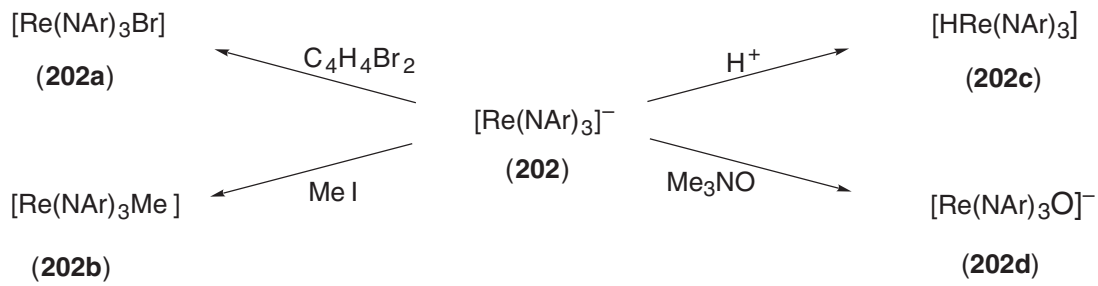
(**201b**)

A series of cationic methylimidorhenium(V) complexes, *trans*-$[Re(NMe)(py)_2(PPh_3)Cl(OEt)]^+$, *cis*-$[Re(NMe)(py)_2(PPh_3)Cl(OEt)]^+$, $[Re(NMe)(py)_3Cl(OEt)]^+$, and $[Re(NMe)(4\text{-}Me\text{-}py)_2(PPh_3)Cl(OEt)]^+$ have been prepared by ligand exchange starting from $[Re(NMe)Cl_3(PPh_3)_3]$

and the ligands in ethanol.[716] The *cis* isomers were obtained when the reactions are conducted at room temperature.

Another approach to imido complexes makes use of the basicity of terminal nitrido ligands and their reactions with Lewis acids such as carbonium ions. The formation of {$Re(NCPh_3$} units by the reaction of nitridorhenium(VI) compounds with $[CPh_3][PF_6]$ has already been described in Section 5.3.2.2.2, but the general route can also be applied for rhenium(V) compounds and also works with carbonium ions generated *in situ* as has been demonstrated for the reaction of nitridorhenium(V) complexes in acidic acetone. Blue compounds of the composition *fac*-$[Re(NCMe_2CH_2COMe)X_3(PMe_2Ph)_2]$ (X = Cl, Br) have been isolated during such reactions and the formation of the unusual $(NCMe_2CH_2COMe)^{2-}$ ligand can be attributed to a nucleophilic attack of the nitrido ligand on a carbonium ion which is formed from the condensation of two molecules of acetone.[717] Similar results have been obtained during reactions of $[ReNCl_2(PMe_2Ph)_3]$ with other Lewis acids, during which the solvent CH_2Cl_2 decomposes. The released protons reacted with the nitrido function with formation of imido complex $[Re(NH)Cl_2(PMe_2Ph)_3]^+$ which was isolated and structurally characterized as $[SbCl_6]^-$ and $[TaCl_6]^-$ salts.[690,699]

Rhenium(V) compounds containing two or three imido ligands have been prepared by reduction of appropriate rhenium(VII) complexes. $[Re(NAr)_2Cl_3(py)]$ (Ar = C_6H_3-2,6-C_3H_7) reacts with zinc dust in THF in the presence of excess pyridine to give the red–brown complex $[Re(NAr)_2Cl(py)_2]$.[718] This product undergoes ligand exchange with phosphines to yield $[Re(NAr)_2Cl(py)(PR_3)]$ ($PR_3 = PPh_3$ or PMe_2Ph) complexes.[719] Addition of thallium tetrafluoroborate to $[Re(NAr)_2Cl(py)(PMe_2Ph)]$ in the presence of PMe_2Ph yields the cation $[Re(NAr)_2(PMe_2Ph)_2]^+$. $[Re(NAr)_3Cl]$ is cleanly reduced by two equivalents of sodium amalgam in THF to give $[Na\text{-}(THF)_2][Re(NAr)_3]$.[720] The corresponding $[NEt_4]^+$ salt is formed in the presence of $[NEt_4]Cl$. The trisimidorhenium(V) anion (**202**) undergoes a number of reactions which give access to a series of novel imido species (**202a**)–(**202d**) (Scheme 19). When only one equivalent of sodium amalgam is used during the reduction of $[Re(NAr)_3Cl]$, the trimeric compound $[Hg\{Re(NAr)_3\}_2]$ is formed. The crystal structure of the compound shows a Re—Hg distance of 2.62 Å which has been assigned to a metal–metal single bond.



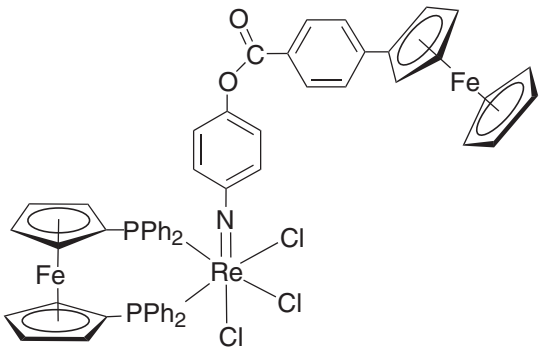
Scheme 19

(ii) Complexes containing chelating ligands

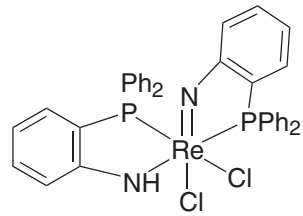
(a) Phosphorus and arsenic donor ligands. Arylimido complexes with chelating P∩P ligands have been prepared with dppe and 1,1′-bis(diphenylphosphino)ferrocene. A ligand exchange procedure starting from $[Re(NPh)Cl_3(PPh_3)_2]$ yields the cation $[Re(NPh)Cl(dppe)_2]^{2+}$,[721,722] and the neutral complex $[Re(NPh)Cl_3(L)]$ with one chelating 1,1′-bis(diphenylphosphino)ferrocene ligand in the equatorial coordination sphere.[723] A similar product, but with an arylamido ligand which is conjugated to another ferrocenyl unit has been reported with trichloro(4-imidophenyl-4′ferrocenyl benzoate){1,1-bis(diphenylphosphine)ferrocene}rhenium(V) (**203**), which has been prepared from the corresponding oxo compound and 4-aminophenyl-4′-ferrocenyl benzoate.[708]

The reaction of $[ReOCl_3(PPh_3)_2]$ in toluene with 2-diphenylphosphinoaniline, H_2dpa, yielded the brown rhenium(V) amido/imido complex $[Re(dpa)(Hdpa)Cl_2]$ (**204**).[724,725] One of the 2-aminophenylphosphine molecules is fully deprotonated to give an N∩P chelated imino ligand, whereas the other acts as monoanionic amidophosphinato ligand. The different bonding in two N∩P ligands can clearly be distinguished by the Re—N bond lengths which are 1.76 Å for the multiple bond and 1.99 Å for the single bond. Analogous reactions with 8-aminoquinoline yield

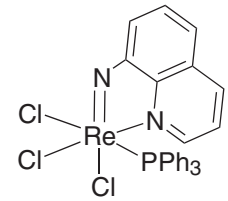
the cationic oxo complex $[ReO(PPh_3)(8\text{-}HNC_9H_6N)_2]^+$ with two amido ligands,[724] or *fac*-trichloro-(quinolin-8-imido-*N*,*N*′)(triphenylphosphine)rhenium(V) (**205**), depending on the conditions used.[726] With anthranilic acid in ethanol a complex with the iminobenzoate ligand, $[Re(NC_6H_4COO)Cl(OEt)(PPh_3)_2]$, is cleanly formed.[727] The compound contains a chelating imino-benzoate ligand and *trans* Ph_3P ligands which are *cis* to the bent imino function.[728] Simple substitution reactions of $[Re(NPh)Cl_3(PPh_3)_2]$ with 2-diphenylphosphinoaniline gives the neutral compound $[Re(NPh)Cl(Hdpa)_2]$ or the cation $[Re(NPh)Cl(Hdpa)(H_2dpa)]^+$ depending on the solvent polarity.[729] Conversely, the tetradentate ligand *N*,*N*′-bis{2-(diphenylphos-phino)phenyl}propane-1,3-diamine, H_2dppd (**131**), gives only the cationic compound $[Re(NPh)Cl(Hdppd)]^+$. In alkaline alcohols, the neutral complexes $[Re(NPh)(OMe)(Hdpa)_2]$ and $[Re(NPh)(OEt)(dppd)]$ were obtained. The reaction of H_2dpa in a 1:1 ligand to precursor ratio produces the monosubstituted complex $[Re(NPh)Cl_3(H_2dpa)]$.[729]



(**203**)



(**204**)



(**205**)

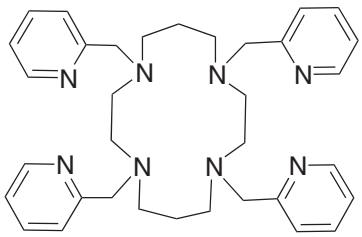
Analogous compounds have been prepared with 2-diphenylphosphinomethyl-4-methylphenol, whereas with 2-diisopropylphosphinophenol,[455] HP⌒O, a mixture of monosubstituted and disub-stituted complexes of the compositions $[Re(NPh)Cl_2(PPh_3)(P⌒O)]$ and $[Re(NPh)Cl(P⌒O)_2]$ were obtained.[456]

(b) Nitrogen donor and mixed N/S and N/O donor ligands. A complex with two *trans* bipyridine, *trans*-$[Re(NPh)(OEt)(bipy)_2]^{2+}$, is formed when $[Re(NPh)Cl_3(bipy)]$ reacts with bipy in ethanol.[721] The bonding situation in this compound contrasts that in the starting complex as well as in an analogous terpyridine compound which possess a nitrogen atom *trans* to the imido ligand.[730] Equatorial coordination of four aromatic nitrogen donor atoms is also observed for a complex with 1,2-bis(2,2′-bipyridyl-6-yl)ethane, *o*-bpy.[731] The rhenium atom in the $[Re(NPh)(o\text{–}bpy)(OEt)]^{2+}$ cation adopts a distorted octahedral geometry. Similar bonding situations are found in $[Re(NPh)(OH)(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane),[442] as in its oxo analogue. Both *trans*-$[Re(NPh)(OEt)(cyclam)]^{2+}$ and *trans*-$[Re(NPh)(OH)(cyclam)]^{2+}$ show a one-electron reduction wave in acetonitrile at potentials of −1.0 V and −1.4 V vs. SCE, respectively. E^0 for reduction of the *trans*-$[Re(NPh)(OEt)(cyclam)]^{2+/+}$ couple is less negative than that of the redox pair of analogous oxo complexes. A completely different coordination mode is obtained with 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (**206**), which reacts with $[Re(NPh)Cl_3(PPh_3)_2]$ in ethanol to give the cationic $[Re(NPh)(L)(EtOH]^{3+}$ which has been iso-lated and structurally characterized as its PF_6^- salt. The metal is coordinated by two aza and two pyridine nitrogen atoms of the ligand while the other four N atoms remain uncoordinated.[732]

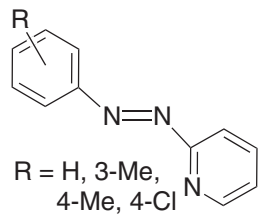
Imido complexes with the tridentate ligand 1,4,7-triazacyclononane (tacn) (**15a**) have been prepared following two different protocols. Whereas the green, dicationic compound $[Re(NPh)(OH)(PPh_3)(tacn)](ClO_4)_2$ was obtained by reacting $[Re(NPh)Cl_3(PPh_3)_2]$ with an excess of the ligand in CH_2Cl_2,[733] mixed-ligand compounds containing additional oxalato or carboxyl-ato ligands of the compositions $[Re(NBu^t)(oxalate)(tacn)]^+$ and $[Re(NBu^t)(CF_3COO)_2(tacn)]^+$ were isolated from the reduction of the rhenium(VII) complex $[ReO_2(NBu^t)(tacn)]^+$ in the pre-sence of oxalic acid or CF_3CO_2H.[190]

Rhenium(V) 4-tolylimido complexes with the hydrotris(pyrazolyl)borate ligand, $\{HB(pz)_3\}^-$, are formed on heating the oxo derivatives $[ReOX_2\{HB(pz)_3\}]$ (X = Cl, I) with 4-toluidine, whereas reactions with amines at ambient temperatures only give oxo complexes of the composition $[ReO(NHR)Cl\{HB(pz)_3\}]$. The $[Re(NC_6H_4\text{-}4\text{-}Me)X_2\{HB(pz)_3]$ complexes react with $ZnEt_2$ with formation of imido-ethyl complexes of the composition $[Re(NC_6H_4\text{-}4\text{-}Me)Cl(Et)\{HB(pz)_3\}]$.[734]

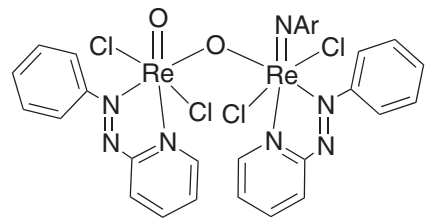
Azo splitting is observed during reactions of 2-(arylazo)pyridines, $RC_6H_4N{=}NC_5H_4N$ (**207**), with K_2ReCl_6 in boiling 2-methoxyethanol and violet crystals of the composition $[Re(NC_6H_4R)Cl_3(RC_6H_4N{=}NC_5H_4N)]$ are formed.[236] The coordinated arylimido moiety originates from the splitting of the azo function of a second azopyridine ligand. The complexes display a nearly reversible one-electron oxidation at $E^0 = 1.3$–1.4 V vs. SCE in acetonitrile. Oxorhenium(V) complexes of the composition $[ReOCl_3(RC_6H_4N{=}NC_5H_4N)]$ are formed when perrhenate is used as precursor. They can be quantitatively converted into violet imido species by reactions with excess of aromatic primary amines.[406,410] Reaction of equimolar amounts of oxo complex and amine gives the bluish violet binuclear complexes $[ReOCl_2(L)\text{-}O\text{-}Re(NAr)Cl_2(L)]$ (**208**). They possess an unusual structure with the oxorhenium(V) and imidorhenium(V) units connected by a μ-oxo ligand. A similar chemistry has been established for related 2-(arylazo)-1-methylimidazoles[407] and Schiff base ligands derived from pyridine-2-carbaldehyde and substituted anilines.[237,238,735]



(**206**)



(**207**)



(**208**)

The reaction of $[Re(NR)Cl_3(PPh_3)_2]$ (R = Me or 4-Me-C_6H_4) with salicylaldehyde (SalH) gives the imido complexes $[Re(NR)Cl_2(Sal)(PPh_3)]$.[736] The corresponding PMe_2Ph derivatives *cis*- and *trans*-$[Re(NMe)Cl_3(PMe_2Ph)_2]$ and *trans*-$[Re(NC_6H_4\text{-}4\text{-}Me)Cl_3(PMe_2Ph)_2]$ do not react with SalH or SalLi under the same experimental conditions. By reactions of $[Re(NC_6H_4\text{-}4\text{-}Me)Cl_2(Sal)(PPh_3)]$ with PR_3 ($PR_3 = PMe_2Ph$, PEt_2Ph, PEt_3, or $PMePh_2$) the complexes $[Re(NC_6H_4\text{-}4\text{-}Me)Cl_2(CHOSal)(PR_3)_2]$ are obtained in which the ligand is monodentate. Addition of toluidine to $[Re(NC_6H_4\text{-}4\text{-}Me)Cl_2(CHOSal)(PR_3)_2]$ and heating in ethanol results in the formation of a Schiff base which coordinates to the rhenium atom via the aldimine nitrogen and the phenolic oxygen.[736] A tridentate Schiff base coordination is obtained in $[Re(NR)(O^{\frown}N^{\frown}O)(O^{\frown}N^{\frown}OH)]$ complexes where R = Ph or C_6H_4-4-OMe and $H_2O^{\frown}N^{\frown}O$ is 2-hydroxybenzaldehyde-((1*R*,2*S*)-1-amino-2-indanol)imine or 3-(1-adamantyl)-2-hydroxy-5-methylbenzaldehyde-((1*R*,2*S*)-1-amino-2-indanol)imine.[498] The main characteristic of these complexes is the presence of two coordination modes for the Schiff base ligands on rhenium. In the latter, the hydroxy group of the indanol is free and is directed away from the coordination sphere.

Reactions of sterically hindered 3-TMS-pyridine-2-thiol (Me_3pySH) with $[Re(NPh)Cl_3(PPh_3)_2]$ yield the green rhenium(V) complex $[Re(NPh)(PPh_3)(Me_3pyS)_2]^+$, in which the rhenium atom has a distorted octahedral geometry with the imido and the phosphine ligands *cis*. An analogous reaction with the unsubstituted pyridine-2-thiol gives a product of similar composition.[724]

(c) Sulfur and oxygen donor and mixed S/O donor ligands. Organoimido compounds of rhenium(V) with sulfur and oxygen donor ligands can be prepared adopting the approaches above: (i) ligand exchange from complexes with a pre-formed imido core such as $[Re(NAr)Cl_3(PPh_3)_2]$, (ii) the replacement of oxo ligands by NAr^{2-} using appropriate nitrogen starting materials such as aromatic amines or iminophosphoranes, or (iii) the electrophilic attack of protons or carbonium ions on nitrido ligands.

A series of $[Re(NAr)Cl(S^{\frown}O)_2]$ complexes where $HS^{\frown}O$ represents *N*,*N*-diethyl-*N*′-benzoylthiourea (**134**) and Ar = C_6H_4-4-C(O)Me, C_6H_4-4-OMe, C_6H_4-2,6-($^iC_3H_7$)$_2$) has been prepared from reaction of the corresponding oxo compounds with substituted anilines in good yields. The green products are air-stable. NMR studies indicate a *cis* arrangement of the oxygen and sulfur atoms of the chelating ligands as has been found in the analogous oxo complex by X-ray structure determination.[478]

Ligand exchange reactions starting from $[Re(NPh)Cl_3(PPh_3)_2]$ and excess maltol in ethanol in the presence of triethylamine give a dark green solution from which the diamagnetic complex

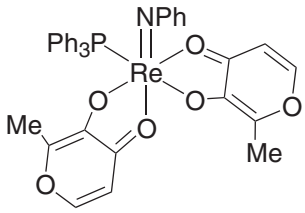
$[Re(NPh)(maltolate)_2(PPh_3)]^+$ has been isolated upon addition of $Na(BPh_4)$.[737] The complex has a pseudooctahedral structure with *cis*-maltolate ligands (**209**).

An electrochemical study on μ-oxo-bridged arylimido complexes with dithiocarbamato ligands of the composition $[\{Re(NAr)(S_2CNR_2)_2\}_2O]$ (Ar = Ph, C_6H_4-4-Me, C_6H_4-4-Cl, C_6H_4-4-OPh; R = Et, Ph) in *N*,*N*-dimethylformamide shows a quasi-reversible one-electron reduction followed by the cleavage of the μ-oxo bond and the release of one dithiocarbamate ligand from the complex.[738] The redox potential for the $[\{Re(NAr)(S_2CNR_2)_2\}_2O]^{0/-}$ couple and the stability of the reduction products strongly depend on the substituents on the imido and the dithiocarbamato ligands. The diphenyldithiocarbamato complexes are easier to reduce by 170 mV than their diethyldithiocarbamato analogues. A comparison with the electrochemical behavior of the analogous oxo complexes $[\{ReO(S_2CNR_2)_2\}_2O]$ shows that the imido complexes are more difficult to reduce as a consequence of the weaker π-bonding abilities of the ReNAr core. A $[\{Re(NAr)(S_2CNR_2)_2\}_2O]$ derivative with $Ar = C_6H_4CO_2N(COCH_2)_2$ and its monomeric analogue $[Re\{NC_6H_4CO_2N(COCH_2)_2\}$ have been prepared as potential precursors for coupling reactions with biomolecules.[711] They resist potential oxidation reactions caused by the *N*-hydroxysuccinimido substituent, but are not suitable for labeling experiments due to hydrolysis of the organoimido groups under the reaction conditions.

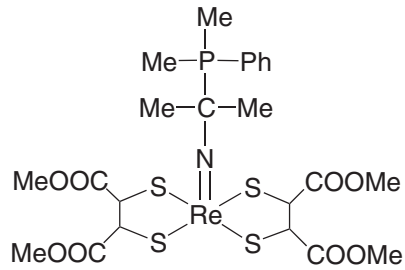
The reactivity of terminal nitrido ligands towards acidic fragments has been used for the synthesis of imido derivatives starting from the neutral rhenium(V) complex $[ReNCl(PPh_3)\{Co(\eta^5\text{-}C_5H_5)\{PO(OEt)_2\}_3\}]$ (**53**). Reactions with CF_3SO_2OMe, $PhCH_2Br$, or $(Ph_3C)BF_4$ afforded imido species with the $(NMe)^{2-}$, $(NCH_2Ph)^{2-}$, or $(NCPh_3)^{2-}$ ligands without changes in the primary coordination sphere of the metal.[229] Similar results have been obtained starting from the dithiocarbamato complex $[ReN(PMe_2Ph)(Et_2dtc)_2]$ and $(Ph_3C)PF_6$ or from a reaction of $[ReN\{N(SPPh_2)_2\}_2]$ with $(Ph_3C)BF_4$, which yield blue crystals of $[Re(NCPh_3)(PMe_2Ph)(Et_2dtc)_2](PF_6)$,[86] and the pale purple complex $[Re(NCPh_3)F\{N(SPPh_2)_2\}_2]$,[668] respectively. The latter compound is presumably formed via the cationic intermediate $[Re(NCPh_3)\{N(SPPh_2)_2\}_2]^+$. Protonation of nitrido ligands has been obtained during reactions of $[ReN\{N(SPPh_2)_2\}_2]$ with trihaloacetic acid anhydrides followed by recrystallization from CH_2Cl_2/hexane in air. The parent imido complexes $[Re(NH)(OCOCX_3)\{N(SPPh_2)_2\}_2]$ (X = Cl, F) have been isolated as yellowish–green crystals in low yields. Air-sensitive orange–red acylimido compounds have been obtained from the same nitrido precursor and acylating agents such as $(CF_3CO)_2O$ or RCOCl (R = $CHCl_2$, CH_2Cl, Me) when the reaction is performed under strictly anaerobic conditions.[668]

Unexpected reactions of released phosphine ligands have been observed during the ligand exchange reactions of $[ReNCl_2(PPh_3)_2]$ with 2-aminothiophenol ($H_2NC_6H_4SH$) and $[ReNCl_2(PMe_2Ph)_3]$ with dimercaptosuccinic acid dimethylester (H_2DMSMe_2). $[ReNCl_2(PPh_3)_2]$ reacts at room temperature in air with a slight excess of 2-aminothiophenol to give the orange–red, air-stable phosphoraneiminato complex $[Re(NPPh_3)(HNC_6H_4S)_2]$.[443] The formation of a phosphoraneiminato ligand from the interaction of a nitrido function represents a major route for the preparation of $\{M(NPR_3)\}$ functionalities for many transition metals, and is not without precedent for rhenium, where it has been described for complexes with sterically hindered thiols,[739] but must be regarded as exception for rhenium in the light of the ready formation of nitrido complexes in reactions of appropriate oxo or chloro complexes with phosphoraneiminato precursors.[679] The formation of the unusual dimethylphenylphosphinoisopropylimido ligand has been observed during the reaction of $[ReNCl_2(PMe_2Ph)_3]$ with H_2DMSMe_2 in acetone which yields the complex $[Re(NCMe_2PMe_2Ph)(DMSMe_2)_2]$ (**210**) in moderate yields.[740,741] This can be understood by the coordination of the phosphine molecule to an intermediately formed product of the addition of acetone to the basic nitrido function. The proposed mechanism is proved by the isolation of a related product when the reaction is performed in methylethylketone and the mass spectrometrical detection of a rhenium complex containing the condensation product of the solvent: $[Re\{NC(Me)(Et)CH_2C(O)C_2H_5\}(PMe_2Ph)(DMSMe_2)_2]$,[740,741] which corresponds to similar products which have been described for rhenium complexes with phosphine ligands.[717,742]

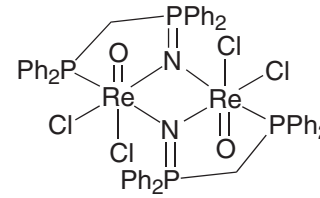
The coordination of a phosphoraneiminato ligand to a rhenium(V) center has been observed during the reaction of $[Bu_4N][ReOCl_4]$ with $TMSNP(Ph)_2CH_2P(Ph)_2$. The dimeric compound $[ReO\{NP(Ph)_2CH_2P(Ph)_2\}Cl_2]_2$ (**211**) deposits as blue crystals when equimolar amounts of the starting materials react at room temperature in dry acetonitrile. Excess of $TMSNP(Ph)_2CH_2P(Ph)_2$ leads to the formation of nitrido species and the cationic phosphoraneimine complex $[ReN(OTMS)\{HNP(Ph)_2CH_2P(Ph)_2\}_2]Cl$ has been isolated when moist acetonitrile or CH_2Cl_2 have been used as solvents.[679]



(**209**)



(**210**)



(**211**)

5.3.2.3.5 Miscellaneous

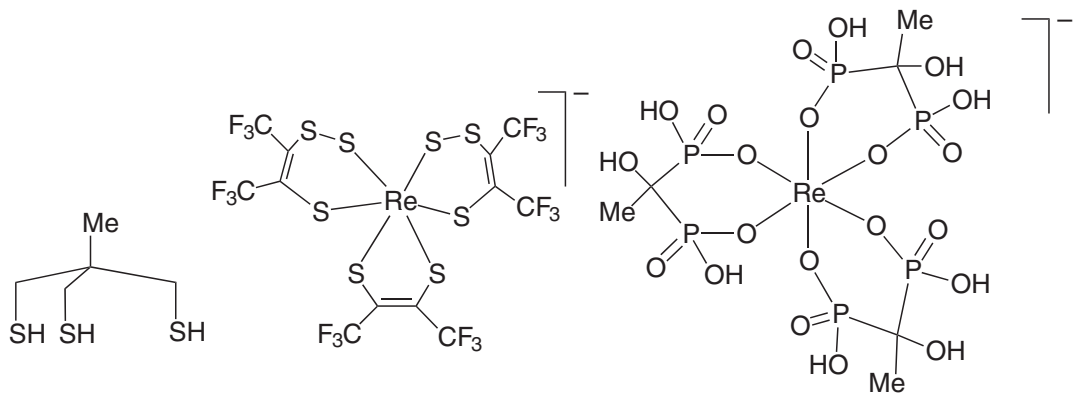
Although the chemistry of rhenium(V) is dominated by multiply bonded ligands such as oxo, nitrido, sulfido or imido groups, a number of compounds are known which contain the metal in other coordination environments. Hydrazido complexes and related compounds will be treated separately in Section 5.3.2.9 since the electronic situation in these complexes and, thus, the formal oxidation state of the metal depends on many factors and cannot be defined unambiguously for each individual compound without detailed knowledge about bond lengths and angles, and the degree of protonation/deprotonation of the arylhydrazine skeleton.

A new and efficient synthesis for the hexachlororhenate(V) anion, $[ReCl_6]^-$, has been reported with the oxidation of $[ReCl_6]^{2-}$ by PbO_2 in a slurry of CH_2Cl_2.[743] The product can be isolated as tetrabutylammonium salt as orange–red crystals. The solution electronic absorption spectrum is dominated by two intense chlorine-to-rhenium(V) charge transfer manifolds. The analogous fluoro anion, $[ReF_6]^-$, is formed when rheniumhexafluoride reacts with $KrF[Sb_2F_{11}]$ or $KrF[SbCl_6]$.[744] The Raman spectrum of the obtained products show characteristic strong bands of $[ReF_6]^-$ at 796 cm^{-1} and 358 cm^{-1}.

The outstanding donor abilities of thiolato ligands allow the stabilization of rhenium(V) complexes even without additional multiply bonded ligands. The known examples, however, suggest that additionally to the charge compensation by the negatively charged ligands chelate formation and steric shielding of the metal ions play an important role. Consequently, stable complexes are preferably formed with bulky chelating ligands such as bi- and tetradentate phosphinothiolates (**128**) or 1,1,1-tris(2-thiomethyl)ethane, $(HSCH_2)_3CCH_3$ (**212**). The anionic complex $[Re\{(SCH_2)_3CCH_3\}_2]^-$ has been isolated as its tetraphenylphosphonium salt from a reaction of K_2ReCl_6 with $(HSCH_2)_3CCH_3$ in air.[357] The complex anion has a geometry which is close to trigonal prismatic. This is surprising since the aliphatic ligand does not belong to the dithiolene ligand class where the preferred formation of trigonal prismatic complexes can be explained by the unsaturated nature of the ligands and S–S interactions along the vertical edges of the prism. The donor atoms of each of the tridentate ligands in $[Re\{(SCH_2)_3CH_2CH_3\}_2]^-$, however, span triangular faces of the prism rather than the vertical edges. Obviously, there are significant contributions from the tripodal nature of the ligand which optimizes interactions between the sulfur 3*p* and the metal 5*d* orbitals and prevents ready disulfide formation due to steric restrictions. Intraligand interactions are discussed to explain the stability of the rhenium(III) tris-chelate $[Re(Ph_2PC_6H_4\text{-}2\text{-}S)_3]$, which has been prepared from several rhenium(III) and rhenium(V) precursors and the phosphinothiol (**128a**) in alkaline methanol.[745] Complexes with the coordination number eight have been isolated from reactions of $[ReS_4]^-$ with three equivalents of tetraethylthiuram disulfide,[163] or by the reduction of perrhenate with HCl and the potentially tetradentate ligand $P(C_6H_4\text{-}2\text{-}SH)_3$ (**128c**), in ethanol and subsequent treatment with Et_3N.[88] The resulting complex cations $[Re(S_2CNEt_2)_4]^+$ and $[Re\{P(C_6H_4\text{-}2\text{-}S)_3\}_2]^+$ both have geometries being between idealized square antiprismatic and dodecahedral. Another oxo-free diethyldithiocarbamato complex has been prepared in high yields starting from the common oxo-bridged dimer $[Re_2O_3(Et_2dtc)_4]$ and TMSCl in dichloromethane. The obtained compounds $[ReCl_2(Et_2dtc)_2]^+$ precursor allows a novel synthetic route into rhenium dithiocarbamate chemistry without an oxo core.[370] An unusual compound, which is most presumably the mixed chelate $[Re\{S_2C_2(CF_3)\}_2\{S_3C_2(CF_3)_2\}_2]$ (**213**) containing two perthio ligands results from the reaction between $[ReS_4]^-$ and bis(trifluoromethyl)-1,2-dithiete, $(CF_3)_2C_2S_2$.[168]

Structural studies on rhenium complexes containing complexone type ligands are of considerable interest in the light of the application of their technetium analogues in diagnostic nuclear

medicine and the interest in rhenium compounds for therapeutic purposes. Thus, rhenium complexes with 1,2-hydroxyethylidenediphosphonate (H_4HEDP) have been synthesized and studied using EXAFS. Products which have been obtained by reduction of perrhenate with tin chloride in the presence of the ligand are characterized by oligomeric structures with bridging HEDP ligands. Depending on the excess of phosphonic acid also products with Re—Re bonds and mixed Sn/Re complexes have been found. An anionic complex with the proposed structure $[Re(H_2HEDP)_3]^-$ (**214**) has been obtained via a ligand exchange approach starting from $[ReO_2(py)_4]^+$ with H_4HEDP in absolute ethanol.[746]



(**212**) (**213**) (**214**)

Oxygen abstraction from the $\{ReO\}^{3+}$ core has been observed during the reaction of $[ReOCl_3(PPh_3)_2]$ with 3-nitro-1,2-diaminobenzene (H_2dab-3-NO_2) which gives $[ReCl(PPh_3)_3(dab\text{-}3\text{-}NO_2)_2]$, whereas the same reaction with 4-nitro-1,2-diaminobenzene (H_2dab-4-NO_2) gives the monosubstitution product $[ReCl_3(PPh_3)_2(dab\text{-}4\text{-}NO_2)]$ in which the incoming ligand is doubly deprotonated at one nitrogen atom and coordinates as imido group.[747] $[ReCl(PPh_3)(dab\text{-}3\text{-}NO_2)_2]$ has an unusual skew-trapezoidal bipyramidal geometry.

The formation of a monomeric amidino complex has been reported for the reaction of rhenium pentachloride with di-isopropylcarbodiimid. A composition of $[ReCl_4(prop^i{}_2N_2CCl)]$ was derived from elemental analysis, spectroscopic data and the crystal structure of the molybdenum analogue.[748]

The tungstorhenate(V) heteropolyanion $[W_9ReO_{32}]^{5-}$ has been isolated as guanidinium and caesium salts from reaction of $[ReOCl_3(PPh_3)_2]^+$ with sodium tungstate. A crystallographic study shows the anion to be isostructural with decatungstate, $[W_{10}O_{32}]^{4-}$. The complex can be oxidized to rhenium(VI) and rhenium(VII) analogues which are less stable against hydrolysis.[208] Rhenium complexes of the $[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$ isomer, a mono-lacunary derivative of the Wells-Dawson ion $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$, have been isolated from the reaction of $K_{10}[\alpha_2\text{-}P_2W_{17}O_{61}]$ with K_2ReCl_6 in water. The resulting $K_7[\alpha_2\text{-}ReOP_2W_{17}O_{61}]$ salt can be oxidized by air to a rhenium(VI) species, oxidation with $Ag(O_3SCF_3)$ results in the rhenium(VII) species $[\alpha_2\text{-}P_2W_{17}O_{61}]^{5-}$.[209]

5.3.2.4 Oxidation State IV

Complexes containing rhenium in the oxidation state +IV are comparatively rare. There is no extended chemistry in aqueous media and many rhenium(IV) complexes tend to hydrolyze when exposed to water. The stabilization of rhenium(IV) centers requires a well-balanced donor-acceptor behavior of the ligands and, thus, none of the classical π-donor ligands such as O^{2-}, N^{3-}, or NR^{3-} or π-acceptors such as carbonyls or nitrosyls are characteristic for this oxidation state.

5.3.2.4.1 Complexes containing exclusively monodentate ligands

(i) Halide and pseudohalide ligands

Hexachlororhenate(IV), $[ReCl_6]^{2-}$, can easily be prepared by the reduction of $[ReO_4]^-$ by H_3PO_2 in HCl and has been explored structurally in more than 20 crystallographic studies.[749–751] An

alternative approach to $[NH_4]_2[ReCl_6]$ has been reported by the reaction between $ReCl_5$ and ammonium chloride which reduces the metal to the oxidation state +IV.[752] The ammonium cations are located on three-fold disordered positions, which allow hydrogen bridges to each four of the chlorine atoms of the hexachlororhenate anions. Hydrogen bridges have also been detected in the solid state structures of the $[ReCl_6]^{2-}$ salts with organic cations such as bipyridinium,[753] triethylammonium,[754] dibutylanilinium,[755] or crown ether-stabilized oxonium.[756]

Solutions of $[ReX_6]^{2-}$ complexes (X = Cl, Br) are phosphorescent at room temperature, with emission maxima of 1,340 nm (chloro complex) and 1,380 nm (bromo complex) at life times between 40 ns and 80 ns. The phosphorescences are assigned to the $\Gamma_8(^2T_{1g}) \rightarrow \Gamma_8(^4A2g)$ transition.[757] Both ions undergo one-electron oxidation on irradiation in the presence of acceptors such as chloranil or benzoquinones. This process is reversible, and back-electron transfer reactions are essentially diffusion-controlled. One-electron oxidation of $[ReCl_6]^{2-}$ has also been studied by thin-layer spectrochemical techniques in CH_2Cl_2 giving high resolution spectra for the generated d^2 ion.[758] Reversible one-electron reduction of $[ReCl_6]^{2-}$ has been performed voltammetrically in the basic aluminum chloride-1-methyl-3-ethylimidazolium chloride melt with a half-wave potential of −0.87 V vs. the Al^{3+}/Al couple. The dimeric metal–metal bonded $[Re_2Cl_9]^-$ ion can be reduced to the $[Re_2Cl_9]^{2-}$ species at a glassy-carbon electrode in a reversible electrode reaction. Like its parent compound $[Re_2Cl_9]^-$ the mixed rhenium(IV)/rhenium(III) anion $[Re_2Cl_9]^{2-}$ exhibits only limited stability in basic melts and converts to $[ReCl_6]^{2-}$ and the rhenium(III) complex $[Re_2Cl_8]^{2-}$ by the incorporation of chloride ions.[759]

Mixed-ligand $[ReCl_nBr_{6-n}]^{2-}$ compounds ($n = 1$–5) are formed when $[ReBr_6]^{2-}$ is dissolved in aqueous HCl followed by a rapid precipitation of the mixture of complex anions with caesium cations. The homogeneous crystalline solid shows luminescence under blue or UV excitation. Analysis of the spectra obtained at low temperatures show the presence of $[ReBrCl_5]^{2-}$, *cis*-$[ReCl_4Br_2]^{2-}$, and *fac*-$[ReCl_3Br_3]^{2-}$. The reverse reaction, starting from $[ReCl_6]^{2-}$ and aqueous HBr, forms predominantly $[ReBr_6]^{2-}$ together with the intermediates *trans*-$[ReCl_4Br_2]^{2-}$ and $[ReCl_2Br_4]^{2-}$.[760] Full separation of all 10 mixed-ligand species of the series $[ReBrxI_{6-n}]^{2-}$ ($n = 0$–6) including the geometrical isomers for $n = 2$–4 was achieved by ion exchange chromatography on diethylaminoethyl cellulose. The IR and Raman spectra of the products have been completely assigned according to point groups O_h, D_{4h}, C_{4v}, C_{3v}, and C_{2v}, as supported by normal coordinate analyses based on a general valence force field.[761] Similar preparation and separation procedures have been applied for the isolation and full structural and spectroscopic characterization of the chloro/iodorhenate(IV) complexes $[ReCl_5I]^{2-}$, *cis*- and *trans*-$[ReCl_4I_2]^{2-}$ and *fac*-$[ReCl_3I_3]^{2-}$. A mean lengthening of the Re–Cl distance by 0.02 Å and a shortening of the Re–I distance by 0.035 Å along the asymmetric Cl–Re–I axes compared with the symmetric X–Re–X axes are due to the stronger structural *trans*-influence of the iodo ligand compared with the chloro ligand.[762]

Mixed halide/isothiocyanato complexes are formed by reactions of hexahaliderhenates(IV) with SCN^- or $(SCN)_2$.[763–766] Bond isomers with nitrogen- and sulfur-bonded thiocyanato ligands have been isolated for the mixed-ligand species und characterized by their vibrational spectra.[763,764] Crystallographic evidence for $SeCN^-/NCSe^-$ bond isomerism has been given for *cis*- and *trans*-$[ReCl_4(NCSe)(SeCN)]^{2-}$ complexes. Based on the molecular parameters of the X-ray data their low temperature IR and Raman spectra have been assigned by normal coordinate analysis. The valence force constants are $f_d(ReN) = 1.68$ mdyn Å^{-1} and $f_d(ReSe) = 1.15$ mdyn Å^{-1}.[767]

(ii) Ligands with P, O, N, S, or As donor atoms

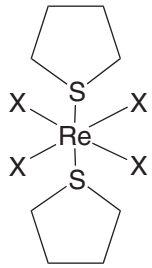
Complexes of the composition *trans*-$[ReX_4(PR_3)_2]$ (X = Cl, Br, I; $PR_3 = PPh_3$, $P(C_6H_4\text{-}3\text{-}Me)_3$, $PMePh_2$, PMe_2Ph, PEt_2Ph, PEt_3, PPr^n_3, PMe_3) are formed by reactions of various rhenium(VII), rhenium(V), rhenium(III), or rhenium(II) precursors.[768–776] The phosphines act as reducing agents and, thus, depending on the conditions applied also phosphine oxide complexes are produced as by-products.[777,778] Complexes with analogous structures have also been obtained with phosphite and phosphonite ligands by oxidation of corresponding $[ReCl_3L_3]$ complexes in air or by Cl_2.[779]

Reactions of common rhenium(V) precursors such as $[ReOCl_3(PPh_3)_2]$ or $[ReNCl_2(PPh_3)_2]$ with TMSNCS give access to unusual rhenium(IV) complexes with isothiocyanato ligands. Whereas the former reaction yields the mixed phosphine/phosphine oxide complex *cis*-$[Re(NCS)_4(PPh_3)(OPPh_3)]$ as red–brown paramagnetic crystals in good yields,[780] the cleavage of the ReN bond of $[ReNCl_2(PPh_3)_2]$ in methanol results in the formation of the hydroxo complex

trans-$[Re(NCS)_3(OH)(PPh_3)_2]$.[781] It is noteworthy that the analogous reaction with $[ReNCl_2(PMe_2Ph)_3]$ yields the thionitrosyl rhenium(I) species $[Re(NS)Cl_2(Me_2PhP)_3]$.[640]

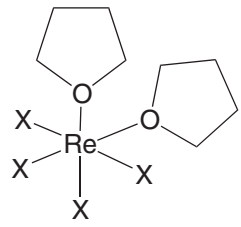
Reactions of $[ReCl_6]^{2-}$ solutions with thiourea does not exclusively yield ligand exchange products with oxidation state +IV. Reducing conditions give access to the class of hexakis{(alkyl) thiourea}rhenium(III) complexes which will be treated more in detail in Section 5.3.2.5.1(ii). Reactions in air result in partial oxidation of thiourea and α,α'-dithiobisformamidinium salts of $[ReCl_6]^{2-}$ and the monosubstitution product $[ReCl_5(tu)]^+$ have been isolated from such solutions. The oxidation requires the presence of air as well as $[ReCl_6]^{2-}$.[782] Ongoing ligand exchange has been observed with acetonitrile and brown crystals of $[ReCl_2(CH_3CN)_4][ReCl_6]$ have been obtained in low yields from acetonitrile solutions of $ReCl_5$ containing triphenylsilanol.[752]

The stable complex *trans*-$[ReX_4(THT)_2]$ (**215**) (X = Cl, Br; THT = tetrahydrothiophene) has been prepared as yellow (chloro complex) or brown crystals (bromo complex) in high yields by heating K_2ReCl_6 in a mixture of THT and aqueous HCl.[783] Both compounds are useful precursors for the synthesis of further rhenium(IV) complexes. *cis*-Arrangement of the organic ligands has been found for the analogous complexes with THF (**216**),[771] a mixed-ligand complex containing phosphine and dimethylaminoadenine,[784] or *N*-phenylacetamidine (**217**).[771,785] The latter compound is formed in high yields when *cis*-$[ReCl_4(CH_3CN)_2]$ reacts with aniline in acetone solutions and shows metamagnetic behavior. At higher temperatures the magnetic behavior is typical of a rhenium(IV) complex, with three unpaired electrons ($\mu = 3.6\,\mu_B$), an almost isotropic *g*-tensor of 1.86 and a large zero-field splitting of $-20(2)$ cm^{-1}. At very low temperatures (T < 9 K) the magnetization behavior as a function of temperature and field strength and direction indicates two magnetically ordered structural phases when the magnetic field is parallel to the *b* axis of the unit cell, but only one along the *a* and *c* axes.[786]

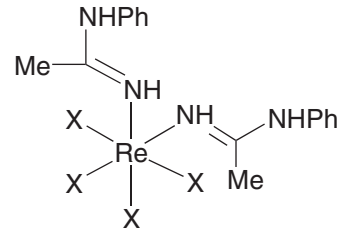


(**215**)

X = Cl, Br



(**216**)



(**217**)

Homoleptic phenoxido complexes of the composition $[Re(L)_4]$ where L = 2,6-diisopropylphenoxide or 2,6-dimethylphenoxide have been prepared by the reaction of $[ReCl_4(THF)_2]$ with the lithium salts of the ligands. The molecular geometry is square planar and the metal center is well protected from above and below the $\{ReO_4\}$ plane by the isopropyl groups and protects the complex from reactions with alkynes, whereas such a reaction and the formation of $[Re(OC_6H_3\text{-}2,6\text{-}Me_2)_4(RC{\equiv}CR)]$ adducts (R = Me, Eth, Ph) has been observed for the dimethyl derivative of the phenoxide.[783,787]

5.3.2.4.2 Complexes with chelating ligands

Formal ligand exchange on $[ReX_4(L)_2]$ complexes (X = Cl, Br ; L = donor solvents such as THF, CH_3CN, or THT) gives ready access to common chelate complexes of the composition $[ReX_4(L)]$ where L is a bidentate neutral ligand. Less common are related reactions with dinegative ligand systems and the formation of corresponding complex anions. A frequently observed structural feature in rhenium(IV) chelate complexes is the $\{Re(\mu_2\text{-}O)_2Re\}^{4+}$ core in which two rhenium atoms are symmetrically connected by two bridging oxo ligands.

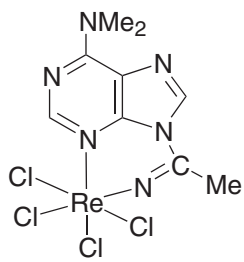
(i) Phosphorus, nitrogen donor and mixed N/S and N/O donor ligands

Rhenium(IV) complexes with only one bidentate ligand have been described for chelating phosphines, Schiff bases, and *N*-heterocycles. The synthetic approaches are different and involve simple ligand exchange procedures as well as reduction of rhenium(V) or oxidation of rhenium(III) compounds.

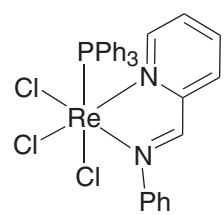
Red crystals of $[ReCl_4(dppe)]$ are obtained when the alkyne complex $[ReCl_4(PhC{\equiv}CPh)(OPCl_3)]$ is treated with the phosphine in dichloromethane.[788] Reduction of the rhenium(V) oxo core with simultaneous oxidation of the phosphine is observed when $[Bu_4N][ReOCl_4]$ reacts with diphenyl(2-pyridyl)phosphine (PPh_2py) in boiling acetone and bright green crystals of $[ReCl_4(OPPh_2py\text{-}O,N)]$ and $[ReCl_3(OH)(OPPh_2py\text{-}O,N)]$ have been isolated in moderate yields.[451] The intermediate formation of the $[ReCl_6]^{2-}$ ion seems to be an important step in the course of this reaction, which gives a mixture of $[Bu_4N]_2[ReCl_6]$, $[ReOCl_3(OPPh_2py\text{-}O,N)]$, and $[ReOCl_3(PPh_2py\text{-}P,N)]$ when it is carried out at room temperature.

Oxidation of the rhenium(III) compound *mer*-$[ReCl_3(PPh_3)(HMe_2Ad)]$, where HMe_2Ad is dimethyladenine, results in the formation of the mixed-ligand complex $[ReCl_4(PPh_3)(HMe_2Ad)]$ with a monodentate dimethyladenine ligand in *cis*-position to PPh_3. A ligand exchange reaction starting from *cis*-$[ReCl_4(CH_3CN)_2]$ and the same ligands gives a completely different product. The CN group of one of the acetonitrile ligands is inserted into the N9-H bond of the N3-bonded dimethyladenine ligand and finally a chelating amidine ligand is formed.[784] The resulting complex $[ReCl_4\{Me_2AdC(Me){=}NH\}]$ (**218**) is stable as solid and in solutions.

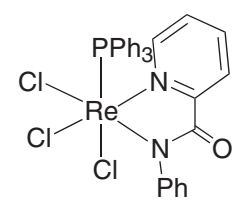
Schiff base complexes with rhenium(IV) centers can be prepared by the reduction of rhenium(V) oxo complexes or by ligand exchange reactions starting from $[ReCl_4(PR_3)_2]$ complexes. A mixed ligand complex containing a salicylideneaminato ligands and PMe_2Ph in an octahedral rhenium(IV) complex has been studied structurally showing that the bonding situation inside the organic ligand is not significantly influenced by the oxidation of the metal as has been derived from comparison with rhenium complexes in the oxidation states +I, +III, and +V.[789] $[ReCl_3(PPh_3)(L)]$ or $[ReCl_3(OPPh_3)(L)]$ complexes with L = pyridine-2-aldimine (**219a**) can be oxidized chemically by dilute nitric acid or electrochemically under formation of pyridine-2-carboxamide ligands (**219b**). The formation of complex cations of the composition $[Re(L)]^+$ has been reported for the reaction of K_2ReCl_6 with tris[2-(2′-hydroxybenzylideneethyl)]amine and related compounds in glacial acid and the sexidentate coordination of the organic ligands has been concluded from spectroscopic data.[790] An unusual decomposition of a rhenium(V) imido complex with the cleavage of the Re—N multiple bond is observed when $[Re(NPh)Cl_3(PPh_3)_2]$ reacts with the potentially pentadentate ligand 2,6-bis(2-thiophenylaminomethyl)pyridine.[791] The resulting ligand (**220**), which is formed from the decomposition of the symmetric pyridine derivative and partial self-condensation followed by oxidation, coordinates the rhenium atom in a tetradentate manner. The coordination sphere of the metal in the neutral rhenium(IV) complex is completed by a dianionic $HN\text{-}C_6H_4\text{-}S^{2-}$ ligand.



(**218**)



(**219a**)

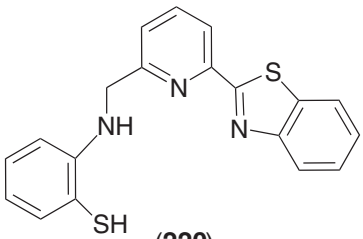


(**219b**)

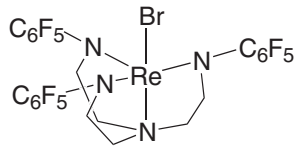
Rhenium(IV) complexes with the potentially tetradentate triamidoamine ligand $\{(C_6F_5)NCH_2CH_2\}_3N^{3-}$ (**115**) are formed when the corresponding rhenium(V) complex $\{ReOCl[\{(C_6F_5)NCH_2CH_2\}_3N]\}$ is reduced. The reaction with $[Ta(CHBu^t)(THF)_2Br_3]$ gives the paramagnetic complex $\{Re[\{(C_6F_5)NCH_2CH_2\}_3N]Br\}$ (**221**) which is useful precursor for the synthesis of numerous rhenium(III) complexes.[432]

Mono- and dinuclear species containing rhenium(IV) have been described with the tripodal ligand tacn (**15a**).[250] Thus, the rhenium(III) complex $[Re(tacn)Cl_3]$ which is formed by the reduction of $[ReO(tacn)(O_2C_2H_4)]Br$ by zinc dust in HCl, can be oxidized in hot CH_3SO_3H in air to give $[Re(tacn)Cl_3]^+$. Disproportionation of $[ReO(tacn)(O_2C_2H_4)]^+$ in HCl or HBr solutions gives the rhenium(VII) compound $[Re(tacn)O_3]X$ and the binuclear rhenium(IV) complexes *anti*-$[(tacn)ClRe(\mu_2\text{-}O)_2ReCl(tacn)]^{2+}$ (**222**). A related binuclear complex has been described with tris(2-pyridylmethyl)amine (**114**). The distorted octahedral coordination spheres of the rhenium atoms of a $\{Re(\mu_2\text{-}O)_2Re\}^{4+}$ core are completed by the four donor atoms of the amine ligand. The tertiary amine and one of the pyridine donor atoms are in *trans* positions to the bridging oxo

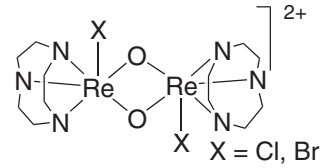
ligands.[792] The dark-brown complex $Ba_2[Re_2(\mu\text{-}O)_2(EDTA)_2]$ has been prepared from the sodium salt of the complex and $BaCl_2$.[793] The binuclear structure is centrosymmetric with each tetradentate $EDTA^{4-}$ ligand having two uncoordinated acetate groups. The $\{Re_2O_2\}$ ring is planar and the short ReRe distance of 2.36 Å indicates multiple metal–metal bonding.



(220)



(221)



(222)

The triply bonded dirhenium(II) complexes $[Re_2X_4(\mu\text{-dppm})_2]$ (X = Cl, Br) have been shown to react with dioxygen with formation of the rhenium(V) oxo complexes $[ReOCl_3(dppmO)]$ (dppmO = $Ph_2PCH_2P(O)Ph_2$). The dirhenium(IV) complex $[ReOCl(\mu\text{-}O)(\mu\text{-}Cl)(\mu\text{-dppm})_2ReCl_2]$ reacts with thionyl chloride to form the centrosymmetric corner-sharing bioctahedral complex $[ReCl_3(\mu\text{-}O)(\mu\text{-dppm})_2ReCl_3]$.[462]

(ii) Sulfur and oxygen donor and mixed S/O donor ligands

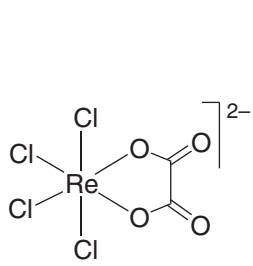
Neutral $[ReCl_4(O^{\frown}O)]$ complexes with O⌒O = dimethoxyethane or 1,4,7,10,13,16-tetraoxaoctadecane (18-crown-6) have been prepared from $ReCl_5$ and the corresponding ligands.[752,788] Only two neighboring oxygen atoms of the crown ether are involved in the complex formation. The Re—Cl bond lengths in *trans* position to the oxygen donors are slightly shorter than those *trans* to Cl which is in accordance with the estimated small *trans*-influence of the ether donor atoms.

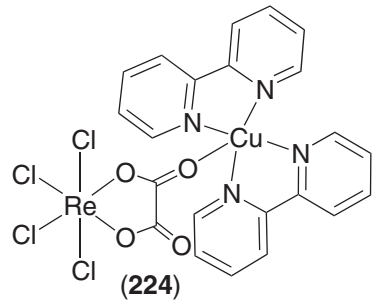
Although oxalato complexes of rhenium(IV) have been known for a long time and the structure of the dimeric, dioxo-bridged complex $[(C_2O_4)_2Re(\mu\text{-}O)_2Re(C_2O_4)_2]^{4-}$ known since 1975,[794] some of the synthetic procedures give only impure products. A synthesis which starts from K_2ReCl_6 and solid oxalic acid in water gives a pure sample of the olive-green complex in 50% yield.[795] The complex is stable in solution at pH 7 over many days, whereas a slow decomposition and the formation of $[ReO_4]^-$ is observed in acidic solutions. A kinetic study of this oxidation indicates a protonation step with an equilibrium constant of $2.4\,M^{-1}$ followed by a reaction with $k = 5.3 \times 10^{-5}\ s^{-1}$.[795]

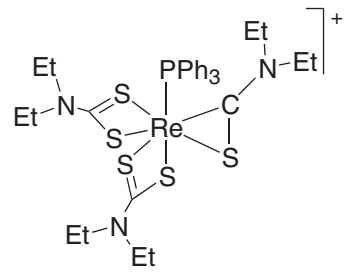
The monosubstitution product of $[ReCl_6]^{2-}$ with oxalate, the $[ReCl_4(C_2O_4)]^{2-}$ anion (**223**) can be prepared by simple ligand exchange procedures and isolated with bulky cations. The complex anion has a distorted octahedral geometry with a chelating oxalato ligand.[796,797] It is an appropriate building block for the synthesis of heterobimetallic complexes with bridging oxalato ligands. This has been demonstrated for a series of compounds containing copper(II) centers. Oxalato (and in some cases additional chloro) bridges connect the metals forming binuclear or tetranuclear units.[796] Examples with bidentate/monodentate (**224**) and bidentate/bidentate oxalato bridges have been isolated and structurally characterized. This results in Re–Cu distances between 5.4 Å and 5.5 Å which allow weak antiferromagnetic couplings between Re^{IV} and Cu^{II}.

Re^{III} and Re^{IV} thiocarbamoyl complexes have been prepared by the reaction of $[ReCl_3(PPh_3)_2(CH_3CN)]$ with a large excess of sodium diethyldithiocarbamate in acetone. The resulting rhenium(III) complex $[Re(S_2CNEt_2)_2(SCNEt_2)(PPh_3)]$ is easily oxidized by $K_3[Fe(CN)_6]$ to the cationic species $[Re(S_2CNEt_2)_2(SCNEt_2)(PPh_3)]^+$ (**225**) which has been isolated and structurally characterized as its perchlorate salt.[799] The structure of the complex cation (**224**) is best described as pentagonal bipyramidal with the PPh_3 ligand and one sulfur atom of a dithiocarbamate in axial positions. The thiocarbamoyl ligand is η^2-*C*,*S* bonded in an equatorial position.

Compounds with the sulfur analogue of the $\{Re(\mu\text{-}O)_2Re\}^{4+}$ core have been obtained during reactions of $[ReS_4]^-$ salts with tetraalkylthiuram disulfides. Dimeric rhenium(IV) complexes of the composition $[Re_2(\mu\text{-}S)_2(S_2CNR_2)_4]$ (**226**) (R = Me, Et, Bu^i) are formed in excellent yields when 1.5 equivalents of thiuram disulfide is used.[162,163] A larger excess gives rhenium(III) species. The dimers $[Re_2(\mu\text{-}S)_2(S_2CNR_2)_4]$ undergo reversible one-electron oxidation to produce $[Re_2(\mu\text{-}S)_2(S_2CNR_2)_4]^+$. This species can also be generated chemically and, in the presence of excess

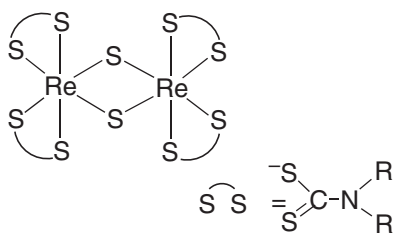

(223)

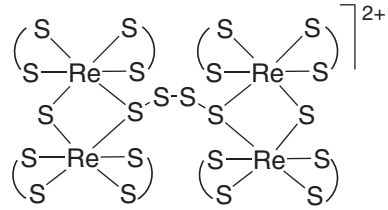

(224)

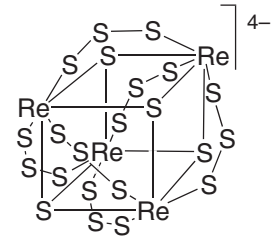

(225)

sulfur, forms a novel rhenium(IV) sulfur-bridged dicationic dimer of dimers $[\{(Re_2(\mu\text{-}S)(S_2CNR_2)_4\}_2S_4]^{2+}$ (**227**).[163]

Reduction of $[ReS_4]^-$ with polysulfide solutions gives a number of products depending on the pH and the solvent used.[151–161] When the reaction conditions are strictly controlled, however, good yields of individual compounds can be obtained as has been demonstrated for the multinuclear rhenium(IV) compound $[NH_4]_4[Re_4S_4(S_3)_6]$ (**228**). It is formed in 40% yield during the reaction of ammonium perrhenate with an aqueous ammonium polysulfide solution at temperatures between 60 °C and 65 °C.[151] The structure of the complex anion can best be described as a distorted $\{Re_4S_4\}$ cube in which the rhenium atoms of each plane are additionally bridged by S_3^{2-} ligands. The shortest Re–Re distance in this compound is 2.76 Å.


(226)


(227)


(228)

5.3.2.5 Oxidation state III

Rhenium complexes containing the metal in the oxidation state +III are comparatively numerous. This may be ascribed to the fact that the d^4 configuration of the rhenium center can readily be stabilized by ligands with pronounced donor and π-acceptor properties. Most of the rhenium(III) compounds are stable against hydrolysis rendering them suitable for nuclear medical applications.

Additionally to the large number of complexes with octahedral or distorted octahedral geometry, compounds containing the metal in trigonal bipyramidal, monocapped trigonal prismatic, or pentagonal bipyramidal coordination environments play an important role. Whereas the most of the octahedral d^4 compounds are paramagnetic, rhenium(III) complexes with the coordination numbers five or seven are diamagnetic as is explained by the orbital energy splitting patterns illustrated in Figure 5.

Organometallic compounds which begin to play a more important role in the chemistry of rhenium with the metal in the oxidation state +III and lower will only be treated in the subsequent sections when the "organometallic parts" of the molecules do not dominate the chemistry of the complexes and can be regarded as co-ligands to halides, phosphines or nitrogen ligands as is often the case for carbonyl or isocyanide ligands. Their behavior as π-acceptors often contributes significantly to the stabilization of rhenium(III) complexes with the coordination number seven.

Seven-coordination is also observed for cyano complexes. The diamagnetic anion $[Re(CN)_7]^{4-}$ is obtained by the reaction of K_2ReCl_6 with KSeCN and KCN under nitrogen.[800,801] The complex anion possesses pentagonal bipyramidal geometry and the Re—CN bonds are kinetically inert as has been demonstrated by an electrochemical study. $[Re(CN)_7]^{4-}$ undergoes a single, fully reversible one-electron oxidation with $E^0 = 0.643$ V. The complex can be singly protonated according to the equilibrium $[Re(CN)_7]^{4-} + H^+ \rightleftharpoons [Re(CN)_7H]^{3-}$ with pH = 1.31. A ^{13}C- and

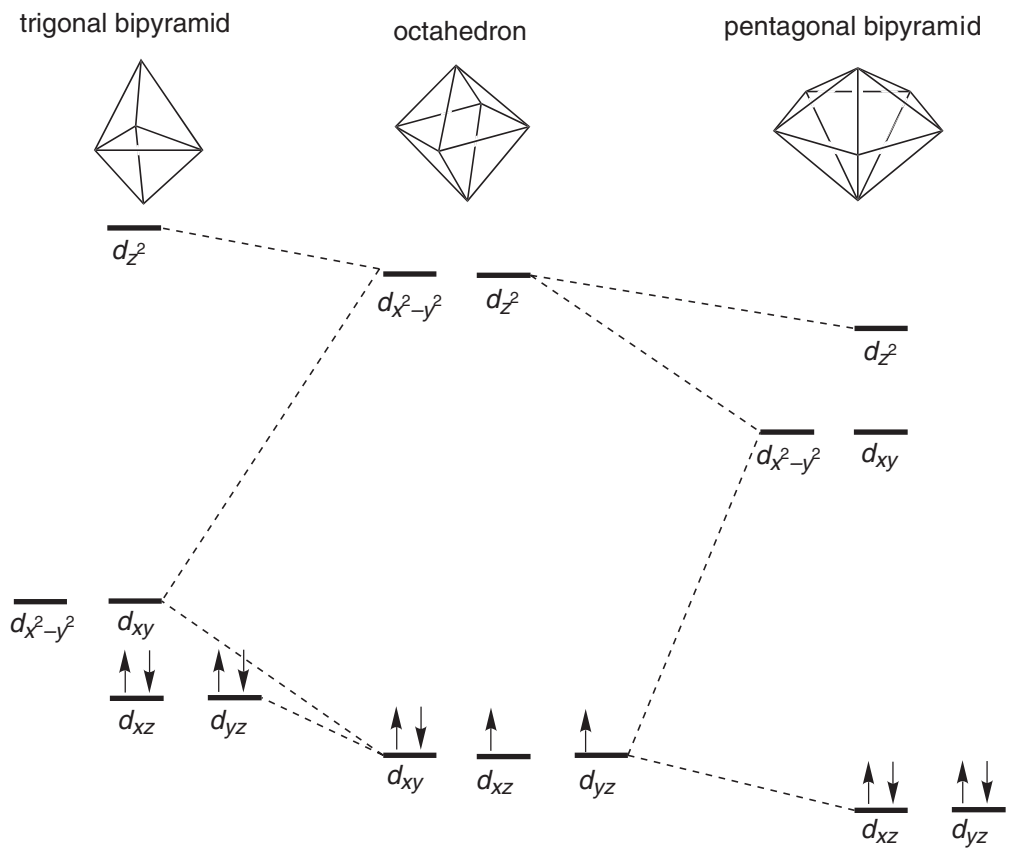


Figure 5 Frequent coordination numbers and energy levels for d^4 rhenium(III) complexes.

^{14}N-NMR study on $K_4[Re(CN)_4]$, however, strongly indicates a fluxional behavior of the cyano ligands in solution at least at the NMR timescale. Only one signal has been observed in the ^{13}C- (140.3 ppm vs. TMS) and ^{14}N-NMR (−95 ppm vs. $NaNO_3$) spectra at ambient temperatures which indicates that the interchange rate of the two nonequivalent ligand sites (two axial and five equatorial) is faster than the NMR timescale and the measured chemical shifts are averaged values for cyano ligands in different chemical environments.[802]

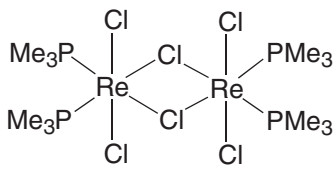
5.3.2.5.1 Complexes containing exclusively monodentate ligands

(i) Ligands with phosphorus or nitrogen donor ligands

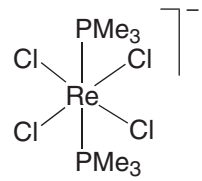
Complexes of the composition *mer*-$[ReX_3(PR_3)_3]$ or $[ReX_3(PR_3)(CH_3CN)]$ (X = halide; PR_3 = ter-tertiary phosphine) have been long established and can easily be prepared as orange–red crystalline solids by the reduction of perrhenate or rhenium(V) oxo compounds with an excess of the corresponding phosphine in HX solutions.[21] The individual composition of the complexes is mainly controlled by the steric requirements of the phosphine ligands. Bulky phosphines such as PPh_3 prefer the formation of $[ReCl_3(PPh_3)_2(L)]$ type compounds where L is a solvent molecule,[803–805] whereas smaller phosphines such as PMe_2Ph, PEt_2Ph, or $PMePh_2$ and related phosphites such as $P(OEt)_3$ or the cyclic $P(OCH_2)_3CEt$ yield *mer*-$[ReCl_3(PR_3)_3]$ compounds.[779,806–809] The paramagnetic d^4 complexes show ^{1}H NMR spectra with narrow lines (≈1 Hz) at low field exhibiting no ^{31}P-H splittings and there are large differences in chemical shifts between geminal methylene protons of the alkyl groups because of the low symmetry at the phosphorus atoms.[772,808] A detailed ^{13}C NMR study has been carried out on $[ReCl_3(PEt_2Ph)_3]$ and $[ReCl_3(PPr^n{}_2Ph)_3]$ and the ^{13}C signals have been assigned based on the known ^{1}H spectra by ^{13}C-^{1}H correlation spectroscopy experiments.[808] The spectra show no coupling between ^{13}C and

^{31}P. The C_1 carbon resonances for the aryl groups, unlike the C_α resonances of the alky groups are too broad for detection. The proton relaxation times T_1^{-1} and T_2^{-1} as well as the linewidths in three different magnetic fields, corresponding to proton frequencies of 250, 400, and 600 MHz, show an increase with the field strength.

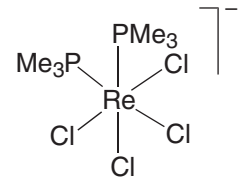
The dichloro bridged complex $[Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4]$ (**229**) which contains no rhenium–rhenium bond is formed from the reaction of the quadruply bonded dimer $[Re_2Cl_8]^{2-}$ with PMe_3 in benzene.[810] This result is remarkable since the same reaction causes reduction of rhenium and the formation of the metal–metal bonded rhenium(III)/rhenium(II) and rhenium(II) dimers $[Re_2Cl_5(PMe_3)_3]$ and $[Re_2Cl_4(PMe_3)_4]$ when it is performed in alcohols.[811,812] $[Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4]$ has an effective magnetic moment of 4.85 μ_B per dirhenium unit which is consistent with the presence of four unpaired electrons. Cyclic voltammetry showed several accessible oxidation and reduction processes, but all of them were irreversible. The use of $[Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4]$ as a synthetic starting material resulted in several reduction products with metal–metal bonds such as $[Re_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4]$, $[Re_2Cl_5(PMe_3)_3]^-$, $[Re_2Cl_4(PMe_3)_4]$, whereas oxidation with $NOBF_4$ gives *trans*-$[ReCl_4(PMe_3)_2]$. When this oxidation is performed in the presence of $[NBu_4]Cl$, the anionic rhenium(III) complex *trans*-$[NBu_4][ReCl_4((PMe_3)_2]$ (**230**) was obtained as a side-product, whereas the *cis* isomer (**231**) has been isolated as $[Co(\eta^5\text{-}C_5H_5)_2]^+$ salt as side-product of the reduction of $[Re_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4]$ with cobaltocene.[775]



(**229**)



(**230**)



(**231**)

Ligand substitution reactions of $[ReCl_3(PR_3)_3]$ or $[ReCl_3(PPh_3)_2(CH_3CN)]$ complexes give access to mixed-ligand complexes with amines or isocyanides or lead to complete replacement of the phosphine ligands. Thus, reactions between $[ReCl_3(PPh_3)_2(CH_3CN)]$ and pyridine-type ligands such as pyridine, 3,5-dimethylpyridine, 4-methylpyridine, and 4-vinylpyridine yield *mer*-$[ReCl_3(L)_2(PPh_3)]$ complexes as major products and the tris-pyridine compounds as side-products.[813] Considerable oxidation to rhenium(V) and the formation of $[ReO_2(py)_4]^+$ complexes is observed when the reaction mixture is exposed to air for a prolonged time.

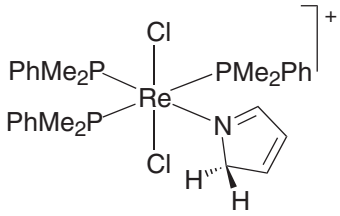
A chloro ligand is replaced when $[ReCl_3(PMe_2Ph)_3]$ reacts with pyrrolyllithium in diethylether. The brown, air-stable product $[ReCl_2(PMe_2Ph)_3(NC_4H_4)]$ contains the remaining chloro ligands in *trans* positions. It reacts with electrophiles under formation of novel rhenium(III) complexes with regioselectively substituted pyrrolyl ligands.[814] For example, the reaction with one equivalent of *N*-chlorosuccinimide gives a compound having a 3-chloropyrrolyl ligand, while the reaction with excess reagent produces 3,4-dichloropyrrolyl and 2,3,4-trichloropyrrolyl complexes. The reaction of $[ReCl_2(PMe_2Ph)_3(NC_4H_4)]$ with methyl triflate yields, depending on the amount of the reactant, the products $[ReCl_2(PMe_2Ph)_3(3\text{-}NC_4H_3Me)]$ and $[ReCl_2(PMe_2Ph)_3(3,4\text{-}NC_4H_2Me_2)]$, whereas triflic acid protonates the pyrrolyl ligand in α-position to form the cation $[ReCl_2(PMe_2Ph)_3(NC_4H_5)]^+$ (**232**). The obtained pyrrol derivatives can be removed from the metal and isolated in good yields by a reaction with a $LiCl/AlCl_3$ mixture in diethylether. The starting material $[ReCl_3(PMe_2Ph)_3]$ is re-formed during this procedure.

An unusual approach to an ammine ligand has been reported by the full protonation of a nitrido ligand.[638] The red–brown complex $[Re(NH_3)I_2(PMe_2Ph)_3]I_3$ is obtained by the reaction of $[ReNCl_2(PMe_2Ph)_3]$ with TMSI in dichloromethane. Decomposition of the solvent is believed to be the source of the protons. It is remarkable that the analogous reaction with TMSBr exclusively results in a Cl/Br exchange and the formation of $[ReNBr_2(PMe_2Ph)_3]$.[637] The synthesis of the cationic tetrammine complex *trans*-$[ReCl_2(NH_3)_4](PF_6)$ was achieved by the reduction of $[ReO_2(NH_3)_4]Cl$ with zinc amalgam in HCl and precipitation of a yellow solid with $[NH_4][PF_6]$.[638]

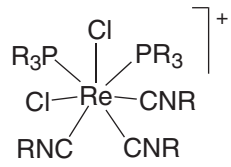
Pyridine complexes of rhenium(III) can be prepared by the reduction of K_2ReX_6 complexes (X = Cl, Br) with $NaBH_4$ in pyridine.[816] Separation of the crude complex mixture by chromatography on Al_2O_3 allows the isolation of the individual $[ReX_{6-n}(py)_n]^{(3-n)-}$ complexes. Apart from the monosubstituted pyridine complexes only the *trans*- and *mer*-isomers are formed for the bis- and tris-pyridine species. This has been proved by crystal structure analyses for *trans*-$[ReBr_4(py)_2]^-$, *mer*-$[ReCl_3(py)_3]$, and *mer*-$[ReBr_3(py)_3]$. An alternative synthesis for the

tris-pyridine derivatives which allow mixed halide coordination has been reported with the isolation of *mer*-$[ReFI_2(py)_3]$ from ReI_3, Tl(OEt), and benzoylfluoride in pyridine.[817]

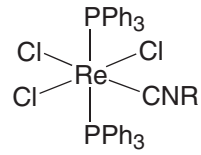
Two different types of mixed-ligand rhenium(III) complexes containing monodentate tertiary phosphines and isocyanides are known. Seven-coordinate cations of the general formula $[ReCl_2(CNR)_3(PR_3)_2]^+$ (**233**) or $[ReCl_3(CNR)_2(PR_3)_2]$ (R = various alky or aryl substituents; $PR_3 = PMe_2Ph$, $PMePh_2$) are formed during ligand exchange procedures starting from $[ReCl_3(PMe_2Ph)_3]$ or $[ReCl_3(PMePh_2)_3]$.[818–821] The coordination geometry of the red, diamagnetic compounds can best be described as capped trigonal-pyramidal with one chloro ligand occupying the capping position. Paramagnetic octahedral compounds of the composition $[ReCl_3(PPh_3)_2(NCR)]$ (R=Bu^t, Cyclohexyl, Ph, $CH_2CH_2N(C_2H_5)_2O$, CH_2COOMe) (**234**) are obtained when triphenylphosphine is used instead of PMe_2Ph or $PMePh_2$.[822,823] Two different routes were employed for the preparation of the compounds: the reduction of $[ReOCl_3(PPh_3)_2]$ with excess of PPh_3 in the presence of the corresponding isocyanide and a ligand exchange approach starting from $[ReCl_3(PPh_3)_2(CH_3CN)]$. The latter procedure gives better yields. The formation of an octahedral rhenium(III) complex with the chelating isocyanide $\{CN(CH_2)_3OCH_2\}_2$ has been reported for the reaction of $[ReOCl_3(PPh_3)_2]$ with $Na_2S_2O_4$ and an excess of the ligand in methanol and a tentative composition of $[ReCl_3(PPh_3)(L)]$ has been derived from spectroscopic data.[824]



(**232**)



(**233**)



(**234**)

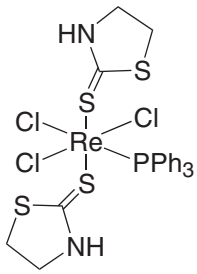
(ii) Ligands with sulfur donors and mixed-ligand complexes

Thiourea complexes of technetium(III) have been shown to be excellent precursors for the synthesis of a large number of Tc^{III} and Tc^{I} complexes.[825] The $[Tc(tu)_6]^{3+}$ cation is readily formed in a mixture of pertechnetate, tu and 12 M HCl and precipitates as chloride. Due to the different redox potentials of the homologous elements technetium and rhenium, the reducing capacity of HCl is not sufficient to apply the same method for rhenium and tin chloride is added as reducing agent.[826] The rhenium atom in the paramagnetic $[Re(tu)_6]^{3+}$ cation has a pseudooctahedral geometry. Analogous complexes have been synthesized with a number of substituted thioureas and structural determinations of the hexakis(alkylthiuourea)rhenium(III) complexes have been reported for *N*-methylthiourea (Metu), *N*,*N*′-dimethylthiourea (Me_2tu) and *N*-ethylthiourea (Ettu).[827,828] The thiourea ligands are labile and the complexes have been tested for their ligand exchange behavior. Reactions with chelating phosphines readily form $[Re(P^{\frown}P)_2Cl_2]^+$ complexes ($P^{\frown}P$ = dppe or bis(diphenylphosphino)propane) and a substitution rate has been found as follows: $[Re(tu)_6]^{3+} < [Re(Ettu)_6]^{3+} < [Re(Metu)_6]^{3+} < [Re(Me_2tu)_6]^{3+}$.[827] $[Re(tu)_6]^{3+}$ hydrolyzes in aqueous solution and pseudo-first order kinetics have been found for the decomposition. The rate constants vary from 1.3×10^{-2} min^{-1} to 9.6×10^{-2} min^{-1} in the pH range 2.80–5.04.[828]

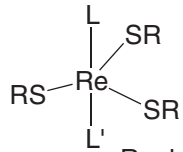
Pseudooctahedral coordination of rhenium(III) centers has also been found for mixed-ligand complexes with tertiary phosphines and *N*-heterocyclic thiols which coordinate as their neutral thione tautomers. A representative example with thiazoline-2-thiol (HSthiaz) has been characterized structurally. The paramagnetic complex $[ReCl_3(HSthiaz)_2(PPh_3)]$ (**235**) contains the HSthiaz ligands in *trans* position.[297]

A series of neutral five-coordinate complexes of the composition $[Re(SR)_3(L)_2]$ (**236**) with trigonal bipyramidal structure has been isolated with sterically hindered thiols such as 2,4,6-triisopropylbenzenethiol (Htipt), 2-triaryl(alkyl)silylbenzenethiol (HR_3Sibt), 2,6-dimethylbenzenethiol (HMe_2bt) or $HSCH_2Ph$-4-OMe.[232,293,294,829–831] The thiolates form the trigonal plane and the axial ligands preferably possess π-accepting properties. Representatives are known with isocyanides,[232,293] CO,[232] phosphines,[293,294,829,831] or dinitrogen.[829] Compounds of the type (**236**) can be prepared starting from $K_2[ReCl_6]$, $[ReOCl_3(PPh_3)_2]$ or $[ReCl_3(PPh_3)_2(CH_3CN)]$. The reaction of $[ReCl_3(PPh_3)_2(CH_3CN)]$ with HSC_6H_4-2-TMS in

acetonitrile yields an unexpected product which contains two thiolimidato ligands, $[Re(SC_6H_4\text{-}2\text{-}TMS)\{NC(SC_6H_4\text{-}2\text{-}TMS)CH_3\}_2(PPh_3)_2]$ (**237**).[291] The formation of this unusual ligand can be understood as the result of a nucleophilic attack on the coordinated acetonitrile and reduction of nitrile to amidine. This unusual feature is attributed to the β-silicon effect of the substituent since neither sterically innocent thiols nor conventionally bulky thiols show this type of reactivity.

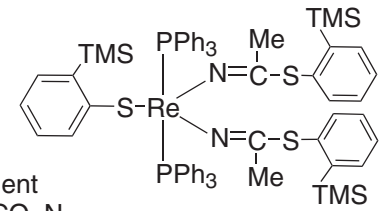


(**235**)



R = bulky substituent
L,L' = PPh_3, NCR, CO, N_2

(**236**)



(**237**)

Rhenium(III) complexes with sulfur dioxide ligands have been obtained by oxidation of dimeric sulfido-bridged complexes either by air or by $NO(PF_6)$. The oxidation of the bridging sulfur atoms is facilitated by the high electron density at these ligands.[152,832]

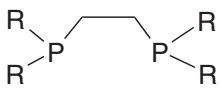
5.3.2.5.2 Complexes with chelating ligands

(i) Phosphorus and arsenic donor ligands

Chelating phosphorus and arsenic ligands have attracted considerable interest for the chemistry of rhenium(III) since cationic technetium(III) complexes with this type of ligand showed considerable myocardial uptake in dogs and were promising candidates for the development of an agent for myocardial imaging for a long time. Finally, no agent was developed, mainly due to problems with the redox behavior of technetium, but this work has contributed significantly to our knowledge about the coordination chemistry of rhenium(III) cations of the general composition *trans*-$[Re(P^{\frown}P)_2X_2]^+$, where $P^{\frown}P$ is one of the ligands (**238**) or related phosphines and X = Cl, Br, or SR. *trans*-$[Re(P^{\frown}P)_2Cl_2]^+$ or *trans*-$[Re(P^{\frown}P)_2Br_2]^+$ complexes can readily be prepared starting from $[ReO_4]^-$ and an excess of the appropriate ligand in HCl or HBr. This general procedure has also been applied for radioactive ^{186}Re.[833] Other protocols start from $[ReX_6]^{2-}$ complexes (X = Cl, Br),[834] the thiourea complex $[Re(tu)_6]Cl_3$,[827] multiply bonded dirhenium precursors,[835] or the rhenium(III) compound $[ReCl_3(PPh_3)_2(CH_3CN)]$.[343] An unusual synthesis has been reported for the fluoro derivative $[Re(dppe)_2F_2]^+$ which is formed as a side-product during the synthesis of the rhenium(I) isocyanide compound $[Re(NCC_6H_4\text{-}4\text{-}Me)_2(dppe)_2]^+$ after treatment of *trans*-$[Re(N_2)Cl(dppe)_2]$ with three equivalents of NCC_6H_4-4-Me in the presence of $TlBF_4$.[836] The cationic complexes are stable in solution and they have been isolated in crystalline form with various anions.

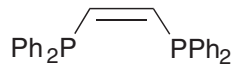
The cationic complexes *trans*-$[Re(\mathbf{238})_2X_2]^+$ (X = Cl, Br) exhibit a diffusion-controlled, reversible one-electron reduction to neutral *trans*-$[Re(\mathbf{238})_2X_2]$ complexes. The formal reduction potential of the Re^{III}/Re^{II} redox couple ranges from -0.205 V to -0.450 V vs. Ag/AgCl depending on the halides and the substituents of the phosphine ligands. Further reduction to Re^{I} anions $[Re(\mathbf{238})_2X_2]^-$ is possible, however, the reversibility of the process depends on the nature of the coordinating ligands and the experimental conditions.[834] In aqueous solutions, insolubility of the electrochemically generated neutral rhenium(II) complexes results in absorption effects when (**238**) is dmpe. However, ionic surfactants effectively solubilize the $[Re(dmpe)_2X_2]$ species such that diffusion-controlled reversible cyclic voltammograms are observed in these media. The more lipophilic $[Re(depe)_2X_2]^+$ (depe = 1,2-bis(diethylphosphino)ethane) complexes behave differently. While the solubility of the cationic complex is enhanced in the surfactant media, the electrogenerated neutral rhenium(II) species are absorbed on the electrode surface which leads to net stabilization of the components of the Re^{III}/Re^{II} redox couple in various surfactant media.[838,839] This stabilization is dependent on (i) the formal charge of the electroactive complex, (ii) the

formal charge of the surfactant molecule in the micelle and (iii) the lipophilicity of the components of the redox couple.



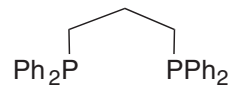
R = Me (DMPE), Et (DEPE)
Ph (DPPE), CH_2Ph (DBPE)

(**238a**)



VDPP

(**238b**)



DPPP

(**238c**)

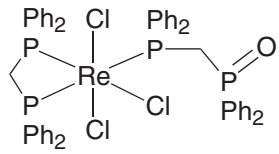
The M—P and M—Cl bond lengths in $[M(dppe)_2Cl_2]^+$ complexes (M = Mo, Re) are sensitive to the number of d electrons. The M–P distances contract by about 0.1 Å for each electron added. In contrast, the Re–Cl distances increase by less than 0.02 Å upon addition of an electron (d^3 to d^4). The results can be interpreted in terms of π-effects.[840]

Another type of rhenium(III) bis-phosphine complex is obtained from reactions of the rhenium(V) precursors $[ReOX_3(AsPh_3)_2]$ (X=Cl, Br) and dppm. The arsine complexes are excellent precursors since $AsPh_3$ binds to Re^V centers less strongly than PPh_3 and the $[ReOX_3(AsPh_3)_2]$ complexes are better soluble in common solvents than their PPh_3 analogues. Treatment of $[ReOCl_3(AsPh_3)_2]$ with two equivalents of dppm in hot benzene under an inert atmosphere gives the yellow rhenium(III) complex *mer*-$[ReCl_3(dppm\text{-}P^1,P^2)(dppmO\text{-}P)]$ (**239**) (dppmO = bis-diphenylphosphino)methane monoxide) in good yields, whilst a similar procedure starting from $[ReCl_3(PPh_3)_2(CH_3CN)]$ results in the formation of $[ReCl_3(dppm\text{-}P^1,P^2)(dppm\text{-}P^1)]$. The bromo analogues $[ReBr_3(dppm\text{-}P^1,P^2)(DPPOM\text{-}P^1)]$ and $[ReBr_3(dppm\text{-}P^1,P^2)(dppm\text{-}P^1)]$ have been prepared using the precursors $[ReOBr_3(AsPh_3)_2]$ and $[ReBr_3(PPh_3)_2(CH_3CN)]$, respectively. During the reaction of $[ReBr_3(PPh_3)_2(CH_3CN)]$ with an excess of dppm a mixture of $[ReBr_3(dppm\text{-}P^1,P^2)(dppm\text{-}P)]$ and *trans*-$[ReBr_2(dppm\text{-}P^1,P^2)_2]^+$ is formed, from which the cation can easily be separated by precipitation with BPh_4^-.[343]

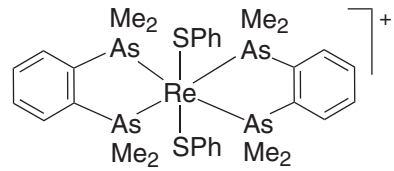
Mixed rhenium(III) complexes of the composition $[Re(SR)_2(P^{\frown}P)_2]^+$ (R = Et, Ph, C_6H_4-4-Cl, $CH_2C_6H_5$, $CH_2C_6H_4$-4-Me) have been synthesized by reactions of $[ReOCl_3(PPh_3)_2]$ or $[ReO_2(py)_4]Cl$ with mixtures of bis-phosphines and aromatic or aliphatic thiols. Only *trans*-isomers have been obtained when $P^{\frown}P$ is dppe or DEPE,[841] whereas a mixture of *cis*- and *trans*-$[Re(SR)_2(dmpe)_2]^+$ complexes is formed when the less bulky chelating phosphine is used.[842] The complexes undergo a reversible one-electron reduction in the range −0.43 V and −0.53 V for the *cis* isomer and −0.48 V and −0.60 V for *trans*-$[Re(SR)_2(dmpe)_2]^{+/0}$ complexes. The individual Re^{III}/Re^{II} couples depend on the nature of the thiolato ligands.

Attempts to prepare Re^{III} diars/thiolato mixed-ligand complexes (diars = 2-phenylenebis-(dimethylarsine)) by the general method which was optimized for the preparation of $[Re(SR)_2(P^{\frown}P)_2]^+$ complexes resulted primarily in the metathesis products $[ReOCl(SR)_2(diars)]$ which indicated that reduction requires more forcing conditions. Heating to 100 °C finally results in the formation of rhenium(III) complexes. In the successful preparation of the alkanethiolato complex $[Re(SEt)_2(diars)_2]^+$, only the red *trans* isomer is apparently formed, whereas in the benzenethiolate case a mixture of *cis*-$[Re(SPh)_2(diars)_2]^+$ (**240**) and *trans*-$[Re(SPh)_2(diars)_2]^+$ complexes have been isolated.[349] Electrochemical measurements show a reversible Re^{III}/Re^{II} redox couple at about −0.55 V for the *trans* complex and −0.52 V for the *cis* thiolato compound, while a cyclic voltammetric study for the $[ReCl_2(diars)_2]^+/[ReCl_2(diars)_2]$ redox couple gives reduction potentials between −0.319 V and −0.263 V depending on the solvent used.[843]

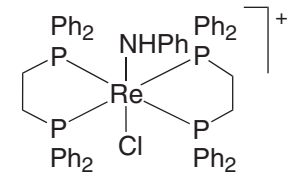
Additional to the rhenium(V) imido complexes $[Re(NAr)Cl_2(dppe)_2]^{2+}$, the amidorhenium(III) compounds $[Re(NHC_6H_4\text{-}4\text{-}R)Cl(dppe)_2]^+$ (R = H, Cl, OMe) (**241**) are formed during the reaction of $[Re(NPh)Cl_3(PPh_3)_3]$ with dppe in ethanol.[722] The brown rhenium(III) species show unusual proton NMR spectra where all of the resonances were found at expected positions except those for the amido protons which is attributed to second-order magnetic contribution that is strongly focused along the axially compressed amido axis. The reducing equivalents for the formation of the rhenium(III) complexes are provided by oxidation of the solvent ethanol which produces acetal and acetaldehyde in amounts as much as 30 equivalents based on the quantity of rhenium starting material. Equal amounts of hydrogen gas are produced suggesting that the catalyzed reaction is the dehydrogenation of ethanol.[722]



(**239**)



(**240**)



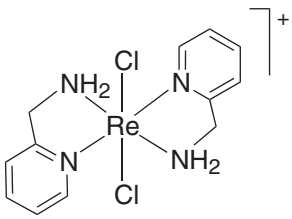
(**241**)

(ii) Nitrogen donor ligands

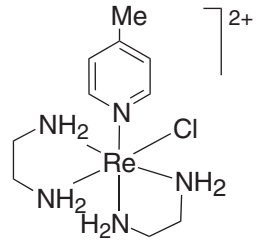
As discussed for bis-phosphine complexes in the previous section, reduction of oxorhenium(V) compounds with chelating amines yields rhenium(III) complexes. The reaction of $[ReO_2(en)_2]Cl$ with excess of zinc amalgam in HCl leads to the formation of *trans*-$[ReCl_2(en)_2]Cl$ which can be precipitated from solution as yellow solid.[638] A similar product is obtained with 2-(aminomethyl)-pyridine (ampy). The orange–red complex $[ReCl_2(ampy)_2]^+$ (**242**) contains all equivalent donor atoms in *trans* arrangement. The cations $[ReCl_2(en)_2]^+$ and $[ReCl_2(ampy)_2]^+$ undergo substitution of chloride by pyridine ligands. This ligand exchange is accomplished with accompanying isomerization to *cis* geometry as has been demonstrated with the structural analysis of $[ReCl(en)_2(picoline)]^{2+}$ (**243**).[638]

A convenient starting material for the synthesis of complexes which contain only one bipyridyl ligand is $[Re^{IV}Cl_4(bipy)]$. Reduction with tertiary phosphines gives the mixed bipy/phosphine rhenium(III) species *fac*-$[ReCl_3(bipy)(PR_3)_2]$ and *trans*,*cis*-$[ReCl_2(bipy)(PR_3)]^+$ ($PR_3 = PPh_3$, PMe_2Ph).[844] The pseudooctahedral complexes show NMR spectra with highly shifted resonances due to temperature-independent paramagnetism. Well-resolved and distinct proton resonances, however, have been found for seven-coordinate terpyridyl rhenium(III) complexes. They possess a capped trigonal-prismatic geometry and, thus, two of the three t_{2g} orbitals are sufficiently lowered in energy to cause diamagnetism. The parent compound of this class, the cationic complex $[Re(terpy)_2(OH)]^{2+}$ (terpy = 2,2′:6′,6″terpyridine), has been synthesized via a reduction/substitution route starting from $[ReO_2(py)_4]^+$.[845] The concomitant production of perrhenate implies the presence of a disproportionation. Replacement of the hydroxo ligands the $[Re(terpy)_2(OH)]^{2+}$ complex by Cl^- or NCS^- is easily achieved by the addition of HCl or KSCN. The structures of the $[Re(terpy)_2X]^{2+}$ cations (X = OH, Cl, NCS) are closely similar with the rhenium atom in the center of a capped trigonal prism. The capping positions are occupied by the anionic ligands in all compounds. An alternative approach to $[Re(terpy)_2Cl]^{2+}$ is the ligand exchange starting from the rhenium(III) benzil complex $[ReCl_3(PPh_3)(benzil)]$ which yields the dark-red product in good yields.[846] This route has been applied also for other polypyridyl complexes of rhenium with the metal in lower oxidation states, such as the rhenium(III) compounds *cis*-$[Re(bipy)_2Cl_2]^+$, *cis*-$[Re(phen)_2Cl_2]^+$, *cis*-$[Re(Bu^t\text{-}bipy)_2Cl_2]^+$ or $[ReCl_3(terpy)]$ (phen = 1,10-phenanthroline). The rhenium(II) and rhenium(I) complexes which can be prepared by a similar procedure and by ongoing ligand exchange reactions from the Re^{III} compounds will be mentioned in Sections 5.3.2.6.2 and 5.3.2.7.2. Generally has been concluded that seven-coordinated polypyridylrhenium(III) complexes can be readily reduced with loss of a ligand to form Re^I complexes and, conversely, rhenium(I) complexes may be oxidized in the presence of appropriate ligands such as Cl^-, CN^- or Bu^tNC to give Re^{III} species with coordination number seven.[846]

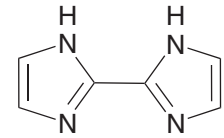
A number of complexes with biimidazole (H_2biim) ligands (**244**) demonstrate the synthetic potential of this class of ligands. Stable rhenium(III) cationic monomers of the composition $[ReX_2(PPh_3)_2(H_2biim)]X$ (X = Cl, Br, I) are obtained from reactions of oxorhenium(V) precursors with H_2biim in boiling chloroform. Crystal structures have been determined for the compounds with the three halogens as well as for the $[ReCl_2(PPh_3)(H_2biim)]$(benzoate) salt.[847] In all cases the counter ion is hydrogen-bonded to NH groups of the coordinated biimidazole. Both NH groups can be deprotonated with sodium methoxide. Competition between monodeprotonated $[ReCl_2(PPh_3)(Hbiim)]$ and various carboxylic acids reveals that the acidity of the first NH proton corresponds to that of acetic acid, whereas the second acidity is estimated to be close to that of phenol.[847] The phosphine ligands in $[ReX_2(PPh_3)(H_2biim)]^+$ complexes can be replaced by PMe_3 with retention of stereochemistry. The resulting complexes are readily deprotonated and the cationic as well as the neutral forms exhibit good stability. The relative high acidity of the NH protons makes these complexes promising candidates to prepare biimidazolato-bridged multinuclear units.[848]



(242)



(243)



(244)

A rhenium(III) complex with a strongly donating coordination environment composed primarily of nitrogen-based ligands has been introduced with the combination of bipyridyl and hydrotris (pyrazolyl)borato ligands, $\{HB(pz)_3\}^-$, in the coordination sphere of one metal atom. The red–purple complex $[ReCl\{HB(pz)_3\}(bipy)]^+$ (**245**) can be prepared in good yields from the oxorhenium(V) compound $[ReOCl_2\{HB(pz)_3\}]$ by reduction with trimethylphosphine and subsequent ligand exchange with bipy.[849] The coordination sphere of the complex allows three fully reversible redox couples in cyclic voltammetric experiments, $E_{1/2} = 1.06$ V (Re^{IV}/Re^{III}), $E_{1/2} = -0.36$ V (Re^{III}/Re^{II}) and $E_{1/2} = -1.42$ V (Re^{II}/Re^{I}). Thus, rhenium complexes comprising four oxidation states of the metal are stabilized by this ligand combination at least in the time-scale of cyclic voltammetry. The first reduction product, $[ReCl\{HB(pz)_3\}(bipy)]$, has also been prepared chemically by the reduction of the Re^{III} complex with zinc amalgam giving a black solid in excellent yields.

A number of rhenium(III) complexes has been described with the tripodal tacn (**15a**), and its *N*,*N*′,*N*″-trimethyl substituted derivative, Me_3tacn. Orange–red complexes of the composition $[Re(tacn)X_3]$ (X = Cl, Br) are obtained when the mixed-ligand species $[Re^{V}O(tacn)(glycolate)]$ is reduced by zinc dust in HCl or HBr.[250] A similar route starting from $[ReO(Me_3tacn)Cl_2]Cl$ and phosphines results in an oxygen transfer from the metal to the phosphorus atom and the formation of the phosphine oxide complexes $[Re(Me_3tacn)Cl_2(OPR_3)]$ (R = Ph, Me). The OPR_3 ligands are readily displaced by other neutral ligands such as acetonitrile, acetone, or pyridine.[199] Oxidation of the rhenium(III) complexes results in a number of different products in which the coordination of the tripodal ligand is retained depending on the conditions applied. Mononuclear rhenium(IV), -(V), or -(VII) compounds have been obtained and the formation of binuclear oxo and chloro bridged species has also been reported.[119,250] The dinuclear complexes exhibit multiple metal–metal bonding with Re–Re distances ranging from 2.36 Å to 2.53 Å.[250]

The ligand tris(2-pyridyl)amine reacts with $[ReCl_3(PPh_3)(benzil)]$ to yield the brown complex $[ReCl_3(L)]$ which has been characterized by spectroscopic methods. The compound possesses a remarkable thermal stability and survives attempted thermolysis at 270 °C.[121]

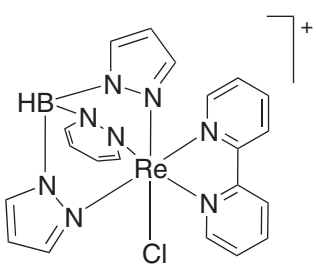
Reduction of a rhenium(V) complex with the trianionic ligand $\{(C_6F_5NCH_2CH_2)_3N\}^{3-}$ (**115**) $[ReOCl\{(C_6F_5NCH_2CH_2)_3N\}]$ with methyllithium or magnesium in the presence of a variety of two-electron ligands such as dihydrogen, ethylene, propylene, CO, N_2, phosphines, pyridine, tetrahydrothiophene, acetonitrile, or silanes give complexes of the general composition $[Re^{III}\{(C_6F_5NCH_2CH_2)_3N\}(L)]$.[432,850] Protonation of the PMe_3 complex $[Re\{(C_6F_5NCH_2CH_2)_3N\}(PMe_3)]$ gives an authentic hydrido phosphine complex $[Re\{(C_6F_5NCH_2CH_2)_3N\}H(PMe_3)]^+$, but protonation of other phosphine complexes result in compounds of the composition $[Re\{(C_6F_5NCH_2CH_2)_3N\}(\eta^2\text{-}HPR_nH_{3-n})]^+$ as has been concluded from the NMR spectra of the products showing relatively large P—H couplings of about 60 Hz.[432]

A phthalocyaninato (pc^{2-}) complex of rhenium(III) has been isolated from reactions of the Re^{II} compound $[Re(pc)(PPh_3)_2]$ with $[NBu_4]F$ in acetone in air.[851] The complex anion *trans*-$[ReF_2(pc)]^-$ can be precipitated with bulky cations. The Re—F bonds are short (1.798 Å) and the Re–F stretching vibration is observed at 746 cm^{-1}. Obviously due to a large spin-orbit coupling, the complex salt is diamagnetic with an electronic d^4 ground state of Re^{III} ($S = 1$) and a sharp ^{19}F-NMR signal at −126.1 ppm has been observed.

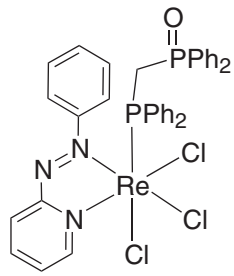
As outlined for rhenium(V) and rhenium(IV) compounds (Sections 5.3.2.3 and 5.3.2.4), 2-(arylazo)pyridines and 2-(arylazo)-1-methylimidazoles are excellent ligand systems for the stabilization of rhenium centers in these oxidation states. Reduction of the oxorhenium(V) complexes (**101**) by phosphines or ligand exchange procedures starting from $[ReCl_3(PPh_3)_2(CH_3CN)]$ provide synthetic routes to rhenium(III) complexes with these N^N chelating ligands.[406,852] The oxygen atom transfer during these reactions which also allows the oxidation of the organic framework of

the aldimines under formation of amides has been studied in a number of papers.[405,853,854] Important intermediates in these reactions are phosphine oxide complexes $[ReCl_3(OPR_3)(L)]$ which can be converted into the phosphine derivatives by subsequent ligand exchange. Transfer of one and two oxygen atoms between azopyridine rhenium(V) oxo complexes and bis(diphenylphosphino)alkanes (P⌒P) has been realized by control of the relative ratios of the two reactants and mononuclear compounds of the compositions [$ReCl_3$(azopyridine-*N*,*N*′)(OP⌒P-P)] or [$ReCl_3$(azopyridine-*N*,*N*′)(OP⌒PO-O)] (for an example see (**246**)) and binuclear products of the formula [$ReCl_3$(azopyridine)(OP⌒PO)$ReCl_3$(azopyridine)] with bridging bis-phosphine dioxide units have been obtained.[409] Related arylazo-1-methylimidazol ligands show a similar chemistry and the synthesis of several rhenium(III) complexes with phosphine or phosphine oxide co-ligands have been described together with their molecular structures.[407,408]

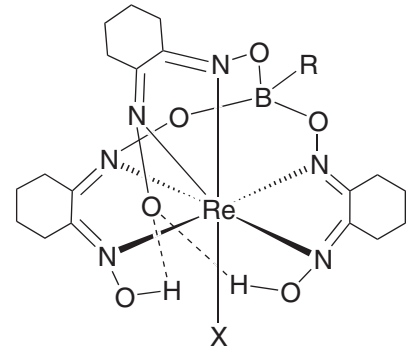
Clathrochelate complexes of the Group VII elements have attracted considerable interest since representatives with boron capped tris(dioxime) ligands have proven to be very useful in the radiopharmaceutical chemistry of technetium. Two compounds from this class of technetium(III) complexes show pronounced myocardial and cerebral uptake. Rhenium analogous tris(dioxime) complexes are known without and with boron caps.[855] Uncapped rhenium(III) tris(dioxime) complexes, [ReCl(dioximeH)$_2$(dioximeH$_2$)] are neutral, seven-coordinate compounds with a chloro ligand occupying the seventh site.[856] They can be capped at one end with a boronic acid to give [ReCl{(dioximeH)$_2$(dioxime)BR}]. Compounds of this type are available with various oximes and boronic acids and can be prepared as orange–red crystals by the combined action of a dioxime and a boronic acid on [$ReCl_3(PPh_3)_2(CH_3CN)$]. The composition of the complexes has been proven by a crystal structure analysis of the 1,2-cyclohexanedione dioxime complex which has been capped by phenylboronic acid (**247**). The geometry around the central rhenium atom can be described as a monocapped trigonal prism. Thus, the rhenium compound is isostructural to the well-known technetium complexes and contrasts to the structure of the Mn^{II} complexes which form a bicapped dioxime complex in which only two of the three oxime oxygen atoms at each end are covalently bonded to the capping boron atoms.[856] An interesting feature, an SCN/NCS bonding isomerism, has been found for monocapped dioxime complexes of type [Re(NCS/SCN){(dioximeH)$_2$(dioxime)BMe}]. Both the isomers are formed during the synthesis, the yellow–brown S-bound complex, however, isomerizes to the deep-red *N*-bound isomer.[857]



(**245**)



(**246**)



(**247**)

(iii) Sulfur and oxygen donor atoms

The number of rhenium(III) complexes with chelating sulfur or oxygen ligands is comparatively small. This may be due to by the fact that stabilization of the d^4 metal center of Re^{III} requires ligands which possess a well-balanced donor/acceptor behavior. These requirements are best met by the combination of ligands with good electron-donating properties and π-acceptors such as phosphines or carbonyls. In some cases this is realized by the decomposition of the sulfur-containing organic ligands.

The latter case has been demonstrated with the reaction of [$ReCl_3(PPh_3)_2(CH_3CN)$] with a large excess of sodium diethyldithiocarbamate which results in sulfur abstraction and in the formation of a mixed phosphine/diethyldithiocarbamato/η^2-thiocarbamoyl complex.[799] For the molecular structure of this compound see formula (**225**) which represents that of the corresponding rhenium(IV) cation which is formed by oxidation of the primarily formed Re^{III} complex and contains one rhenium–carbon bond. The formation of thiocarbamoyl compounds seems to be an essential

step in the decomposition of dithiocarbamates on rhenium(III) centers and can be regarded as intermediate for the formation of thiocarbonyl ligands which has been observed in a similar reaction between $[ReCl_3(PMe_2Ph)_3]$ and sodium diethyldithiocarbamate in ethanol. Prolonged heating of such mixtures under reflux gives the seven-coordinate complex $[Re(CS)(Et_2dtc)_3]$ in form of red crystals, whereas shorter reaction times yield the yellow rhenium(I) complex $[Re(CS)(Et_2dtc)(PMe_2Ph)_3]$.[858] The intermediate formation of a rhenium(I) compound in the course of this reaction is not unexpected in view of the dominance of acceptor ligands in its coordination sphere.

The excellent ability of sulfur-rich ligands to induce internal electron transfer in metal complexes has also been demonstrated for rhenium sulfido and perthio systems. The reduction of $[NEt_4][ReS_4]$ with tetraalkylthiuram disulfides has previously been described in Section 5.3.2.4.2(ii) and gives the binuclear Re^{IV}–Re^{IV} dimer $[Re_2(\mu\text{-}S)_2(R_2dtc)_4]$ in excellent yields when 1.5 equivalents of thiuram disulfide are used.[162,163] This dimer reacts with an additional equivalent of tetraalkylthiuram disulfide in the presence of a Lewis acid to give the dinuclear Re^{III} species $[Re_2(\mu\text{-}S\text{-}S_2CNR_2)_2(S_2CNR_2)_3]^+$ (**248**). The formation of the rhenium(III) complex involves the reduction of Re^{IV} to Re^{III} with the concomitant formation of the S—S bonds. This reaction is induced by the Lewis acidic trimethylsilyltriflate but not by protic acids such as HBF_4. The rhenium–rhenium distance in the dimer is 2.573 Å. The metal atoms in the cationic complex can be re-oxidized with cleavage of the S—S bonds in the bridging trithiocarbamate ligands and re-formation of the sulfido-bridged rhenium(IV) compound $[Re_2(\mu\text{-}S)_2(R_2dtc)_4]$. This formal oxidation of the metal atoms is achieved with reducing agents such as H_2, and may mimic in some extent hydrogenation/dehydrogenation reactions of metal sulfide solids. A similar reactivity has been observed for a reaction between $[ReS_4]^-$ and dithiobenzoate disulfide, which forms the mononuclear, green rhenium(III) complex $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$ with two chelating perthiobenzoate ligands in excellent yields.[859] This reaction can be regarded as a text-book example for an internal redox reaction in which Re^{VII} is reduced by four electrons to Re^{III} and two equivalents of dithiobenzoate disulfide are also reduced by four electrons to form dithiobenzoate. The required electrons come from the sulfido ligands of $[ReS_4]^-$ which finally form elemental sulfur which has been found to be produced during this reaction. Addition of phosphines or CN^- to $[Re(S_2CC_6H_5)(S_3CC_6H_5)_2]$ results in abstraction of sulfur and the formation of seven-coordinated rhenium(III) complexes of the compositions $[Re(S_2CC_6H_5)_3(PPh_3)]$ or $[Re(CN)(S_2CC_6H_5)_3]^-$.[859]

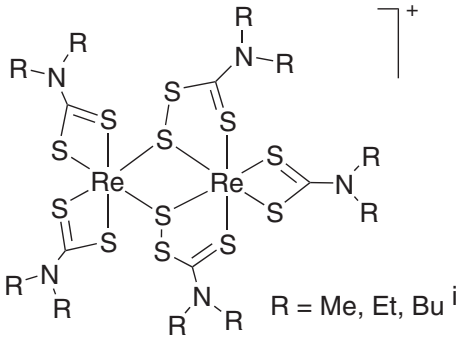
In contrast to the reactivity of numerous rhenium(V) oxo complexes towards tertiary phosphines which has been described in the previous sections, the dimeric dithiocarbamato complex $[Re_2O_3(Et_2dtc)_4]$ is unreactive in this way. Reduction to rhenium(III) products of the composition (**249**) could only be obtained, when the dimer had first been converted into the mixed catecholato/dithiocarbamato complex $[ReO(Et_2dtc)_2\{HO(O)C_6H_4)]$. $[ReO(Et_2dtc)_2\{HO(O)C_6H_4)]$ is a rare example of a complex containing catecholato ligands in monodentate coordination and readily reacts with bidentate tertiary phosphines such as bis(dimethylphosphino)ethane (dmpe) or dppe to give the green rhenium(III) cations $[Re(Et_2dtc)_2(dmpe)]^+$ or $[Re(Et_2dtc)_2(dppe)]^+$ which have been isolated and characterized as tetraphenylborate salts.[370]

An unusual reaction pattern has been found for the electrochemical and chemical (by ascorbic acid) reduction of the rhenium(II) thioether complex $[Re(9S3)_2]^{2+}$ (9S3 = 1,4,7-trithiacyclononane). Instead of the formation of the corresponding rhenium(I) complex, C—S bond cleavage and the release of ethene was observed and the brown rhenium(III) species $[Re(9S3)(SC_2H_4SC_2H_4S)]^+$ (**250**) was isolated as a BF_4^- salt.[860,861] Upon electrochemical reduction of $[Re(9S3)(SC_2H_4SC_2H_4S)]^+$ further loss of ethene was observed while the analogous technetium complex can be reversibly reduced to $[Tc(9S3)(SC_2H_4SC_2H_4S)]$.

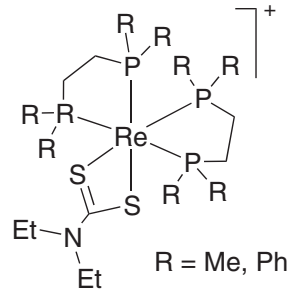
An octahedral rhenium(III) complex of the composition $[ReCl_2(PPh_3)_2(O^{\frown}O)]$ with the chelating $O^{\frown}O$ ligand 4,4,4-trifluoro-1-(2′-thienyl)butane-1,3-dionate has been prepared.[862] The PPh_3 ligands are *trans* in this complex.

(iv) Mixed-donor N/O- and N/S-ligands

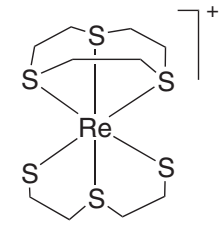
The coordination abilities of *N*-heterocyclic thiols such as 2-thiopyridine, HSpy (**66a**), 2-mercaptopyrimidine, Hspym (**66b**), or 2-mercaptothiazoline (**67**) with rhenium centers has already been described for oxorhenium(V) complexes is Section 5.3.2.3.1. It has been outlined that ligands with five-membered rings preferably coordinate as monodentate neutral thiones whereas chelate formation is possible for mercaptopyridine or mercaptopyrimidine. Similar complex formation



(**248**)



(**249**)

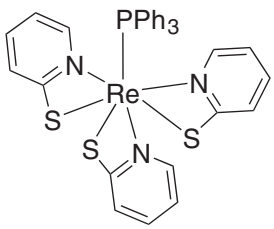


(**250**)

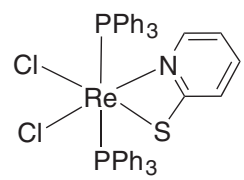
patterns can also be discussed for rhenium(III) compounds with these ligands which can be prepared either by reduction of the corresponding rhenium(V) oxo compounds with excess of the ligands or by ligand exchange procedures starting from common Re^{III} precursors such as $[ReCl_3(PPh_3)_2(CH_3CN)]$.[253,297,613–615] Two different types of products have been obtained depending on the synthetic route. Reactions of $[ReOCl_3(PPh_3)_2]$ or $[ReOCl_2(OEt)(PPh_3)_2]$ with an excess of 2-mercaptopyridine give the seven-coordinate complex $[Re(Spy)_3(PPh_3)]$ (**251**) in almost quantitative yields.[253] Avoiding a large excess of the thiol results in the formation of $[ReCl_2(PPh_3)(Spy)]$ (**252**) or $[ReCl_2(PPh_3)(Spym)]$ in similar reactions in moderate yields.[297,613] A better synthetic route for the pseudooctahedral complexes, however, is the ligand exchange starting from $[ReCl_3(PPh_3)_2(CH_3CN)]$.[297]

The oxorhenium(V)/rhenium(III) interconversion of the species $[ReOX_2(PPh_3)(SpymMe_2)]$ and $[ReX_2(PPh_3)_2(SpymMe_2)]$ ($HspymMe_2$ = 4,6-dimethylpyrimidine-2-thiol; X = Cl, Br, I) by treatment with PPh_3 or atmospheric oxygen and the related oxygen transfer from rhenium to phosphorus has extensively been studied by several spectroscopic methods and suggests this system to be an efficient catalyst.[614] In contrast to the behavior of the dimethyl-substituted mercaptopyrimidine, no rhenium(V) oxo species could be isolated during the reaction of HSpym under the same experimental conditions and exclusively rhenium(III) compounds of the composition $[ReX_2(PPh_3)_2(Spym)]$ were isolated.[615] Re-oxidation to Re^{V} was not observed for these species, but seven-coordinate species of the type (**251**) were obtained when the reaction was performed with addition of an excess of the thiol and triethylamine as proton scavenger.

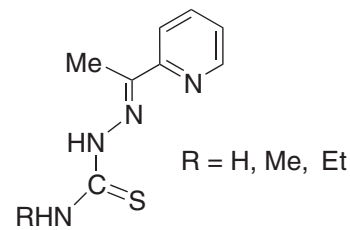
Another synthetic approach to the octahedral complexes of type (**252**) is provided by the thermal decomposition of the hydrido complex $[ReH_7(PPh_3)_2]$ in the presence of 2-mercaptoquinoline or 2-hydroxyquinoline in 1,2-dichloroethane solutions.[863] The solvent is source of the chloro ligands and, thus, essential for the formation of the rhenium(III) products. Comparable reactions in THF afford hydridorhenium(V) complexes (see Section 5.3.2.11).



(**251**)



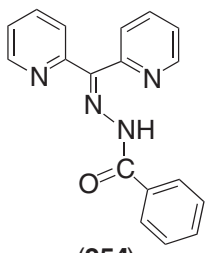
(**252**)



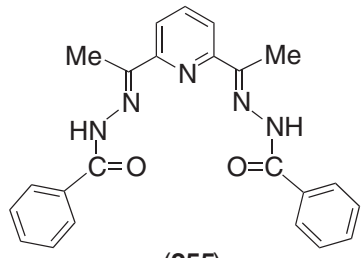
(**253**)

A series of rhenium(III) complexes with the almost planar 2-formylpyridine thiosemicarbazone (**253**) and related ligands have been synthesized from reactions of $[ReOCl_3(PPh_3)_2]$ with the potentially tridentate ligands. An alternative synthesis is a one-pot reaction between $[ReO_4]^-$ and the ligands with Ph_3P as reducing agent.[864,865] The ligands deprotonate and form dark pseudooctahedral cationic $[Re(L)_2]^+$ complexes. Decomposition of the ligands has been detected during the complex formation which results in a reductive cleavage of the hydrazinic N—N bond. The resulting ketone imine has been trapped by the formation of a rhenium complex of the composition $[ReCl_2(PPh_3)_2(py\text{-}2\text{-}C(Me)=NH)]$. The composition of this paramagnetic product has been identified unambiguously by mass spectrometry and X-ray crystallography which

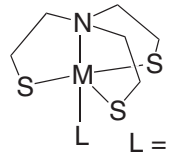
allowed the detection of the imine hydrogen atoms.[864] A product having a completely different structure has been obtained in a similar reaction of $[ReOCl_3(PPh_3)_2]$ with the analogous ligand dipyridylketone benzoylhydrazone, Hpy_2bhyd (**254**). As with the thiosemicarbazones, reduction of the metal atom and formation of a rhenium(III) species has been observed. This, however, contains additionally to two deprotonated, tridentate organic ligands one chloro ligand and a seven-coordinate $[ReCl(py_2bhyd)_2]$ complex is formed.[629] Its structure can best be described as a distorted capped trigonal prism with each of the benzoylhydrazones forming one trigonal plane and the chloro ligand capping the tetragonal plane formed by the oxygen and the pyridine nitrogen atoms. This structure contrasts that observed for a related rhenium(III) complex with 2,6-diacetylpyridinebis(benzoylhydrazone), $H_2py(benzhyd)$ (**255**). This ligand coordinates in a doubly deprotonated, pentadentate manner in the equatorial plane of the complex and the five donor atoms form an almost planar pentagon. The axial positions in the pentagonal bipyramid are occupied by a triphenylphosphine and a chloro ligand giving a composition of $[ReCl(PPh_3)\{py(benzhyd)_2\}]$.[866]



(**254**)



(**255**)



L = PR_3, CO, CNR

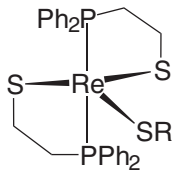
(**256**)

Rhenium(III) complexes with the tetradentate ligand 2,2′2″-nitrilotris(ethanethiolate) can readily be obtained by reduction of $[ReO_4]^-$ with phosphines or phosphite in the presence of the tris-thiol or by ligand exchange on $[ReCl_3(PPh_3)_2(CH_3CN)]$.[867,868] The resulting $[Re\{N(CH_2CH_2S)_3\}(PR_3)]$ complexes (**256**) ($PR_3 = PPh_3$, PMe_2Ph, $PMePh_2$, PBu^n_3, $POEt_3$) demonstrate the outstanding abilities of the chelating ligand to accommodate rhenium(III) in a trigonal-bipyramidal manner by providing four of the five donors. The axial phosphine ligand can be replaced by other monodentate π-acceptor ligands as has been demonstrated for a large number of isocyanides. The activated carbon atoms of the isocyanides are subject to nucleophilic attack and can be converted into CO.[869]

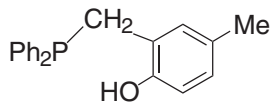
(v) Mixed-donor P/O-, P/N-, P/S-, and S/O-ligands

Whereas the tetradentate ligand $P(C_6H_4\text{-}SH\text{-}2)_3$ forms the anionic rhenium(V) complex $[Re\{P(C_6H_4\text{-}S\text{-}2)_3\}_2]$, the potentially bi- or tridentate analogues $Ph_2P(C_6H_4\text{-}SH\text{-}2)$ and $PhP(C_6H_4\text{-}SH\text{-}2)_2$ are more flexible and additionally to the oxo- and imidorhenium(V) chelates which have been described in Section 5.3.2.3, a number of rhenium(III) complexes are stabilized. Reactions of $Ph_2P(C_6H_4\text{-}SH\text{-}2)$ with various rhenium(III) or rhenium(V) precursors result in the formation of the neutral tris-chelate $[Re\{Ph_2P(C_6H_4\text{-}SH\text{-}2)\}_3]$.[745] The complex shows two reversible oxidation and one reversible reduction processes by cyclic voltammetry. Another complex with $Ph_2P(C_6H_4\text{-}SH\text{-}2)$ has been obtained from a reaction with the dimeric oxo-bridged rhenium(V) compound $[Re_2O_3(Et_2dtc)_4]$ ($Et_2dtc^- = N,N$-diethyldithiocarbamate).[370] The product is the orange–red rhenium(III) complex $[Re\{Ph_2P(C_6H_4\text{-}S\text{-}2)\}_2(Et_2dtc)]$ which has a distorted octahedral geometry with the sulfur atoms of the phosphinothiolate in a *trans* arrangement.

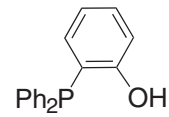
A series of five-coordinate rhenium(III) complexes containing the related ligand $Ph_2P(C_2H_4S)^-$ together with a monothiol have been synthesized and characterized. The diamagnetic compounds of the composition $[Re(Ph_2PCH_2CH_2S)_2(SR)]$ (**257**) with a trigonal-bipyramidal structure are formed by the combined action of $Ph_2P(C_2H_4SH)$ and RSH (R = Ph, Pr^n, $CH_2C_6H_5$, $CH_2CH_2PPh_2$, $CH_2CH_2P(O)Ph_2$) on the Re^{III} precursor $[ReCl_3(PPh_3)_2(CH_3CN)]$.[870] Attempts to prepare the products by reduction/substitution procedures starting from rhenium(V) precursors or perrhenate failed. The trigonal bipyramidal coordination sphere contains the three sulfur atoms in the trigonal plane and two axial PPh_3 ligands in accordance with the general structural motif for this class of complexes.



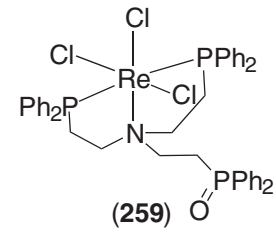
(**257**)



(**258a**)



(**258b**)



(**259**)

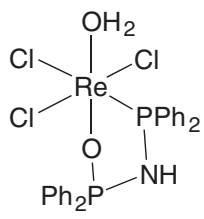
Rhenium(III) tris-chelates are formed by the reaction of 2-(diphenylphosphinomethyl)-4-methylphenol, P_1-OH (**258a**), or 2-diphenylphosphinophenol, P_2-OH (**258b**) with $[ReCl_3(PPh_3)_2(CH_3CN)]$ in a 1:3 ratio. $[Re(P_1\text{-}O)_3]$ is stable as solid and in solutions while $[Re(P_2\text{-}O)_3]$ is easily oxidized in air giving the rhenium(V) oxo complex $[ReO(P_2\text{-}O)_2(OP_2\text{-}O]$.[871] This behavior is also reflected in the electrochemical behavior of the compounds, where each one well-defined redox couple for one-electron oxidation and reduction steps are observed for both compounds. A second oxidative wave (Re^{IV}/Re^{V}) is only reversible for $[Re(P_1\text{-}O)_3]$.

Whereas the oxidation state of the rhenium atom is maintained during the reaction of the potentially tetradentate ligand tris(2-diphenylphosphinoethyl)amine, NP_3 (**179**), with the nitrido complex $[ReNCl_2(PPh_3)_2]$, the rhenium(III) complex $[ReCl_3(\eta^3\text{-NPP-}(N\{CH_2CH_2PPh_2\}_2\{CH_2CH_2P(O)Ph_2\})]$ (**259**) is obtained when the oxo compound $[ReOCl_3(PPh_3)_2]$ is used as starting material.[648] The oxidation of the noncoordinated phosphorus atom is related to the reduction of the rhenium atom. A similar product has been isolated for the related ligand with two side-arms, $PhN(CH_2CH_2Ph_2)_2$. The red–brown complex $[ReCl_3\{PhN(CH_2CH_2Ph_2)_2\}]$ is paramagnetic and most probably has a structure similar to that of $[ReCl_3(\eta^3\text{-NPP-}(N\{CH_2CH_2PPh_2\}_2\{CH_2CH_2P(O)Ph_2\})]$ (**259**).[450]

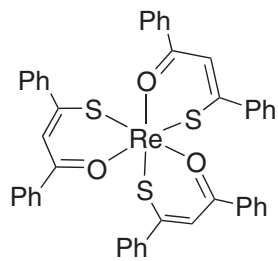
More rhenium(III) compounds with neutral chelating P^N ligands have been reported with bis(diphenylphosphino)amine, $HN(PPh_2)_2$ (**178**), and 2-(diphenylphosphino)-*N*,*N*′-dimethylaniline, $Ph_2PC_6H_4\text{-}NMe_2$-2 (**123b**). Reactions of $HN(PPh_2)_2$ with $[ReOCl_4]^-$ give various rhenium(IV) and -(III) complexes depending on the reaction conditions applied and the Re^{III} product $[ReCl_3(H_2O)\{HN(PPh_2)(OPPh_2)\}]$ (**260**) has been studied structurally showing the aqua ligand *trans* to the oxygen atom of the P=O unit. A reaction starting from $[ReCl_3(PPh_3)_2(CH_3CN)]$, however, results in the cation $[ReCl_2\{HN(PPh_2)_2\}_2]^+$.[463] Complexes of similar types are formed with ligand (**123b**) or 2-(diphenylphosphino)aniline: $[ReCl_3(P^{\frown}N)(PPh_3)]$ and $[ReCl_2(P^{\frown}N)_2]^+$.[449]

Relatively rare examples of octahedral tris-complexes of rhenium(III) with mononegative bidentate ligands have been reported for a series of monothio-β-diketonates.[872] The neutral complexes (**261**) have been prepared by a ligand exchange procedure from a thiourea precursor. An attempted synthesis starting from perrhenate was not successful. The NMR spectra of the paramagnetic complexes are well resolved and the chelate ring protons show a low-field shift what in contrast to the analogous technetium complexes where a high-field shift is observed.

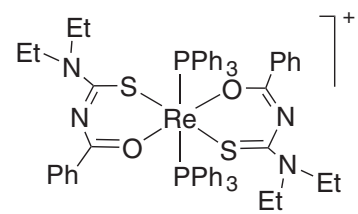
Reduction of the rhenium(V) oxo complex $[ReOCl(DEBT)_2]$ (HDEBT = *N*,*N*′-diethyl-*N*′-benzoylthiourea) with PPh_3 results in the Re^{III} cation $[Re(PPh_3)_2(DEPT)_2]^+$ (**262**).[478] The structure of the compound has been concluded from spectroscopic data.



(**260**)



(**261**)



(**262**)

5.3.2.6 Oxidation state II

Rhenium (II) complexes with the metal in the formal oxidation state +II are relatively rare. The d^5 configuration requires ligands with pronounced acceptor abilities to reduce the electron density at the metal atom. Thus, soft donor atoms such as phosphorus or π-binding ligands such aromatic amines or isocyanides dominate the rhenium chemistry of this oxidation state. Organometallic compounds are not very numerous for the Re^{II} state, and will only be regarded in exceptional cases, e.g., when they complete the coordination spheres of typical coordination compounds or represent "borderline cases" such as isocyanides. Nitrosyl and thionitrosyl complexes, which doubtlessly can be assigned to the rhenium(II) family due to their magnetic properties and the detection of well-resolved EPR spectra which are characteristic for the d^5-low-spin-configuration, will be treated separately together with all other rhenium nitrosyl complexes in Section 5.3.2.9. Generally, electron paramagnetic resonance is a useful tool to study rhenium(II) compounds and gives direct information on the geometry of the complexes and the composition of the equatorial coordination sphere in axially symmetric complexes.

The main routes for the synthesis of rhenium(II) compounds involve oxidation of rhenium(I) or the reduction of rhenium(III) complexes. Additionally a few examples are known where Re^{II} species are formed during the cleavage of Re—Re bonds of bimetallic units.

5.3.2.6.1 Phosphorus donor ligands

A major group of rhenium(II) complexes is characterized by two chelating bis-phosphines forming the equatorial plane of a distorted octahedron (**263**). The axial ligands can be varied and representatives with halides, pseudohalides, thiolates, and nitriles have been studied extensively.

Complexes of the general composition $[Re(P^{\frown}P)X_2]$ ($P^{\frown}P$ = bis(phosphines) with formula (**238**) or 1,2-bis(diphenylphosphino)benzene, X = halides or pseudohalides) are formed upon reduction of rhenium(III) species of the same composition. The formal reduction potential ranges from −0.25 V to −0.45 V vs. Ag/AgCl depending on the individual ligands.[834,837] Detailed electrochemical studies draw attention to the importance of the lipophilicity and the solubility of the electrogenerated species on the potential and the reversibility of the redox processes.[838,839] Further reduction of the rhenium(II) species generated is not reversible and, most probably, results in cleavage of rhenium–halogen bonds which has been followed by ramp-clamp voltammetry.[840] The resulting 16-electron rhenium(I) compounds $[ReCl(P^{\frown}P)]$ are unstable and readily add ligands which are present in the solution to re-form octahedral complexes as has been demonstrated for *t*-butylisocyanide with formation of the complex $[ReCl(CNBu^t)(dppe)_2]$ from such reactions.[838]

The Re—Cl bond lengths in the neutral rhenium(II) complexes of the composition $[ReCl_2(P^{\frown}P)_2]$ ($P^{\frown}P$ = ligands of formula (**238**) or 1,2-bis(diphenylphosphino)benzene) are significantly longer than in their rhenium(III) analogues $[ReCl_2(P^{\frown}P)_2]^+$, whereas a shortening of the metal–phosphorus bonds has been observed.[834,840,874,875]

The oxidative approach to rhenium(II) compounds has been reported for mixed $P^{\frown}P$/cyano complexes. The reactivity of the anionic rhenium(I) complex $[Re(CN)_2(dppe)_2]^-$ has been studied in detail showing that the CN^- ligands can readily be alkylated or protonated.[876,877] Oxidation in air yields the neutral rhenium(II) compound $[Re(CN)_2(dppe)_2]$. This red, paramagnetic compound is also obtained on dissolution of the mixed cyano/isocyanide $[Re(CN)(CNH)(dppe)_2]$ complex in solvents such as CH_2Cl_2 or THF, even under an atmosphere of dinitrogen. In order to get more insight into the interaction of rhenium cyanide species with acids, a solution of *trans*-$[Re(CN)(CNH)(dppe)_2]$ was treated with an excess of trifluoroacetic acid. The resulting violet solid was identified as the adduct complex *trans*-$[Re(CN\cdots HO_2CCF_3)_2(dppe)_2]$ (**264**) containing strong hydrogen bonds between two cyano ligands and two molecules of $HOOCCF_3$.[877] Hydrogen bonding has also been detected in similar adducts with MeOH or $HNEt_2$. The reactions doubtlessly involve the oxidation of the metal. The liberation of dihydrogen, however, has not been observed. The cyano groups in the rhenium(II) complexes do not undergo protonation due to the less electron-rich character of the oxidized rhenium atom which results in a weaker activation of the CN^- ligands to electrophilic attack.

Oxidation of rhenium(I) species has also been observed during reactions of $[ReCl(N_2)(dppe)_2]$ with thiolates which gives $[ReCl(SR)(dppe)_2]$ ($R = C_6H_4$-4-Me),[878] or $[ReCl(NCR)(dppe)_2]$ with electrophiles. Whereas the latter type of reactions with $[Et_2OH][BF_4]$ or $TMSCF_3SO_3$ lead to the formation of methylenamide rhenium(I) complexes which will be treated more in detail in Section 5.3.2.7.2(i),

reaction with $[Et_3O][PF_6]$ results in oxidation and isomerization of *cis*-$[ReCl(NCC_6H_4\text{-}4R)(dppe)_2]$ to afford *trans*-$[ReCl(NCC_6H_4\text{-}4R)(dppe)_2][PF_6]$ (R = H, Me, Cl).[879]

Translucent red crystals of the tris-chelate $[Re(dmpe)_3][F_3CSO_3]_2$ are formed when the corresponding rhenium(I) complex $[Re(dmpe)_3][F_3CSO_3]$ is oxidized by H_2O_2 in acetonitrile in the presence of CF_3SO_3H.[880] The electrochemistry of the $[Re(dmpe)_3]^{n+}$ ($n = 1$–3) is described by three interrelated oxidation steps and an associated chemical decomposition pathway. Sequential one-electron oxidation steps are dominant features in aqueous and nonaqueous solutions. Dissociation of phosphine ligands occurs for the oxidized complexes in a stepwise fashion to yield finally the species $[Re(dmpe)_2(solv)_2]^{3+}$ which is reduced at negative potentials.[881] A detailed study of the relative self-exchange rate of the $[Re(dmpe)_3]^{+/2+}$ redox couple has been performed in comparison with the analogous technetium complexes. It shows a slightly greater exchange rate for the rhenium complexes which is adequately described by the Marcus equation.[882]

The $[Re(dmpe)_3]^{2+}$ cation is one of the rare examples of a d^5 complex that is luminescent in fluid solution. It has a reducible metal and an oxidizable strong field π-acid ligand, and is highly emissive in acetonitrile solution with a high quantum efficiency.[883]

The cleavage of Re—Re multiple bonds represents an alternative route for the synthesis of rhenium(II) compounds with phosphine ligands. The reaction of $[NBu_4][Re_2Cl_8]$ with an excess of 1,2-bis(diphenylphosphino)benzene (dppbe) in refluxing nitriles gives orange–red crystals of $[ReCl_2(dppbe)_2]$ in moderate yields.[835] Further examples of reductive cleavage of Re—Re bonds yield binuclear compounds without metal–metal bonds. This has been shown by the reaction of $[Re_2(O_2CCH_3)_2X_4L_2]$ complexes (X = Cl, Br; L = py or H_2O) with the tripodal ligand $CH_3C(CH_2PPh_2)_3$ (triphos) in refluxing ethanol. The resulting bioctahedral dirhenium(II) complexes $[Re_2(\mu\text{-}X)_3(triphos)_2]Y$ where Y = Cl, Br, or BPh_4 show long Re—Re distances of about 3.2 Å which implies the absence of metal–metal bonds.[884] The paramagnetic cations display four redox processes, each two one-electron oxidations and reductions. A similar reactivity has been observed for the triply bonded dirhenium(II) complexes $[Re_2X_2(\mu\text{-}Y^{\frown}Y)_2]$ ($Y^{\frown}Y = Ph_2AsCH_2AsPh_2$ or $Ph_2PCH_2PPh_2$; X = Cl, Br) which react with carbon disulfide at room temperature with formation of thiocarbonyl and sulfido ligands.[885]

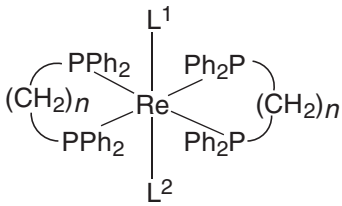
A mixture of the orange–red rhenium(I) complex $[Re(CNBu^t)_2(NCCH_3)_2(PPh_3)_2][BF_4]$ and the purple rhenium(II) species $[Re(CNBu^t)_2(NCCH_3)_2(PPh_3)_2][BF_4]_2$ is obtained when the monohydrido compound $[ReH(NCCH_3)_4(PPh_3)_2][BF_4]_2$ is treated with *t*-butylisocyanide.[886] The related reactions of $[ReH(NCCH_3)_4(PPh_3)_2][BF_4]_2$ with isopropyisocyanide and of the pyridine derivative $[ReH(NCCH_3)_3(py)(PPh_3)_2][BF_4]_2$ with *t*-butylisocyanide or isopropylisocyanide proceed in an analogous fashion to afford pairs of rhenium(II) and rhenium(I) complexes. The paramagnetic rhenium(II) compounds with μ_{eff} values between 1.2 μ_B and 1.5 μ_B have been characterized structurally and show all-*trans*-arrangement for the ligands.

Electrochemical oxidation of $[Re(CO)_2(P^{\frown}P)_2]^+$ cations ($P^{\frown}P$ = chelating bis-phosphine such as dppm yields rhenium(II) carbonyl species. The stabilities of the 17-electron compounds are dependent upon charge and ligand types. A particularly high stability has been found for *trans*-$[Re(Ph_2PCH_2PPh_2)_2(CO)X]^+$ (X = Cl, Br).[887] Another type of rhenium(II) monocarbonyl complex has been introduced by treatment of the dinitrogen complex $[Re(N_2)(CO)_2Cl(PPh_3)_2]$ with monoanionic bidentate 2-aminothiazole ligands which can be used to conjugate amino acids. The resulting red paramagnetic products of the composition $[Re(CO)Cl(PPh_3)(L)]$ (**265**) are formed as the only oxidation products in high yields when benzene is used as solvent, whereas a mixture of the rhenium(II) complex with complexes having rhenium in higher oxidation states is formed in polar solvents.[888] The PPh_3 ligands are *trans* to each other.

5.3.2.6.2 Nitrogen and sulfur donor ligands

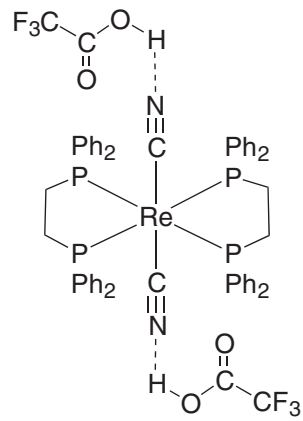
Polypyridyl ligands are able to stabilize electron-rich metal centers as has been shown for the d^6-systems Ru^{II} and Os^{II}. This suggests this class of ligands also to be appropriate for rhenium(I) compounds, and this will be discussed more in detail in Section 5.3.2.7.2, and rhenium(II) complexes which represent intermediates in the syntheses of the Re^I species or are accessed by oxidation of Re^I.

Air-stable blue–black crystals of $[Re(bipy)_3][ReO_4]_2$ have been isolated from reaction mixtures containing $K_2[ReF_6]$ and bipy (bipy) in moderate yields.[889] A more facile synthesis for the $[Re(bipy)_3]^{2+}$ cation and the related complexes $[Re(Bu^t\text{-}bipy)_3]^{2+}$ and $[Re(phen)_3]^{2+}$ starts from the rhenium(III) complex $[ReCl_3(benzil)(PPh_3)]$ and $Tl[PF_6]$ as chloride scavenger.[846] At low concentrations and the addition of one equivalent of $Tl[PF_6]$ only ligand exchange and the formation of

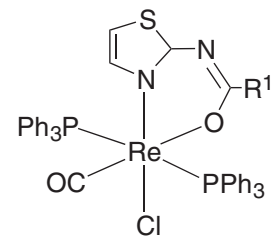


$L^1 = L^2 = Cl, Br, CN, SR$
$n = 1–3$

(**263**)



(**264**)



R^1 = Ph,C(R^2)NHCOOBu^t
C(R^2)NHCOOCH$_2$Ph

(**265**)

the rhenium(III) product *cis*-[Re(N$^\frown$N)$_2$Cl$_2$][PF$_6$] is observed, whereas at high concentrations of [ReCl$_3$(benzil)(PPh$_3$)] and excess of Tl[PF$_6$] the rhenium(II) dications are the major products. Another useful precursor for the synthesis of [Re(N$^\frown$N)$_3$]$^{2+}$ dications is *cis*-[Re(N$^\frown$N)$_2$Cl$_2$][PF$_6$] as has been demonstrated for the bipy derivative. The transformation is achieved stepwise where [Re(bipy)$_2$Cl$_2$]$^+$ is first reduced to [Re(bipy)$_2$Cl$_2$] with zinc amalgam and then the chloro ligands are removed by Tl[PF$_6$] in the presence of bipy. [Re(bipy)$_3$]$^{2+}$ can also be obtained directly from [ReCl$_3$(PPh$_3$)$_2$(CH$_3$CN)] and excess of bipy in refluxing ethanol as reducing agent.

An oxidative approach to rhenium(II) amine complexes is represented by the reaction of the dinitrogen complex *fac*-[Re(PPh$_3$)(PF$_3$)(dien)(N$_2$)]$^+$ (dien = diethylenetriamine) with silver triflate which forms *fac*-[Re(PPh$_3$)(PF$_3$)(dien)(F$_3$CCOO)][F$_3$CCOO] as a yellow solid. The compound is paramagnetic as expected for a mononuclear rhenium(II) complex and shows a broad EPR signal, but no coupling could be resolved.[890] An attempt to prepare a rhenium(II) dihydrogen complex starting from *fac*-[Re(PPh$_3$)(PF$_3$)(dien)(F$_3$CCOO)][F$_3$CCOO] in acetone resulted in the substitution of the triflate ligand and a complex with η^1-bonded acetone, *fac*-[Re(PPh$_3$)(PF$_3$)(dien)(OCMe$_2$)]-[F$_3$CCOO]$_2$. The desired dihydrogen complex is obviously unstable as is suggested by the electrochemical oxidation of the analogous rhenium(I) compound which results in a chemically irreversible wave at $E = +1.28$ V vs. NHE.[890]

A useful precursor for the synthesis of rhenium(I) and rhenium(III) compounds has been prepared in an unusual reaction, the interaction of the rhenium(V) hydrazido complex [Re{NNC(Ph)O}Cl$_2$(PPh$_3$)$_2$] with terpy, which gives the black rhenium(II) complex [ReCl(PPh$_3$)$_2$(terpy)]$^+$ (**266**) in almost quantitative yield.[891] The phosphine ligands occupy the axial positions with the nitrogen atoms of the terpy ligand and Cl$^-$ lying in the equatorial plane. The chloro salt can readily be converted into the triflate salt without changes in the structure of the complex cation.

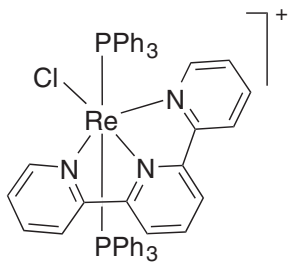
Treatment of the rhenium(III) complex [Re{HB(pz)$_3$}Cl(bipy)][F$_3$CCOO] with zinc amalgam in MeOH gives the one-electron reduction product [Re{HB(pz)$_3$}Cl(bipy)] (**267**) in excellent yields. The reduction results in a color change from red to almost black. The isolated rhenium(II) complex belongs to a series of rhenium {HB(pz)$_3$}$^-$/bipy mixed-ligand complexes which stabilize the metal in four different oxidation states.[849] This flexibility is attributed to the ability of the nitrogen heterocyclic ligands to act as both weak π-donors and π-acceptors depending on the demand of the metal.

Monomeric and dimeric porphyrinato and phthalocyaninato complexes of rhenium(II) have been prepared starting from high-valent precursors such as dirheniumheptoxide or rhenium(V) oxo compounds and appropriate reducing agents such as phosphines. A typical reaction is that of [ReO(OEP)Cl] (OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion) with PMe$_3$ at a temperature of 110 °C for 24 h which gives the orange–red complex *trans*-[Re(OEP)(PMe$_3$)$_2$] in good yields.[892] Similar procedures have been applied to other phosphine/porphyrinato complexes. Magnetic measurements show that the d^5 complexes are in a low-spin configuration. EPR spectra consist of a six-line pattern due to the nuclear spin of 5/2 of the rhenium ^{185,187}Re nuclei at $g = 2.33$. No nitrogen or phosphorus hyperfine couplings have been observed. Pyrolysis of the *trans*-[Re(porphyrinate)(PR$_3$)$_2$] complexes results in cleavage of the Re—P bonds and the formation of triply bonded dimers of the composition [Re(porphyrinate)]$_2$.[893] Solid-state magnetic measurements indicate that the compounds are diamagnetic despite some unusual ^{1}H NMR

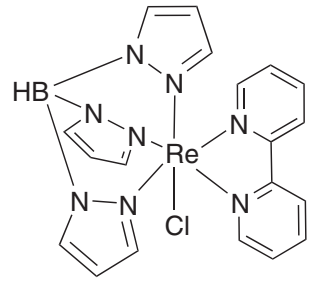
chemical shifts have been observed in solution. $[Re(porphyrinate)]_2$ can be oxidized to give mono- and dicationic dimeric complexes. UV–vIS and vibrational spectroscopic data indicate that these oxidations occur at the metal–metal bond rather than at the porphyrin ligands.

Dirheniumheptoxide reacts with phthalonitrile in boiling 1-chloronaphthalene and subsequent reprecipitation of the green crude products from concentrated sulfuric acid gives an oxo-phthalocyaninate of rhenium, which is reduced by molten PPh_3 forming dark-green *trans*-$[Re(pc)(PPh_3)_2]$ (pc^{2-} = phthalocyaninato dianion).[894] The rhenium atom is situated in the center of the plane which is defined by the nitrogen atoms of the phthalocyaninato ring. Thermal decomposition of *trans*-$[Re(pc)(PPh_3)_2]$ results in the formation of the blue dimer $[Re(pc)]_2$ in which two cofacial phthalocyaninates are bonded together by a Re—Re bond with a length of 2.285 Å.[895] The rhenium atoms are located distinctly outside the center of the N_4 plane by 0.4 Å which contrasts the situation in the monomeric compound *trans*-$[Re(pc)(PPh_3)_2]$.

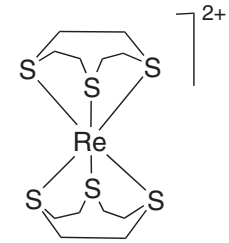
A homoleptic thioether complex can be prepared by the reaction of perrhenate with 9S3 (**15b**) in glacial acid in the presence of $SnCl_2$.[860,896] Red–brown crystals of $[Re(9S3)_2][PF_6]_2$ have been isolated and studied structurally showing a mean Re—S distance of 2.37 Å. Treatment of $[Re(9S3)_2][PF_6]_2$ (**268**) with ascorbic acid does not result in reduction of the rhenium atom but in its oxidation and the release of ethene by decomposition of the cyclic thioether. The resulting rhenium(III) complex $[Re(9S3)(SCH_2CH_2SCH_2CH_2S)][PF_6]$ has been isolated and studied by X-ray crystallography.[860]



(**266**)



(**267**)



(**268**)

5.3.2.7 Oxidation state I

The chemistry of rhenium(I) is dominated by organometallic compounds which are not covered by this review. Thus, cyclopentadienyl and related compounds, where the "organometallic part" of the molecule dominate the properties will generally not be considered. Nevertheless, compounds with carbonyl or isocyanide co-ligands will be treated when they can be regarded as constituents of a "typical coordination compound" or the compounds are of fundamental interest in a radiopharmaceutical context such as the hexakis(isocyanide)rhenium(I) cations. For the same reason a separate section has been included which gives a brief summary of recent attempts to develop synthetic routes to tricarbonylrhenium(I) complexes for nuclear medical applications.

The d^6 configuration of rhenium(I) requires ligand systems which are able to accept electron density from the electron-rich metal center. Thus, frequently phosphines, nitrogen heterocycles, carbonyls, or isocyanides are encountered. Most of the octahedral products possess a high thermodynamic stability and kinetic inertness as is expected for 18-electron d^6 systems.

5.3.2.7.1 Complexes containing exclusively monodentate ligands

(i) Phosphorus donor ligands

The rhenium(V) complex $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$ containing a chelating benzoylhydrazido ligand is a known suitable starting material for the synthesis of rhenium(I) dinitrogen complexes with phosphine ligands.[897] Extension of this work to phosphite and phosphonite ligands allows the synthesis of compounds of the compositions $[ReCl(N_2)(PPh_3)(L)_3]$ (**269a**) or $[ReCl(N_2)(L)_4]$ (**269b**) (L = $P(OMe)_3$, $PPh(OEt)_2$, $PPh(OMe)_2$) depending on the reaction conditions and the solvents used.[898,899] The dinitrogen complexes react with isocyanides to afford the complexes

$[ReCl(CNR)_3(L)_2]$ (R = C_6H_4-4-Me, C_6H_2-2,4,6-Pr^i_3 for L = $P(OMe)_3$ and R = Me for L = $PPh(OMe)_2$). Direct treatment of $[Re(NNCH_2Ph)Cl_2\{P(OMe)_3\}_3]$ or $[Re(NNCH_2Ph)Cl_2(PPh_3)\{P(OEt)_3\}_2]$ with isocyanides in refluxing methanol gives the mixed-ligand dinitrogen complexes $[ReCl(N_2)(CNR)\{P(OMe)_3\}_3]$ (R = Me, Et, Bu^t, C_6H_4-4-Me, C_6H_4-4-Cl) or $[ReCl(N_2)(CNMe)(PPh_3)\{P(OEt)_3\}_2]$.[900]

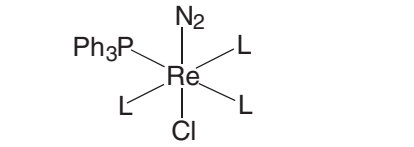
Whereas reactions of the rhenium(III) precursors $[ReCl_3\{PPh(OEt)_2\}_3]$ with arylhydrazines give arylhydrazido complexes in good yields, similar reactions with alkylhydrazines $RNHNH_2$ (R = H, Me, Bu^t) afford the bis(dinitrogen) complexes $[Re(N_2)_2\{PPh(OEt)_2\}_4]^+$, the dinitrogen complex $[ReCl(N_2)\{PPh(OEt)_2\}_4]$ or methyldiazenido derivatives $[ReCl(NNCH_3)(CH_3NHNH_2)\{PPh(OEt)_2\}_3]^+$ in moderate yields.[901] An X-ray structural analysis of the bis(dinitrogen) complex $[Re(N_2)_2\{PPh(OEt)_2\}_4][BPh_4]$ shows the two N_2 ligands in *trans*-arrangement with a N—N distance of 1.09 Å. Only one $\nu(N_2)$ band is observed in the infrared spectrum of the compound at 2,094 cm^{-1}. The neutral mono(dinitrogen) complex $[ReCl(N_2)\{PPh(OEt)_2\}_4]$ also shows $\nu(N_2)$ as a sharp strong band at 2,027 cm^{-1} and only one sharp singlet in the ^{31}P-NMR spectrum of the compound, strongly suggesting a *trans*-arrangement for the Cl^- and dinitrogen ligands. Analogous bis(dinitrogen) complexes of rhenium(I) are obtained with phosphite co-ligands by treating $[ReOCl_3(AsPh_3)_2]$ first with $P(OMe)_3$ or $P(OEt)_3$ and then with an excess of *t*-butylhydrazine.[902] The reaction of $[ReOCl_3(AsPh_3)_2]$ with phosphites probably proceeds to give rhenium(III) intermediates of the composition $[ReCl_3(L)_3]$ which have not been isolated, but readily react with *t*-butylhydrazine to give the yellow bis(dinitrogen) complexes in 30–40% yield. Reactivity studies show that the dinitrogen compounds are stable and the N_2 ligands cannot be substituted by CO, phosphines, or other donor ligands.

The reactivity of coordinated dinitrogen molecules, however, has been demonstrated by the reaction of $[ReCl(N_2)(PMe_2Ph)_4]$[903] with one equivalent of the iron porphyrinato complexes [Fe(porph)(triflate)] (H_2porph = octaethylporphyrine or tetra(4-tolyl)porphyrine) which gives the dinitrogen-bridged species $[(Cl(PMe_2Ph)_4ReNNFe(porph)][triflate]$ (**270**).[904] The dissociation of the labile triflate ligand from the iron porphyrine is crucial for the formation of the bridged species and no comparable reaction has been observed when [Fe(porph)Cl] is used as starting material. The Re–N–N–Fe linkage is essentially linear with a π-delocalized system showing bond lengths of 1.832 Å for the Re—N bond and 1.17 Å for the N—N bond, respectively. The relatively long Fe–N distance of 1.93 Å indicates that only a weak Fe–N_2 π-interaction is present which is consistent with the magnetic moment of 4.4 μ_B at room temperature. Nitrogen-15 NMR spectroscopy has been shown to be a useful tool to study the formation of dinitrogen-bridges with acceptor molecules. Bi- and trinuclear adducts which are formed between $[ReCl(N_2)(PMe_2Ph)_4]$ and π-acceptors such as $TiCl_4$, $ZrCl_4$, $HfCl_4$, $NbCl_5$, and $TaCl_5$. The chemical shifts observed reflect the bonding modes and to some extent the reactivity of the dinitrogen ligand.[905] Another ^{15}N-NMR study on $[ReCl(N_2)(PMe_2Ph)_4]$ emphasizes the importance of shielding anisotropy for the $^{15}N_2$ ligand at higher magnetic fields and the presence of dipole–dipole mechanisms at lower fields.[906]

A facile one-pot synthesis for the synthesis of the dicarbonylrhenium(I) complex $[Re(CO)_2Cl(N_2)(PPh_3)_2]$[907] has been developed which gives this compound in good yields. It starts from a mixture of perrhenate, HCl, PPh_3, and benzoylhydrazine in CH_2Cl_2/methanol. When CO gas is bubbled into this mixture, the known pale-yellow complex $[Re(CO)_2Cl(N_2)(PPh_3)_2]$ precipitates from the solution. This compound represents a useful precursor for the synthesis of a number of rhenium(II) and (surprisingly) rhenium(V) complexes.[888]

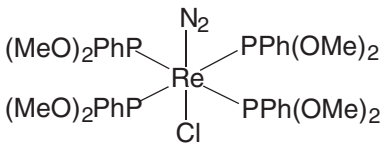
A series of dihydrogen complexes of rhenium(I) has been prepared showing that the binding strength of the H_2 ligand is comparable to that of N_2. Since most of this chemistry is "organometallic", it is not considered here in detail. Typical compounds are $[ReCl(H_2)(PMe_2Ph)_4]$ which has been subject of a detailed structural study,[908] $[Re(H_2)(CNBu^t)_3(PPh_3)_2]^+$, or $[Re(H_2)(CNBu^t)_5]^+$.[909] A number of reviews are available which cover this chemistry in all its facets.[910–913]

The dihydrogen complexes $[Re(H_2)(CNBu^t)_3(PPh_3)_2]^+$ and $[Re(H_2)(CNBu^t)_5]^+$ are members of a series of mixed-ligand rhenium(I) complexes which can be derived from the hydrido species $[Re(CNBu^t)_3(PR_3)_2H]$ (PR_3 = PPh_3, P(cyclohexyl)$_3$). These compounds react with halocarbons with formation of $[ReCl(CNBu^t)_3(PR_3)_2]$ complexes which can be oxidized to the corresponding 17-electron rhenium(II) complexes.[909] The cleavage of rhenium-hydrido bonds has also been applied for the synthesis of a number of compounds with trimethylphosphine. Reactions of $[Re(PMe_3)_5H]$ with CO_2 yields white crystals of $[Re(PMe_3)_4(CO)(O_2CH)]$ (**271**) with an unidentate formato ligand, whereas a similar reaction with MeI yields $[Re(PMe_3)_4(CO)I]$.[914]

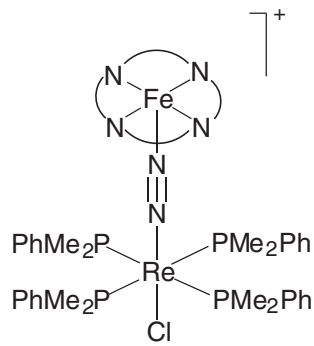


L = $P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$

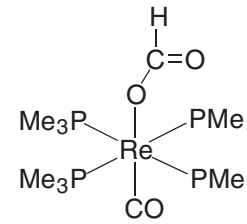
(**269a**)



(**269b**)



(**270**)



(**271**)

(ii) Selected isocyanide complexes

Isocyanide complexes are usually defined as being organometallic. Nevertheless, some of the rhenium(I) representatives are treated here in the light of the application of their technetium analogues in diagnostic nuclear medicine. Hexakis(isocyanide) complexes of technetium can readily be prepared from ligand exchange procedures starting from $[Tc(tu)_6]^{3+}$ or by direct reduction of pertechnetate with sodium dithionite in the presence of excess of the corresponding ligands.[915] The latter procedure is not appropriate for rhenium analogues due to the insufficient reducing power of the $[S_2O_4]^{2-}$ anion. $[Re(CNR)_6]^+$ complexes (R = Bu^t, Ph, Cyclohexyl, Me, C_6H_3-2,6-Me_2) can be prepared from reactions of $[ReOCl_3(PPh_3)_2]$ with an excess of the ligands,[915] or by the reductive cleavage of the Re—Re bonds in the binuclear complex $[Re_2(O_2CCH_3)_4Cl_2]$.[916] The cations can be precipitated as air-stable, white solids as $[PF_6]^-$ salts. The ν(CN) vibrations are detected at about 2,090 cm^{-1}. From a detailed analysis of the vibrational spectra of $[Re(CNBu^t)_6][PF_6]$, force constants of $k_{(NC)} = 1{,}684\ nm^{-1}$ and $k_{i(NC)} = 21\ Nm^{-1}$ have been derived.[917]

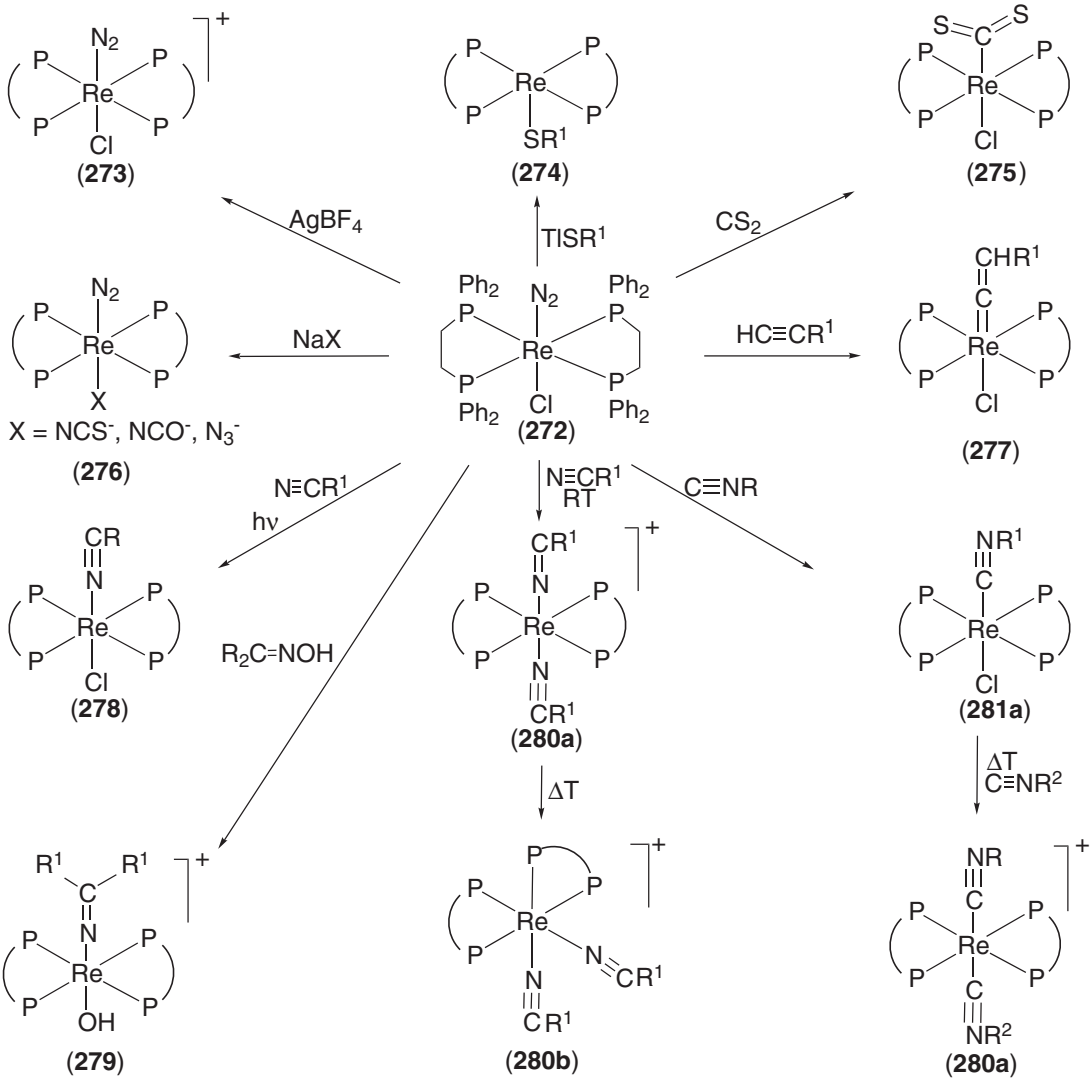
$[Re(CNR)_6]^+$ complexes are robust as expected for d^6 complexes and undergo reaction only under drastic conditions. Thus, they can be chlorinated or brominated to give the seven-coordinate rhenium(III) cations $[Re(CNR)_6X]^{2+}$ (X = Cl, Br). The products of this reaction readily dealkylate to form cyano species of the composition $[Re(CNR)_5(CN)X]^+$.[918]

Irradiation of $[Re(CNC_6H_3$-2,6-$Me_2)_6]^+$ with UV light in CH_2Cl_2 in the presence of halide ions yields complexes of the type $[Re(CNC_6H_3$-2,6-$Me_2)_5X]$ (X = Cl, Br, or I). The quantum yield of this reaction is high and results in chemical yields between 30% and 40%.[916] Products of the same composition have been obtained directly from the cleavage of the metal–metal bond in quadruply bonded rhenium complexes of various compositions in the presence of isocyanides.[919]

5.3.2.7.2 Complexes with chelating ligands

(i) Phosphorus donor ligands

Chelating bis(phosphines) of the general composition (**238**) which play an important role in the chemistry of rhenium(V), rhenium(III), and rhenium(II) are also of special interest for the coordination chemistry of the d^6 centers in rhenium(I) compounds. A combination with appropriate co-ligands which preferably have acceptor properties allows a perfect compensation of the high electron density at the metal center. An almost planar equatorial $\{Re(dppe)_2\}^+$ coordination sphere is a common structure motif. The dinitrogen complex *trans*-$[Re(N_2)Cl(dppe)_2]$ (**272**) is representative of a whole family of such complexes (Scheme 20). The pale-yellow compound can be prepared from the benzoylhydrazidorhenium(V) complex $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$, dppe, and NaOMe in refluxing methanol in good yields. A huge number of derivatives containing different P⌒P ligands have been prepared following this method.[920] Significant amounts of the five-coordinate species of the type $[ReCl(P⌒P)_2]$[921] are only obtained when P⌒P is bis{(4-trifluoromethyl)phenylphosphino} ethane. Interestingly, the five-coordinate complex with trigonal-bipyramidal structure does not react with N_2, though it reacts with CO or $CNCH_3$.



Scheme 20

Both the dinitrogen and the chloro ligands of *trans*-[Re(N_2)Cl(dppe)$_2$] are potential reaction sites. Electrochemical oxidation shows a reversible one-electron step which confirms the stability of a rhenium(II) dinitrogen species as has been described in an early work.[897] Chemical oxidation by Ag[BF_4] results in the formation of the rhenium(II) species *trans*-[Re(N_2)Cl(dppe)$_2$][BF_4] (**273**) and $NCCH_3$ readily replaces the N_2 ligand to afford *trans*-[Re(CNMe)Cl(dppe)$_2$][BF_4].[922] Photochemical chlorination of [Re(N_2)Cl(dppe)$_2$] with CH_2Cl_2 gives [Re_2Cl_8(dppe)$_4$].[922] Substitution of the dinitrogen ligand is also observed during reactions with thiolates and products of the compositions [Re(SC_6H_4-4-Me)(dppe)$_2$] (**274**) and [Re(SC_6H_4-4-Me)Cl(dppe)$_2$] have been isolated containing rhenium in the oxidation states "+1" and "+2", respectively.[878] A complex which has been assigned to [ReCl(η^2-CS_2)(dppe)$_2$] (**275**) was isolated from the reaction of [Re(N_2)Cl(dppe)$_2$] with CS_2 in THF under irradiation with UV light. The structure of this yellow solid is somewhat uncertain since an IR band at 1,205 cm^{-1} favors formulation as thiocarbonyl species.[878]

The coordination of the dinitrogen ligand is maintained when *trans*-[Re(N_2)Cl(dppe)$_2$] is exposed to NaX salts (X = NCS^-, NCO^-, N_3^-) in THF/MeOH solutions. The isothiocyanato and azido complexes of type (**276**) have been studied by X-ray structural analysis.[923] A Re—N_2 bond length of 1.951 Å is observed for the NCS^- compound which is somewhat shorter than that in the starting material and indicates a considerable degree of double bond character.

Reactions of *trans*-[Re(N_2)Cl(dppe)$_2$] with 1-alkynes HC≡CR (R = Ph, Et, Bu^t, TMS, CO_2Me) cause replacement of the dinitrogen ligand giving access to the vinylidene compounds [ReCl(=C=CHR)(dppe)$_2$] (**277**).[924] The molecular structure of the red phenylvinylidene complex shows that the rhenium–carbon bond (Re—C = 2.046 Å) has double-bond character and the Re=C=C bond is slightly bent. Since the vinylidene ligand is coordinated on the electron-rich metal site {ReCl(dppe)$_2$} it is subject to β-electrophilic attack which allows conversion of a carbyne species by protonation.[925] A structurally related compound is obtained when *trans*-[Re(N_2)Cl(dppe)$_2$] reacts with trimethylsilylcyanide. The initially formed ligand exchange product *trans*-[ReCl(CNTMS)(dppe)$_2$] undergoes a secondary reaction which cleaves the N—Si bond when it is treated with MeOH or HBF_4 to give the neutral compound *trans*-[ReCl(CNH)(dppe)$_2$] and the aminocarbyne species *trans*-[ReCl(CNH_2)(dppe)$_2$]$^+$.[926]

Treatment of *trans*-[Re(N_2)Cl(dppe)$_2$] with nitriles in boiling solvents affords *trans*-[Re(NCR)Cl(dppe)$_2$] (**278**) complexes with nitriles with various substituents (R = Me, C_6H_4-4-Me, C_6H_4-4-OMe, C_6H_4-4-F). Protonation of the products with H[BF_4] gives [ReCl(N=CHR)(dppe)$_2$] complexes, and provides a novel route to methyleneamido ligands.[927] The same products are obtained during reactions of the nitrile complexes with [Et_2OH][PF_6] and have been unambiguously characterized as azavinylidene compounds by spectroscopic methods and the X-ray crystal structure of one example.[879] The resulting CNHR ligands behave as three-electron donors and as strong π-acceptors. The ligated methyleneamide has a linear coordination and thus resembles the linear coordination mode of NO^+. Previous reports by the same authors, which discussed the formation of a hydrido complex,[928–930] have been refused.[879] Another approach to methylenamide complexes is possible by the oxidative addition of an oxime with N—O bond cleavage as in the reaction of Me_2C=NOH with *trans*-[Re(N_2)Cl(dppe)$_2$] in the presence of a Tl[BF_4]/Tl[HSO_4] mixtures. The resulting methylenamide complex *trans*-[Re(OH)(N=CMe_2)(dppe)$_2$]$^+$ (**279**) undergoes ready replacement of the OH^- ligand by F^- upon reaction with H[BF_4].[931] The linearly bound N=CMe_2 ligand behaves as a π-acceptor and exerts a significant *trans* influence.

The configuration of [Re(NCR)$_2$(dppe)$_2$]$^+$ complexes (**280**) can be controlled by the reaction conditions and the temperature of the ligand exchange reaction starting from *trans*-[Re(N_2)Cl(dppe)$_2$]. When the reaction with NCC_6H_4-4-Me is performed in boiling THF in the presence of Tl[BF_4], the *trans* isomer (**280a**) is isolated together with the rhenium(III) cation [ReF_2(dppe)$_2$]$^+$. The $\nu_{(CN)}$ band in *trans*-[Re(NCC_6H_4-4-Me)$_2$(dppe)$_2$]$^+$ is found at 2,140 cm^{-1} which points to the electron-rich nature of the {Re(dppe)$_2$}$^+$ site and a considerable electron transfer from the metal to the ligand[836] The corresponding bands in the *cis* isomer, which is obtained when the reaction is performed at ambient temperatures, are found between 2,200 cm^{-1} and 2,185 cm^{-1}.[932,933] Isomerization of *cis*-[Re(NCR)$_2$(dppe)$_2$]$^+$ complexes into their *trans* analogues is observed upon heating of solutions of the salts, activation by sunlight or by electrochemical activation.[934,935] *cis*-Arrangement of two dppe ligands has also been assigned for [Re(η^2-BH_4)(dppe)$_2$] based on spectroscopic data. The compound is formed when *trans*-[Re(N_2)Cl(dppe)$_2$] reacts with Na[BH_4] in the presence of Tl[BF_4] as chloride scavenger.[936]

As with their *trans* isomers, treatment of the nitrile complexes *cis*-[ReCl(NCR)(dppe)$_2$] (R = aryl) with [Et_2OH][BF_4] or $TMSCF_3SO_3$ in CH_2Cl_2 leads to the formation of the methylenamide compounds *cis*-[ReCl{NC(E)R}(dppe)$_2$]$^+$ (E = H, TMS) and *trans*-[ReCl(NCHR)-(dppe)$_2$]$^+$. The products undergo deprotonation by bases such as [NBu_4]OH to form the *trans* isomers of the corresponding nitrile complexes [ReCl(NCR)(dppe)$_2$]. Reactions of *cis*-[ReCl(NCR)(dppe)$_2$] complexes with [Et_3O][PF_6] result in oxidation and isomerization to afford the rhenium(II) complexes *trans*-[ReCl(NCR)(dppe)$_2$][PF_6].[836]

Alkyl- and arylisocyanide complexes of the type (**281**) are formed by treatment of *trans*-[Re(N_2)Cl(dppe)$_2$] with the corresponding ligands CNR (R = Me, Bu^t, Ph, C_6H_4-4-Me, C_6H_4-4-Cl, C_6H_2-2,4,6-Pr$^i_3$) and *trans* geometry is maintained after monosubstitution (**281a**).[937] Disubstitution and the formation of symmetric or asymmetric *trans*-[Re(CNR^1)CNR^2)(dppe)$_2$]$^+$ (**281b**) complexes is observed when *trans*-[ReCl(CNR^1)(dppe)$_2$] complexes are treated with CNR^2 ligands either in the presence of Tl[BF_4] or Tl[PF_6] or in boiling solvents such as CH_2Cl_2 or THF. In the latter case the presence of a thallium salt is not required and this approach can also be used for the synthesis of symmetrical complexes starting directly from the dinitrogen complex (**272**).[938] The disubstituted derivatives (**281b**) undergo at least one reversible one-electron oxidation as assessed by cyclic voltammetry.

The above examples demonstrate the enormous synthetic potential of the electron-rich complex fragment {Re(dppe)$_2$}$^+$ which allows well-defined ligand substitutions in the axial positions and a variety of reactions at the coordinated ligands. This has also been observed for other ligands

including cyanamide,[939,940] cyanoguanidine and its derivatives.[941] Special attention has also been drawn to the coordination chemistry of cyano ligands bonded to the $\{Re(dppe\}_2\}^+$ center which are activated and give access to an number of protonation and alkylation reactions.[876,877,942–946] The course of the reactions can be controlled by the substrate as well as by co-ligands which influence the electronic situation at the reactive site. This opens the door to a new exciting area of organometallic chemistry.

Whereas the rhenium coordination chemistry with dppe is dominated by the formation of bis-complexes which normally contain the chelating bis(phosphine) ligands in one plane, the formation of tris-chelates has been observed for the methyl derivative bis(dimethylphosphino)ethane (dmpe) and, surprisingly, for dppm. The $[Re(dmpe)_3]^+$ cation is formed in good yields when either $[ReO_2(py)_4][CF_3SO_3]$ or $[ReOCl_2(OEt)(PPh_3)_2]$ is treated with excess of dmpe.[947] The phosphine itself acts as reducing agent and the cationic complex can be isolated with bulky anions. The redox behavior of $[Re(dmpe)_3]^+$ in DMF is described in terms of three interrelated one-electron oxidations and the chemistry from decomposition of the electrogenerated rhenium(III) species.[881] The formation of the tris-chelate $[Re(dppm)_3]^+$ is remarkable with regard to the steric requirements of the ligand. The compound is formed as yellow iodide salt from the reaction of $[ReO_2(PPh_3)_2I]$ with a large excess of the phosphine in refluxing methanol in 30% yield. The coordination geometry is a strongly distorted octahedron with *cis*-P–Re–P angles between 69° and 107°.[948]

(ii) Nitrogen donor ligands

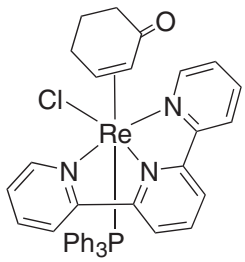
The ability of polypyridyl ligands to accept electron density from electron-rich rhenium centers and, thus, to contribute to the stabilization of rhenium complexes with the metal in low oxidation states has already been discussed for rhenium(II) compounds. Only small modifications to the polypyridyl ligand or the metal center can create dramatic differences in the properties of the resulting complexes. Generally, the starting materials which have been introduced as precursors for rhenium(II) polypyridyl complexes in Section 5.3.2.6.2, are also appropriate for the synthesis of related rhenium(I) compounds.

$[ReCl_3(PPh_3)(benzil)]$ reacts with bipy and related ligands or terpy to form a number of rhenium(III) and rhenium(II) compounds which are useful precursors for the synthesis of lower-valent rhenium complexes.[846] Thus, reduction of $[Re(bipy)_3][PF_6]_2$ with zinc amalgam results in the rhenium(I) compound $[Re(bipy)_3][PF_6]$ in excellent yields. The corresponding terpyridyl bis-chelate $[Re(terpy)_2][PF_6]$ has been prepared in a similar manner.[846] The electrochemistry of the products provides a convenient measure of the chemical reactivity associated with the redox processes. Thus, the one-electron oxidation of $[Re(bipy)_3]^+$ is reversible at -0.33 V, whereas the Re^{II}/Re^{III} redox couple is irreversible and occurs at relatively low potentials (+0.61 V) which is consistent with the instability of $[Re(bipy)_3]^{3+}$ in solution.[889] However, in the presence of a small coordinating molecule such as $CNBu^t$, oxidation to the rhenium(III) state is readily available by the formation of seven-coordinate complexes of the composition $[Re(bipy)_3(L)]$.[846]

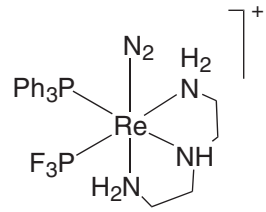
The rhenium(II) complex $[Re(terpy)(PPh_3)_2Cl]^+$, which can be prepared from the rhenium(V) benzoylhydrazido species $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$, is a useful precursor for the synthesis of rhenium(I) complexes containing the terpy ligand.[891] Reaction in the presence of cyclohexenone yields the green rhenium(I) compound $[Re(terpy)Cl(PPh_3)(cyclohexenone)]$ (**282**) in good yields. The compound undergoes a number of ligand exchange reactions during which preferably the alkene or the chloro ligands are replaced and products of the composition $[Re(terpy)(PPh_3)(cyclohexenone)(L)]^+$ with $L = CNBu^t$, $NCCH_3$, 4-*t*-butylpyridine or $HN{=}CMe_2$, $[Re(terpy)(bipy)(PPh_3)]^+$, $[Re(terpy)(PMe_3)_2(cyclohexenone)]^+$, or $[Re(terpy)(cyclohexenone)\{P(OCH_2)_3CCH_3\}_2]^+$ have been isolated and spectroscopically characterized.[891]

Whereas no formation of dinitrogen complexes has been found during the reaction of $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$ with terpy in the examples mentioned above, the coordination of N_2 has been found in the products of similar reactions with bipy and related ligands. This is not unexpected in the light of the early work of Chatt,[949,950] and the successful application in the synthesis of the rhenium(I) dinitrogen complex $[Re(N_2)Cl(dppe)_2]$, the chemistry of which has been described in the previous section. Rhenium(I) amine complexes can be obtained in a similar way. Treatment of $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$ with ethylenediamine (en) or 2-aminomethylpyridine (ampy) gives the cationic species $[Re(N_2)(PPh_3)(N^{\cap}N)]^+$ which can be isolated as their triflate salts. Related reactions give access to the structurally characterized complex $[Re(N_2)(PPh_3)(PF_3)(dien)]^+$ (**283**) which readily replaces the N_2 ligand by acetone to give the

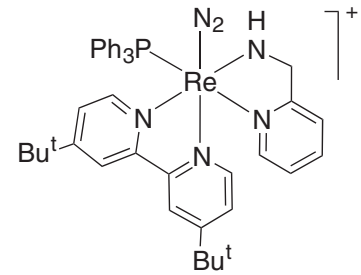
yellow derivative $[Re(OCMe_2)(PPh_3)(PF_3)(dien)]^+$. A number of related dinitrogen complexes with mixed amine/phosphine or amine/phosphite coordination sphere have also been prepared in a similar fashion which includes the reduction of the rhenium(V) precursor and subsequent ligand exchange reactions.[890] The synthetic route also allows approach to chiral rhenium(I) amine compounds as has been demonstrated for $[Re(N_2)(PPh_3)(ampy)(Bu^t\text{-bipy})][CF_3COO]$ (**284**) and related complexes.[951]



(**282**)



(**283**)



(**284**)

The stability of the polypyridyl rhenium(I) compounds mentioned above stimulated applications of this coordination chemistry. Thus, new heterotopic bis(calix[4]arene)rhenium(I) bipyridyl receptor molecules have been prepared and shown to bind a variety of anions at the upper rim and alkali metal cations at the lower rim.[952,953] A cyclodextrin dimer, which was obtained by connecting two permethylated β-cyclodextrins with a bipy ligand, was used for the preparation of a luminescent rhenium(I) complex. The system is discussed as a model compound to study the energy transfer between active metal centers and a bound ditopic substrate.[954] The fluorescence behavior of rhenium(I) complexes containing functionalized bipy ligands has been applied for the recognition of glucose.[955]

The extraordinary electronic flexibility of the mixed-ligand set $\{HB(pz)_3\}^-$/bipy which allows the stabilization of rhenium complexes in four oxidations states has already been mentioned in the previous sections. This flexibility is attributed to the ability of the nitrogen heterocyclic ligands to act as both weak π-donors and π-acceptors depending on the demand of the metal. The structure of the black rhenium(II) complex is given in formula (**267**). Further reduction results in rhenium(I) compounds and the replacement of the chloro ligand and gives access to a whole series of rhenium(I) compounds with coordinated alkenes.[849] Related complexes with the $\{HB(pz)_3\}^-$ ligand stabilizing rhenium(I) centers are subject of a number of organometallic studies.[85,957–959]

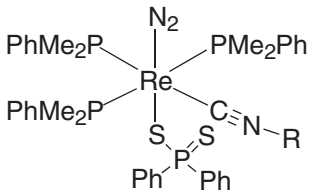
(iii) Miscellaneous

A number of rhenium(I) compounds with sulfur-containing ligands have been prepared. They are stable when the ligands are able to reduce the electron density of the d^6 metal center or acceptor co-ligands are present. The latter case can be discussed for the thiocarbonyl complex *mer*-$[Re(CS)(PMe_2Ph)_3(Et_2dtc)]$ which results from the reaction of $[ReCl_3(PMe_2Ph)_3]$ with sodium diethyldithiocarbamate in methanol.[858] The thiocarbonyl ligand is formed by decomposition of diethyldithiocarbamate.

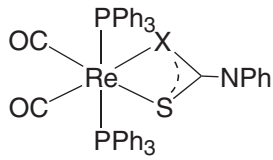
Treatment of dinitrogen mixed-ligand complexes of the type $[Re(N_2)(PMe_2Ph)_3(Et_2dtc)]$ with methylisocyanide results in replacement of the dinitrogen ligands and the formation of the products $[Re(CNMe)(Et_2dtc)(PMe_2Ph)_2]$ and $[Re(CNMe)_2(Et_2dtc)(PMe_2Ph)_2]$ depending on the conditions applied.[960] A similar reaction with $[Re(N_2)(PMe_2Ph)_3(S_2PPh_2)]$ ($S_2PPh_2^- =$ diphenyldithiophosphinate) affords the mixed-ligand species $[Re(N_2)(S_2PPh_2)(CNMe)(PMe_2Ph)_3]$, $[Re(N_2)(S_2PPh_2)(CNMe)_2(PMe_2Ph)_2]$, or $[Re(S_2PPh_2)(CNMe)(PMe_2Ph)_3]$. The rhenium atom in the yellow compound $[Re(N_2)(S_2PPh_2)(CNMe)(PMe_2Ph)_3]$ (**285**) is six-coordinate and has a pseudo-octahedral coordination sphere. The diphenyldithiophosphinato ligand is only monodentate.[960]

Pseudo-allyl compounds are formed from reactions of $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4\text{-}4\text{-}Me)]$ with excess of PhNCO or PhNCS. Whereas carbamate compounds are formed in the former case, a mixture of monothio- and dithiocarbamate compounds is obtained with the sulfur analogue. The formation of the latter complex proceeds via the intermediate formation of the first. The related compounds show similar structural features with distorted octahedral rhenium atoms and

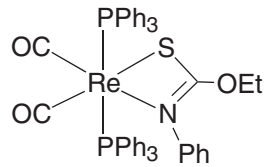
trans-arrangement of the phosphine ligands (**286**).[961] When the reaction of $[Re(CO)_2(PPh_3)_2(OCHNC_6H_4\text{-}4\text{-}Me)]$ with PhNCS is performed in benzene and the product exposed to EtOH, formal insertion of the heterocumulene molecule into the Re—N bond is observed. A second product of this procedure is the thiazedine rhenium(I) derivative $[Re(CO)_2(PPh_3)_2\{PhN{=}C(OEt)S\}]$ (**287**).[962] Electrochemical studies on pseudoallyl complexes of rhenium(I) show the Re^I/Re^{II} redox couples to occur at potentials between +0.60 V and +0.90 V and competing chemical reactions of the oxidized species.[963]



(**285**)



(**286**)



(**287**)

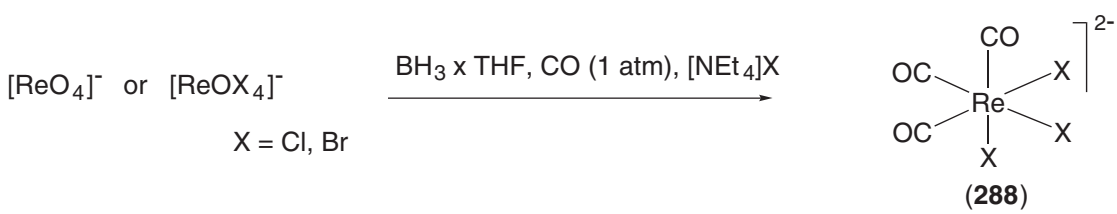
Reduction of $[ReOCl_3(PPh_3)_2]$ with sodium dithionite in the presence of a bidentate isocyanide ligand and the isolation of a cationic tris-chelate of the composition $[Re\{CNC_3H_6OC_2H_4OC_3H_6NC\}_3]^+$ has been reported. The product was isolated as its $[BPh_4]^-$ salt and characterized based on elemental analysis and spectroscopic data.[824]

5.3.2.7.3 Rhenium(I) tricarbonyl complexes

Although carbonyl complexes are considered as "organometallic" and are therefore not the subject of this review, a brief summary of rhenium(I) tricarbonyl chemistry is given. This is mainly justified by the progress in the exploration of "aqueous carbonyl chemistry" during the last decade and the fact that carbonyl compounds of technetium (and rhenium) have been involved in nuclear-medical research.[964,965] The focus is on synthetic aspects and other interesting facets of rhenium(I) tricarbonyl chemistry such as luminescence, the photosensitizing properties of many complexes and their roles as building blocks in supramolecular frameworks will not be regarded.

The traditional syntheses of metal carbonyls by autoclave reactions is time-consuming and causes numerous problems in terms of radiation protection when radioactive materials (such as $^{186,188}Re$ or $^{99,99m}Tc$) are used. However, a protocol which produces rhenium(I) tricarbonyl compounds in a one-pot synthesis using carbon monoxide at normal pressure as established by Alberto and co-workers[252] is a breakthrough which opens up to the aqueous coordination chemistry of the *fac*-$\{Re(CO)_3\}^+$ core.

The *fac*-$[Re(CO)_3X_3]^{2-}$ dianions (X = Cl, Br) (**288**) are formed by the reduction of $[ReO_4]^-$ with the tetrahydrofuran adduct of BH_3 in the presence of $[NEt_4]X$ while CO gas is bubbled through the solution (Scheme 21). The three carbonyl ligands are in facial positions and due to their strong *trans*-influence they labilize the halide ligands strongly and these are readily replaced by solvent molecules to give species *fac*-$[Re(CO)_3(solv)_3]^+$. This has been demonstrated by spectroscopic experiments and by the stepwise deprotonation of the complex *fac*-$[Re(CO)_3(OH_2)_3]^+$ by means of titration with OH^-.[252,967] The intermediate hydroxo complex subsequently dimerizes or oligomerizes. Two of the species, which have been formed at higher pH, have been characterized crystallographically, the dimeric anion $[(CO)_3Re(\mu\text{-}OH)_3Re(CO)_3]^-$ and the trimeric complex $[Re_3(\mu^2\text{-}OH)_3(\mu^3\text{-}OH)(CO)_9]^-$ which forms an incomplete cube with three $\{Re(CO)_3\}^+$ cores alternating with four HO^- groups.[252]



(**288**)

Scheme 21

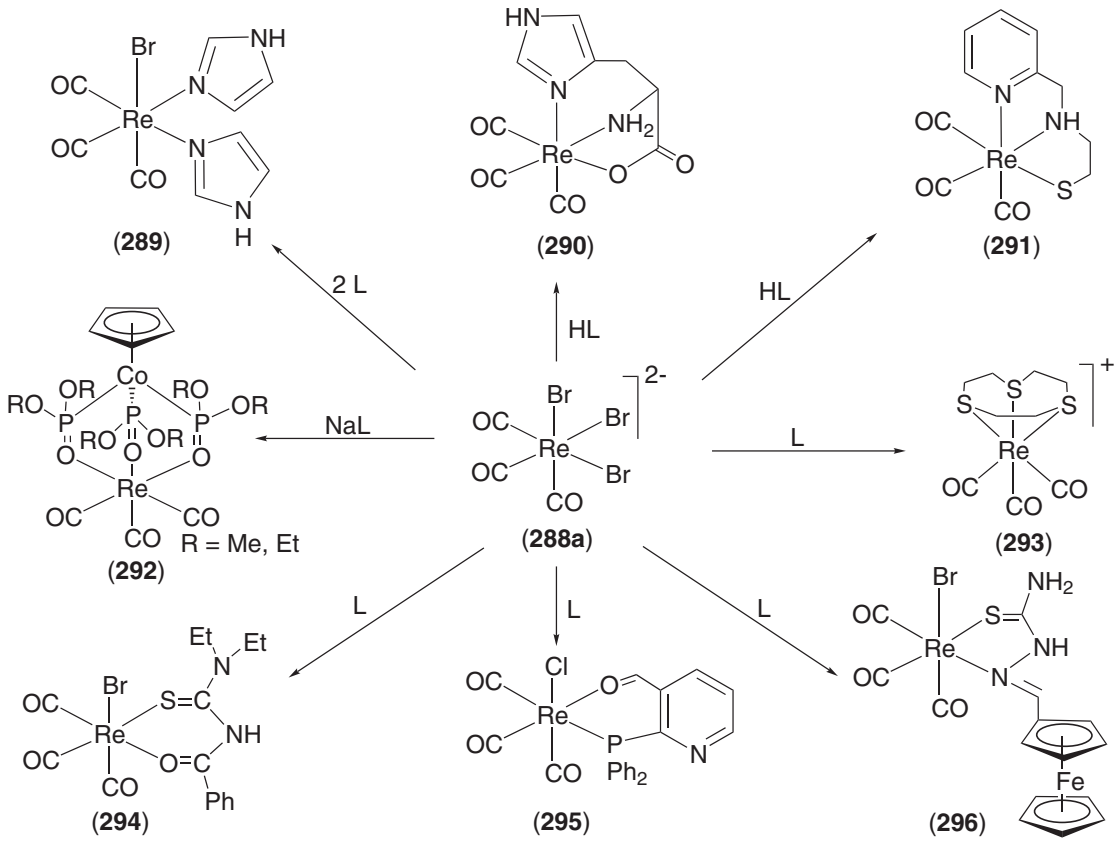
The tricarbonyl rhenium(I) core is extremely inert and does not take part in ligand exchange reactions under mild conditions, but cleavage of a Re—C bond can be observed when *fac*-$[Re(CO)_3Br_3]^{2-}$ (**288a**) is treated with elemental Br_2 which results in oxidation and the formation of the rhenium(III) anion *cis*-$[Re(CO)_2Br_4]^-$.[968]

Ligand exchange experiments have been performed with a large number of ligands and special attention has been directed to ligands and ligand systems which mimic biological binding sites and, thus, contain oxygen, nitrogen or sufur donor atoms (Scheme 22). A detailed study with the heterocyclic ligand imidazol (Im), which is present in the side-chain of the amino acid histidine, showed that all three possible ligand exchange products, $[Re(CO)_3Br_2(Im)]^-$, $[Re(CO)_3Br(Im)_2]$, and $[Re(CO)_3(Im)_3]^+$ can be isolated when appropriate reaction conditions are used. A surprising feature is, that the third imidazole ligand only coordinates when all bromide ions have been removed from the solution. This result has been confirmed by a solution NMR study which supports that the re-coordination of Br^- to the species $[Re(CO)_3(Im)_2(solv)]^+$ and the formation of the neutral complex $[Re(CO)_3(Im)_2Br]$ (**289**) is favored over the coordination of a third nitrogen donor.[964] Histidine (Hhist) forms a neutral rhenium(I) tricarbonyl complex of the composition $[Re(CO)_3(hist)]$ (**290**) contributing all three potential donor functions for facial coordination to the $\{Re(CO)_3\}^+$ core. This facial coordination, of course, can not be achieved with histidine when it is integrated in a peptide sequence or in a native protein, but its extraordinary stability guides the way to a formation of stable bioconjugates by facially coordinating ligand systems. Other examples are the neutral complexes with *N*-(2-thioethyl)picolylamine and derivatives thereof (**291**),[969] chelates with Kläui-type ligands such as the yellow crystalline complex $[Re(CO)_3\{cpCo\{P(OR)O\}_3\}]$ (R = Me, Et) (**292**),[970] or $[Re(CO)_3\{py_2(O)OH\}]$ which is formed from the hydrolysis of di(2-pyridyl)ketone in the presence of $[Re(CO)_3(OH_2)_3]^+$ in a $MeOH/H_2O$ mixture.[971,972] A manifold of compounds have been prepared with cyclic thioether ligands which ranges from common monomeric cations such as $[Re(CO)_3(9S3)]^+$ (9S3 = 1,4,7-trithiacyclononane) (**293**) to dimeric units where large thiacrowns coordinate to two tricarbonylmetallates as has been confirmed by the crystal structure of technetium analogues.[973] Thiolato ligands often act as η^2-bridging ligands giving access to a number of binuclear complexes,[629] while ligands with thiocarbamoylbenzamidinato (**170**) or benzoylthiourea groups (**134**) act as chelating ligands. Dialkylthiocarbamoylbenzamidines deprotonate during the reaction with $[Re(CO)_3Br_3]^{2-}$ and monomeric anions of the composition $[Re(CO)_3(L)Br]^-$ or neutral dimers of the composition $[Re_2(CO)_6(L)_2]$ with the sulfur atoms of the organic ligands connecting two metal centers with four-membered $\{Re_2S_2\}$ rings are formed. Contrasting the complexing behavior with rhenium(V) and rhenium(III) centers, HDEBT does not deprotonate upon reaction with $[Re(CO)_3Br_3]^{2-}$ even with addition of triethylamine, but coordinates bidentately to give $[Re(CO)_3Br(HDEPT)]$ (**294**) in form of air-stable yellow crystals.[974] The bromo ligand is situated *trans* to carbonyl. Similar complexes with Cl^- ligands *trans* to CO are formed with 2-(diphenylphosphino)benzaldehyde ($P^{\frown}O$) (**295**) or its Schiff base 2-(diphenylphosphino)benzylideneaniline ($P^{\frown}N$).[975] Thiosemicarbazone ligands are coordinated to rhenium(I) tricarbonyl centers in two different ways. Whereas ferrocenylaldehyde thiosemicarbazone acts as bidentate, neutral ligand and forms a complex of the composition $[Re(CO)_3Br(HL)]$ (**296**) in reactions starting from $[Re(CO)_3Br_3]^{2-}$ or $[Re(CO)_5Br]$, deprotonation is achieved upon addition of sodium methanolate to afford doubly sulfur-bridged dimers of the composition $[\{Re(CO)_3(L)\}_2]$.[629,976] Tridentate coordination, however, is observed when acetylpyridinethiosemicarbazone is used and the resulting neutral complex $[Re(CO)_3(L)]$ contains deprotonated ligand in a facial arrangement.[629]

The examples discussed above are only representatives of many rhenium(I) tricarbonyl complexes and hopefully demonstrate the versatility and stability of the $\{Re(CO)_3\}^+$ core. This has significant implications for applications in nuclear medical research and this topic is discussed further in Section 5.3.3.

5.3.2.8 Oxidation state 0

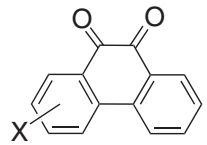
Rhenium(0) compounds are rare and frequently lie in the realm of the organometallic chemistry. A simple example is decacarbonyldirhenium(0) in which two staggered, square-pyramidal $\{Re(CO)_5\}$ fragments are held together by a single rhenium–rhenium bond. Substitution of carbonyl ligands is possible by tertiary phosphines and arsines, silanes and isocyanides, and binuclear Re–Re, Mn–Re, and Co–Re complexes have been studied.[977–984] Successive replacement of CO ligands can readily be observed by vibrational spectroscopy. This has been demonstrated



Scheme 22

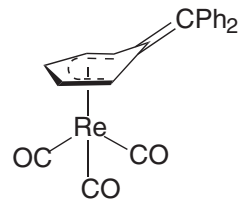
for $[Re_2(CO)_{10-n}(CNR)_n]$ ($n = 1$–4; R = Me, Bu^t, benzyl) and results in gradual shift of the $\nu_{(CO)}$ modes to lower wave numbers which is in agreement with the stronger σ-donor and poorer π-acceptor capacities of isocyanides compared to CO.[985]

Cleavage of the Re—Re bond in $[Re_2(CO)_{10}]$ by photolysis results in the formation of the short-lived paramagnetic species $\{Re(CO)_5\}$. This radical exhibits an optical absorption band in the visible region with a maximum at 535 nm and readily reacts with organic substrates.[986,987] A series of rhenium(0) radicals were spin-trapped by 9,10-phenanthroquinone ($C_{14}H_8O_2$) (**297**) and its derivatives. Paramagnetic species of the compositions $[Re(CO)_4(O_2C_{14}H_{8-n}X_n)]$, $[Re(CO)_3(O_2C_{14}H_{8-n}X_n)(PPh_3)]$, and $[Re(CO)_2(O_2C_{14}H_{8-n}X_n)(PPh_3)_2]$ ($n = 1$, X = H, OMe-3, Cl-3, Br-3, Pr^i-3, CN-3, NO_2-2; $n = 4$, $X_4 = Me_4$-1,3,6,8) were studied by EPR spectroscopy.[988] The rhenium hyperfine coupling constants of the $[Re(CO)_4(O_2C_{14}H_7X)]$ radicals correlate well with the Hammett σ_p parameters of the substituents.

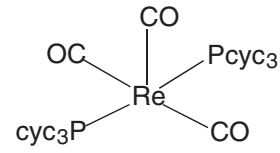


X = H, 3-OMe, 3-Cl, 3-Br, 3-Pr^i, 2-NO_2,1,3,6,8-Me_4

(**297**)



(**298**)



cyc = cyclohexyl

(**299**)

Without addition of spin traps, the photochemically generated $\{Re(CO)_n\}$ radicals dimerize quickly. More persistent rhenium(0) radicals have been prepared by replacement of two carbonyl groups by bulky phosphines to give the species $[Re(CO)_3(PR_3)_2]$. The restrictions due to the photochemical route, however, prevents isolation of the products in the solid state. This can be

achieved by a synthesis starting from the organometallic precursor $[Re(CO)_3(\eta^5\text{-}CPh_3)]$ (**298**) which can be prepared by thermal decarbonylation of $[Re(CO)_4(\eta^3\text{-}CPh_3)]$.[989–991] $[Re(CO)_4(\eta^3\text{-}CPh_3)]$ reacts with tri(cyclohexyl)phosphine ($Pcyc_3$) and other bulky tertiary phosphines to give deep-blue solutions. In each case the presence of radicals was detected by EPR spectroscopy. Deep blue crystals of *mer*-$[Re(CO)_3(Pcyc_3)_2]$ (**299**) precipitate from such solutions and the structure of the product has been determined by X-ray crystallography. The structure of the rhenium(0) complex is a distorted square pyramidal. The monomeric compound reacts with CO to give the dimeric complex $[Re_2(CO)_8(Pcyc_3)_2]$. Reaction with tin hydrides affords the neutral hydride $[Re(CO)_3(Pcyc_3)_2H]$.[991]

5.3.2.9 Nitrosyl, Thionitrosyl, and Related Complexes

Nitrosyl ligands have relatively poor σ-donor capabilities, but are excellent π-acceptors. There are synthetic routes to nitrosyl complexes using NO gas, $[NO][BF_4]$ or $[NO][PF_6]$, hydroxyamine hydrochloride, HNO_3, $NaNO_2$, or *N*-nitrosoamides.

Thionitrosyl compounds are less common, but the few structurally characterized representatives suggest a close similarity to the chemistry of nitrosyl complexes.

5.3.2.9.1 Halide and pseudohalide ligands

Paramagnetic rhenium anions of the composition $[Re(NO)X_5]^{2-}$ have been known for 30 years.[992,993] These compounds are excellent precursors for the synthesis of other rhenium nitrosyl complexes and some attempts have been made to improve the yields of the original procedures. Analytically pure $[NEt_4]_2[Re(NO)Br_5]$ can be obtained from a reaction of $[NEt_4][ReO_4]$ with NO gas in the presence of $[NEt_4]Br$, HBr and H_3PO_2 as reducing agent as an apple-green solid with a yield of 90%.[994] The $\nu_{(NO)}$ vibration has been detected at 1,732 cm^{-1}. The formal oxidation states of the products depend on the nature of the incoming ligands. Thus, reduction occurs with phosphines and other reducing ligands. Surprisingly, the dihydrogen compound $[Re(NO)(\eta^2\text{-}H_2)Br_2(PPr^i_3)_2]$ is produced when $[Re(NO)Br_5]^{2-}$ reacts with tri(isopropyl)phosphine in ethanol despite the formation of $[Re(NO)Br_3(PPh_3)_2]$ in an analogous reaction with triphenylphosphine.[994]

Reductive nitrosylation of perrhenate has also been reported for the reaction with hydroxyamine hydrochloride in aqueous solution. The primary product is believed to be the hydroxo complex $[Re(NO)(OH)_4]^-$ which has been isolated as the green $[AsPh_4]^+$ salt. The product is paramagnetic and shows an axially symmetric EPR spectrum with an unusual coupling pattern.[995] $[Re(NO)(OH)_4]^-$ and its derivatives with polypyridyl ligands disproportionate when heated in HX (X = Cl, Br) producing $[Re(NO)X_5]^-$ and $[Re(NO)_2X_4]^-$. The same reaction in HI, however, exclusively yields the rhenium(IV) complex $[ReI_6]^{2-}$. C_{4v} symmetry is suggested for the mononitrosyl complexes based on infrared data.[995] This has been confirmed by the X-ray crystal structure of $[AsPh_4]_2[Re(NO)(CN)_4(OH_2)]$ showing a distorted octahedral geometry for the complex anion with a Re–NO distance of 1.73 Å.[996] A *trans*-influence of comparable magnitude to that of the oxo ligand is proposed for the linear NO^+ ligand based on the experimentally determined bond lengths.

The generation of pentacoordinate dinitrosylrhenium compounds is reported from the reduction of $[ReO_4]^-$ with hydroxylamine hydrochloride and NCS^- in alkaline solutions and subsequent treatment with NO_2^- in acidic solutions.[997] The products are paramagnetic and EPR-active which suggests the oxidation states "+2" or "0".

A hypothetic NO/NO coupling reaction has been regarded by extended Hückel calculation for the *cis*-dinitrosylrhenium complex $[Re(NO)_2Cl_4]^-$. The results show that couplings between the neighboring NO ligands are disfavored in general, but might occur via *N*–*N* coupling.[998] This situation contrasts that in the analogous thionitrosyl compound in which two thionitrosyl ligands have been coupled to form a five-membered metallacycle.

5.3.2.9.2 Phosphorus donor ligands

The treatment of $[ReOCl_3(PPh_3)_2]$ with NO gas is a complex reaction and yields a number of paramagnetic rhenium(II) nitrosyl complexes depending on the conditions. This has been checked

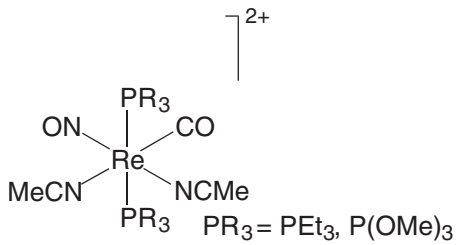
by EPR spectroscopy. When the reaction is performed in CH_2Cl_2, the sparingly soluble starting material dissolves forming a brown solution which turns green when it is exposed to air. Subsequently the complexes $[Re(NO)Cl_2(PPh_3)(OPPh_3)(OReO_3)]$, $[Re(NO)Cl_2(OPPh_3)_2(OReO_3)]$, and $[Re(NO)Cl_2(OPPh_3)_3][ReO_4]$ have all been isolated and characterized by their crystal structures.[999] Other products such as $[Re(NO)Cl_3(PPh_3)(OPPh_3)]$, $[Re(NO)Cl_2(PPh_3)(OPPh_3)]Cl$, and $[Re(NO)Cl_3(PPh_3)_2]$ have also been isolated as side-products of this reaction. The formation of perrhenate-containing products can be avoided when the reaction is performed under an inert atmosphere, but also in these cases phosphine oxide ligands are found in the products as has been shown by the full characterization of the complexes: $[Re(NO)Cl_3(PPh_3)(OPPh_3)]$ and $[Re(NO)Cl_3(OPPh_3)_2]$.[1000,1001] Cationic species have not been isolated during the latter reactions despite the fact that $[Re(NO)Cl_2(OPPh_3)_3]^+$ is the final product of reductive nitrosylation by NO gas in air and can be isolated as green crystals in 30% yield.[999] A Q-band-EPR study shows a slightly rhombic spectrum which confirms the deviations of the molecular geometry from the ideal axial symmetry as has been found in the solid state structure.[1002]

Similar conditions for the nitrosylation of oxorhenium(V) compounds have also been applied to prepare the analogous bromo complexes $[Re(NO)Br_3(PPh_3)_2]$ and $[Re(NO)Br_3(OPPh_3)_2]$ which have been obtained from benzene solutions and fully characterized by spectroscopic data and their crystal structures.[1003] The same reaction in CH_2Cl_2 is reported to lead to dinitrosyl complexes.[1004] Nitrosyl halides such as [NO]Cl or the [NO]Br are less appropriate for the nitrosylation of oxorhenium compounds. Whereas the chloride reacts with $[ReOCl_3(PPh_3)_2]$ to give the rhenium(IV) complex *trans*-$[ReCl_4(PPh_3)_2]$,[769] the less stable nitrosyl bromide, which is said to be formed by the reaction of $[ReOBr_3(PPh_3)_2]$ with NO, causes decomposition of triphenylphosphine and the formation of a nitrosyl/aryl complex of the composition $[Re(NO)Br_3(Ph)(PPh_3)]$.[1005]

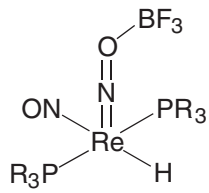
Reactions of the rhenium(II) mixed phosphine/phosphine oxide complex $[Re(NO)Cl_3(PPh_3)(OPPh_3)]$ allows access to further nitrosylrhenium derivatives such as $[Re(NO)Cl_3(PPh_3)_2]$, $[Re(NO)(CO)Cl_2(PPh_3)_2]$, or $[Re(NO)H_2(PPh_3)_3]$, when the starting material is treated with PPh_3, CO gas, or $NaBH_4$ in the presence of PPh_3.[1006] Related trimethylphosphine and trialkylphosphite complexes have been subject of extensive studies and show remarkable structures and reactivities.[993,1007–1011] The reaction of $[Re(NO)(CO)Cl_2(PR_3)_2]$ ($PR_3 = PEt_3$ or $P(OMe)_3$] with excess $Ag[F_3CCO_2]$ in boiling acetonitrile leads to an isomeric mixture of cationic $[Re(NO)(CO)Cl(NCCH_3)_2(PR_3)][F_3CCO_2]$ complexes which can be used as precursors for further ligand exchange reactions. When the same reaction is performed in toluene using one or two equivalents of $Ag[F_3CCO_2]$, mono- and disubstituted complexes of the composition $[Re(NO)(CO)Cl(F_3CCO_2)(PR_3)_2]$ and $[Re(NO)(CO)(F_3CCO_2)(PR_3)_2]$ are obtained. The replacement of the triflate ligands in the latter compounds proceeds very slowly and with retention of the molecular geometry. The resulting ionic compounds $[Re(NO)(CO)(NCCH_3)_2(PR_3)_2]^{2+}$ (**300**) contain the PR_3 ligands in *trans*-positions to each other with a *cis*-arrangement of the acetonitrile ligands, as shown by the X-ray crystal structure of $[Re(NO)(CO)(NCCH_3)_2\{POMe)_3\}_2][F_3CCO_2]_2$.[1011]

The trimethylphosphine derivative $[Re(NO)Cl_2(NCCH_3)(PMe_3)_2]$ has an extraordinary solid state structure with a dense net of intermolecular hydrogen bonds which is responsible for the unusual number of 44 independent molecules in the monoclinic unit cell. Methyl groups serve exclusively as hydrogen donor groups, leading to hydrogen bonds of the type C—H···O and C—H···Cl.[1012]

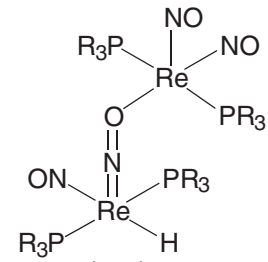
The paramagnetic rhenium(II) complex $[Re(NO)Br_5]^{2-}$ has been used to prepare a series of mononitrosyl hydride and dihydrogen rhenium complexes including $[Re(NO)Br_2(\eta^2\text{-}H_2)(PR_3)_2]$ and $[Re(NO)(BH_4)(H)(PR_3)_2]$ ($R = Pr^i$, cyclohexyl).[994] The BH_4^- ligand in the latter complex is replaced by H_2 or another NO ligand yielding tetrahydrido or dinitrosyl species. The dinitrosyl species react with Lewis acids such as BF_3 which is abstracted from BF_4^- anions giving access to acid–base adducts of the composition $[Re(NO)(NOBF_3)(H)(PR_3)_2]$ (**301**). Many other examples of dinitrosylrhenium complexes are derived from cationic $[Re(NO)_2(PR_3)_2]^+$ fragments ($R = Pr^i$, cyclohexyl) which can be prepared from $[Re(NO)_2(H)(PR_3)_2]$ and $[Ph_3C][B\{C_6H_3\text{-}(CF_3)_2\text{-}3,5\}_4]$ in benzene in excellent yields.[1013] The isolated complexes of the general composition $[Re(NO)_2(PR_3)_2(L)]$ ($L = CO$, C_6H_5CHO, $[ONRe(NO)(PR_3)_2(H)]$) also include examples of dimeric species which contain bridging nitrosyl ligands. One of the NO ligands in the latter is slightly bent with Re–N–O angles between 150° and 160°. Dimeric compounds of composition $[Re_2(H)(\mu,\eta^2\text{-}NO)(NO)_3(PR_4)]^+$ are formed by abstraction of the hydride in the dinitrosyl complexes $[Re(NO)_2(H)(PR_3)_2]$ ($R = Pr^i$ or cyclohexyl). The metal centers are connected via a bridging nitrosyl ligand (**302**).[1014] The products not only react with classical two-electron donor ligands such as $NCCH_3$, CO, C_6H_5CHO, and THF, but also with H_2 and $HSiEt_3$. In the last two cases rupture of the hydrogen–hydrogen or hydrogen–silicon bonds is achieved.[1014]



(300)



(301)



(302)

Nitrosylrhenium complexes with the chelating ligand dppe have been obtained by the reaction of $[ReOBr_3(dppe)]$ with NO,[1015] or by treatment of the rhenium(I) dinitrogen complex $[Re(N_2)Cl(dppe)_2]$ with $[NO][BF_4]$ or NO gas.[1016] The latter reaction involves a facile oxidation of NO to form nitrate as has been shown by the crystal structure of the product $[Re(NO)Cl(dppe)_2][NO_3]_2$. The complex contains a linear NO^+ ligand. A very similar reaction, that of $[Re(N_2)Cl(dppe)_2]$ in THF with NO and $Tl[BF_4]$ under irradiation with UV light, yields a yellow solid which has been assigned to the structure *trans*-$[Re(NO)_2(dppe)_2][BF_4]$ on the basis of elemental analysis and spectroscopic data.[1017] The compound readily reacts with acids HX ($X = BF_4$, Cl, HSO_4) to afford *trans*-$[Re(NO)F(dppe)_2]$, *trans*-$[Re(NO)Cl(dppe)_2]$, and *trans*-$[Re(NO)(HSO_4)(dppe)_2]$, respectively.

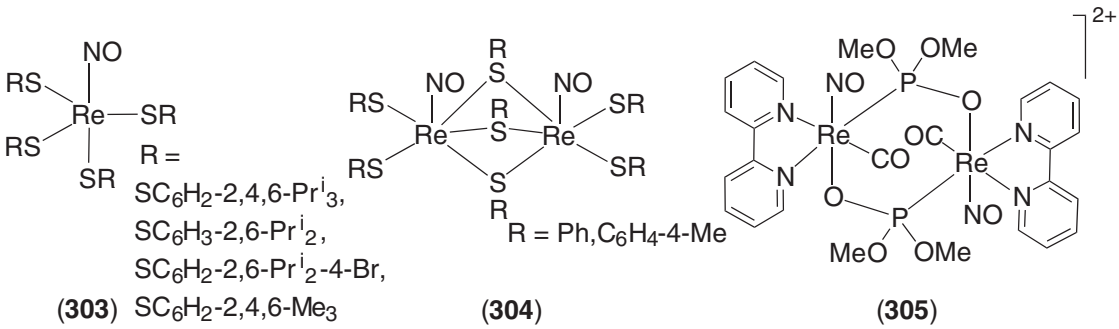
5.3.2.9.3 *Sulfur, nitrogen, and oxygen donor ligands*

Reactions of the rhenium(II) nitrosyl precursor $[Re(NO)Cl_2(OMe)(PPh_3)_2]$ with a range of thiophenols under basic conditions gives three different types of products depending on the steric requirements of the thiols. Thiophenols with methyl and isopropyl substituents in their 2-position yield monomolecular rhenium(III) complexes of the composition $[Re(NO)(SR)_4]$ (**303**),[1018,1019] whereas sterically less demanding ligands without substituents in 2-position give dimeric compounds with μ^2-coordinated thiolates of the composition $[Re_2(NO)_2(SR)_7]$ (**304**). A rhenium(I) complex has been isolated during a similar reaction with 2-triphenylsilylthiophenol.[293]

The rhenium(I) anion $[Re(NO)(CN)_4(OH_2)]^{2-}$ substitutes the aqua ligand upon reactions with nucleophiles such as SCN^-, N_3^-, and tu.[1020] A kinetic study of the ligand substitutions reveals that both the aqua and the hydroxo ligands in the corresponding complex $[Re(NO)(CN)_3(OH)]^{3-}$ are substituted with respective rate constants of 3.6×10^{-3} $M^{-1}s^{-1}$ and 1.6×10^{-3} $M^{-1}s^{-1}$ at 40 °C in the case of SCN^-. The X-ray structure of the product of the ligand exchange with thiourea, $[AsPh_4]_2[Re(NO)(CN)_4(tu)]$ has been determined showing a *cis*-arrangement of the thiourea ligand with respect to the NO group.

Nitrosyl complexes with amine ligands are formed by reactions of $[Re(NO)(CO)(CNCH_3)Cl(PR_3)][F_3CCO_2]$ ($PR_3 = PEt_3$, $P(OMe)_3$) with bipy which yield stable $[Re(NO)(CO)Cl(PR_3)(bipy)]$ type complexes. The IR spectra of the products support the assumption that different isomers co-crystallize.[1011] The neutral precursors $[Re(NO)(CO)(CF_3CO_2)_2\text{-}(\{P(OMe)_3\}_2]$ undergo Arbuzov-type phosphite dealkylation in the presence of bipy producing a dinuclear complex in which the two rhenium fragments are linked by two phosphonite moieties, forming a planar six-membered ring (**305**).[1011] Reduction of $[Re(NO)(CO)Cl_2\{P(OPr^i)_3\}_2]$ with $LiCMe_3$ results in an unstable compound with two *trans* trimethylphosphite ligands which reacts with *trans*-azobenzene to give $[Re(NO)Cl\{P(OPr^i)_3\}_2(PhN{=}NC_6H_4)]$ containing orthometallated azobenzene.[1010] Another approach to rhenium nitrosyls with bipy ligands involves the reduction of perrhenate with hydroxyamine hydrochloride in alkaline solutions in the presence of bipy.[995]

The complex $[Re(NO)(CO)(NCO)(tacn)][BF_4]$ has been synthesized from $[Re(NO)(CO)_2\text{-}(tacn)][BF_4]$ in methanol with a number of nucleophiles such as N_2H_4, H_2NNHMe, H_2NNMe_2, H_2NOH, or N_3^-. A general mechanism for these reactions has been proposed involving a nucleophilic attack at a coordinated carbonyl to give carbazoyl intermediates.[1021] $[Re(NO)(CO)(NCO)(tacn)][BF_4]$ undergoes a series of reactions at the coordinated isocyanate ligands, e.g., concentrated HBr forms $[Re(NO)(CO)(tacn)(NH_3)]Br_2$, whereas reactions with formic acid or trifluoromethane sulfonic acid gives complexes of the type $[Re(NO)(CO)(tacn)(HCO_2)]^+$ and $[Re(NO)(CO)(tacn)(CF_3SO_3)]^+$. In the presence of iodide anions, $[Re(NO)(CO)(NCO)(tacn)][BF_4]$ undergoes addition reactions in methanol or ethanol to form complexes containing coordinated



methyl- or ethylcarbamato ligands, [Re(NO)(CO){NHCO(OR)}(tacn)]I. [Re(NO)(CO)-(tacn)(NH_3)]Br_2 can be oxidized electrochemically or chemically with Br_2 to give [Re(NO)(CO)-(tacn)(NH_3)]Br_3.[1021]

A series of nitrosylrhenium phthalocyaninates has been prepared by reactions of [Re(PPh_3)$_2$(pc)] (pc^{2-} = phthalocyaninato dianion) with NO_2^-. Green–blue [Re(NO)(NO_2-O)-(pc)] has been obtained with bis(triphenylphosphine)iminium nitrite, while during a similar reaction with [NBu_4][NO_2] the red dinitrosyl compound [NBu_4][Re(NO)$_2$(pc)] was isolated.[1022] [NBu_4][Re(NO)$_2$(pc)] and PPh_3 yield at 300 °C the blue–green compound [Re(NO)($OPPh_3$)(pc)], that can be oxidized with I_2 to give [Re(NO)($OPPh_3$)(pc)]I_3. The nitrosyl ligands are almost linearly bound and $\nu_{(NO)}$ vibrations between 1,571 cm^{-1} and 1,724 cm^{-1} have been detected.[1022]

Acetylacetonato complexes of various composition have been reported as the products of reactions between acetylacetone (Hacac) and rhenium nitrosyl precursors. Compositions of [Re(NO)Cl(acac)$_2$(H_2O)] and [Re(NO)(acac)$_3$(Hacac)(H_2O)$_2$] have been assigned to the products.[1023]

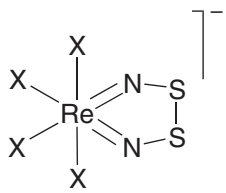
5.3.2.9.4 Thionitrosyl complexes

Compared with the large number of nitrosyl complexes, only a few examples of thionitrosyl complexes have been studied. Although NS does not exist, a number of synthetic approaches to thionitrosyl complexes have been reported: the reaction of nitrido complexes with S_2Cl_2 or TMSNCS, treatment of chloro or oxo complexes with trithiazyl chloride or S(NTMS)$_2$, or the use of heterocyclic nitrogen–sulfur rings. Pre-formed thionitrosyl cations in [NS][SbF_6] or [NS][AsF_6] have been used to prepare the cationic complex [Re(NS)(CO)$_5$]$^{2+}$ in liquid SO_2.[1024]

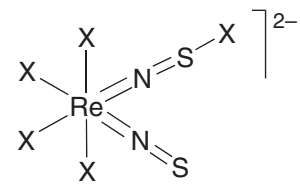
Reactions of (chlorothio)nitrene complexes [$ReCl_3$(NSCl)$_2$($POCl_3$)] or [$ReCl_4$(NSCl)$_2$]$^-$ with reducing agents such as PPh_3, $SbPh_3$, diphenylalkyne, or TMSBr give the complex [$ReCl_4$(N_2S_2)]$^-$ (**306**) which has been studied crystallographically.[1025–1027] In this reaction a reductive dehalogenation is likely to occur prior to the formation of a new sulfur–sulfur bond. Thus, the intermediate formation of two *cis* thionitrosyl ligands is favored, followed by a thionitrosyl/thionitrosyl coupling. A theoretical consideration based on extended Hückel theory calculations supports this assumption.[998] The mixed chloro/fluoro derivative [PPh_4][Re(N_2S_2)Cl_2F_2] can be obtained by the reaction of [PPh_4][Re(NSCl)Cl_4] with sodium fluoride in acetonitrile.[1028] Black, moisture-sensitive crystals of [Re(NSCl)$_2$$Cl_3$($NCCH_3$)] are obtained from the dimeric [{Re(NSCl)$_2$$Cl_3$}$_2$] and acetonitrile in CH_2Cl_2. The complex is monomeric and contains almost linear ReNS groups with bond lengths that correspond to double bonds.[1029]

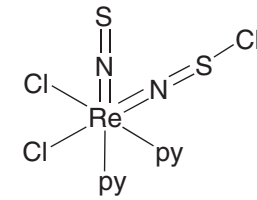
The thionitrosyl/halothionitrene mixed-ligand complexes [Re(NS)(NSX)X_4]$^{2-}$ (X = Cl, Br) (**307**) are obtained by nucleophilic ring cleavage of the {ReN_2S_2} rings in [Re(N_2S_2)X_4]$^-$ complexes with [PPh_4]X in CH_2Cl_2.[1030] [$AsPh_4$]$_2$[Re(NS)(NSCl)Cl_4] can also be obtained by the reaction of [Re(NSCl)Cl_4($OPCl_3$)] with S(NTMS)$_2$ and subsequent addition of [$AsPh_4$]Cl, or by treatment of [$ReNCl_4$] with N_4S_4 and [$AsPh_4$]Cl.[1031] The pyridine derivative [Re(NS)(NSCl)Cl_2(py)$_2$] (**308**) was obtained by the reaction of pyridine with either [Re(NSCl)$_2$$Cl_3$($OPCl_3$)] or [{Re(NSCl)$_2$$Cl_3$}$_2$($\mu$-$N_2S_2$)] in CH_2Cl_2. The distorted octahedral coordination of the rhenium atoms has the pyridine and the chloro ligands in *cis*-geometry (**308**). The Re—N bond length to the thionitrosyl ligand is markedly shorter (1.77 Å) than that to the chlorothionitrene ligand (1.89 Å).[1032] The related bromo complex can be prepared from the chloro compound by halide exchange using TMSBr.[1030] A reaction of [Re(NSCl)$_2$$Cl_4$]$^-$ with an excess of N(TMS)$_3$ gives the dimeric complex anion [(SN)$ReCl_3$)(μ-N)(μ-NSN)$ReCl_3$(THF)]$^{2-}$. The

rhenium atoms are connected by an asymmetric nitrido bridge (ReN bond lengths of 1.883 Å and 2.244 Å) as well as by a $(NSN)^{4-}$ bridge to form a planar $\{Re_2N(NSN)\}$ six-membered heterocycle. Both rhenium atoms are coordinated by three chlorine atoms, one by a thionitrosyl ligand, the other by a THF molecule.[691]



X = Cl, Br





(**306**) (**307**) (**308**)

Thionitrosyl complexes with phosphine co-ligands have been prepared by reactions of rhenium(V) nitrido complexes such as $[ReNCl_2(PMePh_2)_3]$ with $(NSCl)_3$ which yields a mixture of the rhenium(I) and rhenium(II) complexes $[Re(NS)Cl_2(PMePh_2)_3]$ and $[Re(NS)Cl_3(PMePh_2)_2]$ which have been studied structurally as their PMe_2Ph analogues.[1033,1034] Products of the same composition have been isolated from a reaction of the rhenium(V) mixed-ligand complex $[ReN(Cl)(PMe_2Ph)_2\{N(SPPh_2)_2\}]$ with disulfur dichloride which occurs with complete re-arrangement of the coordination sphere of the metal.[666] The rhenium(V) bis-chelate $[ReN\{N(SPPh_2)_2\}_2]$ has been isolated as a second product.

Oxidation of $[Re(NS)Cl_2(PMePh_2)_3]$ with Br_2 results in an exchange of the halide ligands and the isolation of the green thionitrosyl rhenium(II) species $[Re(NS)Br_3(PMePh_2)_2]$. An EPR spectroscopic study of the paramagnetic rhenium(II) compounds $[Re(NS)X_3(PMePh_2)_2]$ proves that the MO of the unpaired electron has $5d_{xy}$ character for both complexes and suggests a stronger extend of covalency of the Re-(equatorial) ligand bonds for the bromo compound.[1033]

An unusual formation of a thionitrosyl ligand has been observed during the reaction of $[ReNCl_2(PMe_2Ph)_3]$ with TMSNCS in CH_2Cl_2 which does not only cause a Cl/NCS ligand exchange, but also an attack on the nitrido ligand giving $[Re(NS)(NCS)_2(PMe_2Ph)_3]$.[640]

5.3.2.10 Hydrazido and Related Complexes

5.3.2.10.1 General considerations

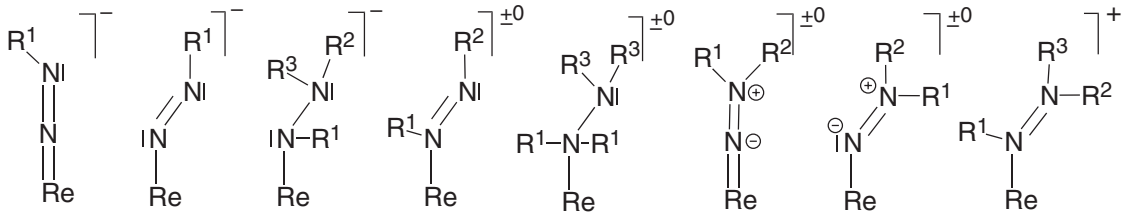
Organohydrazine derivatives play an important role in the coordination chemistry of rhenium since they represent important intermediates in the preparation of nitrido, imido, or dinitrogen complexes as has been described in the previous sections. They are defined as complexes which possess metal–nitrogen–nitrogen bonds, which would (strictly applied) also include dinitrogen complexes, and indeed this class has attracted considerable attention in the exploration of biological nitrogen fixation.

The description of the bonding situation for hydrazido and related ligands is complicated and has been done in different ways which do not always reflect the measured bond lengths and angles in the molecules satisfactory. More problems arise with uncertainties with the location of hydrogen atoms (or the unambiguous evidence of their absence) and the correct assignment of the oxidation state of the metal.

A very helpful attempt to classify organohydrazido and related complexes of Group 7 elements by analysis of their X-ray crystal structure data has been undertaken in a review which also covers the structural chemistry of this type of complexes up to the year 1996.[1035] The convention applied in this article will also be used here to classify hydrazido and related complexes.

Since organohydrazines are reducing, all of the electrons forming the metal–nitrogen bond are considered to be derived from the organohydrazine. In addition the nitrogen is more electronegative than the metal, and consequently the bonding electrons should be assigned to nitrogen for the charge assignment of the ligand. From this considerations eight structural types for "end-on bonded" hydrazide ligands have been derived, the monoanionic, linear four-electron donor (**309a**) (diazenido); the monoanionic, bent two-electron donor (**309b**) (diazenido); the monoanionic, bent two-electron donor (**309c**); the neutral, bent two-electron donor (**309d**) (diazene); the

neutral, bent two-electron donor (**309e**) (hydrazine); the neutral (zwitterionic), linear four-electron donor (**309f**) (isodiazene), the neutral (zwitterionic), bent two-electron donor (**309g**), and the monocationic, bent two-electron donor (**309h**). This assignment avoids the formulation of trinegative azenido ligands which can be found in some original papers, but do not in all cases describe satisfactory the bonding situation inside the ligand and the magnetic behavior of the complexes. A mixture of structural types is often found in chelating diazenido ligands in a sense that they show double bond character for the Re—N and the N—N bonds of (**309a**) and the bent coordination of (**309b**). Rhenium complexes with only one hydrazide in most cases adopt the diazenido form (**309a**), whereas the two-electron donor forms often are accompanied by four-electron donor forms.

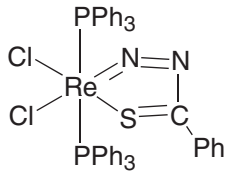


(**309a**) (**309b**) (**309c**) (**309d**) (**309e**) (**309f**) (**309g**) (**309h**)

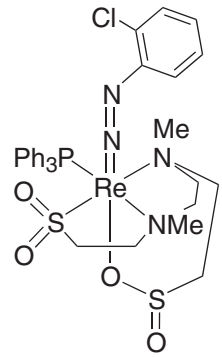
5.3.2.10.2 Complexes with a single hydrazide ligand

A general approach to rhenium hydrazido complexes is the reaction of oxo or chloro compounds with organohydrazines as has been demonstrated in an early report with the synthesis of $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$ (**310**),[949] the molecular structure of which was solved in 1988.[1036] A detailed study on $[Re(NNR)Cl_2(PPh_3)_2]$ complexes with R = COPh or phthalazine shows that the course of subsequent reactions is governed both by the nature of the donor group R responsible for chelate closure and by the type of donor ligand introduced. No simple substitution chemistry has been observed for R = phthalazine. The benzoyl compound $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$, however, is reactive and forms secondary products with common donor ligands such as $NCCH_3$, NH_3, or pyridine, or complexes with different types of hydrazide ligands which will be discussed more in detail in the following section. Thus, $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$ can be regarded as a key compound in the chemistry of hydrazido complexes and has been used as precursor for many ligand exchange reactions and for the preparation of dinitrogen complexes of rhenium(I) (see Section 5.3.2.7). Reactions of $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$ with sulfur-donor ligands result in chelate ring opening and the formation of monodentate diazenido ligands of type (**309a**)).[253] Mononuclear products of the composition $[Re\{NNC(Ph)O\}\{SC_2H_4XC_2H_4XC_2H_4S\}(PPh_3)]$ and related compounds are formed with a variety of ligands of the general composition $HSC_2H_4XC_2H_4XC_2H_4SH$ (X = S, NR).[1037,1038] The oxidation of thiolato groups by air to form sulfinates has been observed during the reaction of $[Re(NNCC_6H_4\text{-Cl-}2)Cl_2(PPh_3)(NH_3)]$ with *N*,*N*′-dimethyl-*N*,*N*′-bis(thioethyl) ethylenediamine and the red, air-stable product $[Re(NNCC_6H_4\text{-Cl-}2)(PPh_3)\{O_2SC_2H_4N(Me)C_2H_4N(Me)C_2H_4SO_2\}]$ (**311**) has been obtained in moderate yields after chromatographic separation of the product mixture. A possible intermediate of this type of oxidation has been characterized with the X-ray crystal structure of $[Re\{NNC(OMe)O\}Cl_2(PPh_3)(O_2)]$ containing a η^2-bonded dioxygen ligand.[1039] The dinuclear, triply thiolato bridged diazenido compound $[Re_2(NNPh)_2(SPh)_7]^-$ (**312**) is formed during the reaction of $[Re(NNPh)_2Cl(PPh_3)_2]$ with thiophenol in quantitative yields.[1040,1041]

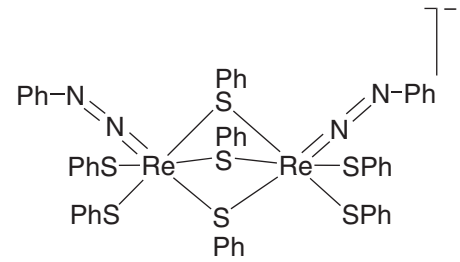
Complexes with chelating phoshines such as dppe, dmpe, or dppm have been prepared from reactions of $[ReCl_4(P^{\frown}P)]$ with phenylhydrazine,[1042] or by ligand exchange procedures starting from $[Re(NNCC_6H_4\text{-X-}4)_2Cl(PPh_3)_2]$ (X = Cl, Me).[1043] The latter reactions allow the isolation of species of the compositions $[Re(NNCR)Cl(P^{\frown}P)_2]^+$ and $[Re(NNR)_2(P^{\frown}P)_2]^+$ containing one or two diazenido ligands with a bonding characteristic lying between the types (**309a**) and (**309b**). Binuclear heterometallic complexes with a rhenium diazenido unit have been obtained by treatment of $[Re(NNC_6H_4\text{-Me-}4)Cl(CO)(dppm\text{-}P^1,P^2)(dppm\text{-}P^1)][PF_6]$ with trans-$[PtH(Cl)(PPh_3)_2]$.[1044] Related compounds are also formed with copper and rhodium complexes and other bridging bis(phosphines).



(**310**)



(**311**)



(**312**)

Reaction of $[Re\{NNC(C_6H_4\text{-}R\text{-}4)O\}Cl_2(PPh_3)_2]$ complexes (R = H, Me, NO_2) with *N*,*N*- and certain *N*-substituted hydrazines gives the ammine complexes $[Re\{NNC(C_6H_4R4)O\}(NH_3)Cl_2(PPh_3)_2]$. An intermolecular homolytic cleavage of the N—N bond is assumed to be involved in the mechanism of the NH_3 formation.[176] Cleavage of a nitrogen–nitrogen bond has also been observed during reactions of $[ReOCl_3(PPh_3)_2]$ with 1,1-diphenylhydrazine hydrochloride or $Me_2C{=}NNHCOPh$ and both reactions give nitrido compounds. The product of the former reaction, $[ReNCl_2(NNPh_2)(PPh_3)]$ (**313**) contains a co-ligated diazene ligand in *cis*-position to the nitride.[176]

Dark-orange crystals of $[Re\{NNC(Ph)O\}Cl(PPh_3)_2(maltol)]$ have been isolated from a reaction of $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$ with excess maltol in ethanol upon addition of triethylamine.[737] The octahedral complex contains the chelating maltol ligand in one plane with a monodentate diazenido and a chloro ligand. Opening of the chelate ring in $[Re\{NNC(Ph)O\}Cl_2(PPh_3)_2]$ has also been observed during its reaction with $TMSCH_2NC$ or substituted 2-aminothiazoles. Only one isocyanide ligand is present in the coordination sphere of the resulting complex $[Re\{NNC(O)Ph\}Cl_2(PPh_3)_2(TMSCH_2NC)]$.[1045] Mono- or disubstitution is observed with the chelating substituted 2-aminothiazoles which allow couplings to amino acids.[888]

A paramagnetic diazenido complex has been obtained from the oxidation of $[Re(NNPh)_2Cl(PPh_3)_2]$ with elemental bromine. The resulting green solid has been identified as $[Re(NNPh)Br_3(PPh_3)_2]$ with the two triphenylphosphine ligands in *trans* positions.[1046] The complex reacts with dithiocarbamates or isocyanides, undergoing bromide or phosphine replacement, to give $[Re(NNPh)Br(S_2CNR_2)(PPh_3)_2]$ or $[Re(NNPh)Br_2(PPh_3P)(CNR)_2]$.

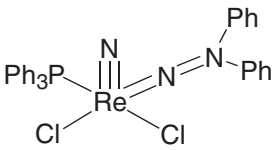
A mixed imide/hydrazide complex of the composition $[Re(NH)(NHNH_2)Cl_2(PPh_3)_2]$ (**314**) is formed upon extended heating of $[ReOCl_3(PPh_3)_2]$ and thiosemicarbazides $H_2NNHC(S)NHR$ (R = Me, Ph) in refluxing ethanol. It represents one of the intermediates in the reaction which finally yields the nitrido compound $[ReNCl_2(PPh_3)_2]$. Another intermediate, $[ReCl_2\{NNC(S)NHR\}(PPh_3)_2]$, contains an *S*,*N*-chelated thiosemicarbazido ligand.[1047]

Depending on the experimental conditions and the nature of the hydrazine, reactions of the phosphonite rhenium(III) complex $[ReCl_3\{PPh(OEt)_2\}_3]$ and H_2NNHR (R = H, Me, Bu^t) afford bis(dinitrogen), dinitrogen, and methyldiazenido $[Re(NNMe)Cl(H_2NNHMe)\{PPh(OEt_2)\}_3]^+$ derivatives. In contrast, reactions with arylhydrazines H_2NNHAr (Ar = Ph, C_6H_4Me-4) give the aryldiazenido cations $[Re(NNAr)Cl(H_2NNHAr)\{PPh(OEt)_2\}_3]^+$ and $[Re(NNAr)\text{-}Cl\text{-}\{PPh(OEt)_2\}_4]^+$, and the bis(diaryldiazenido) compounds $[Re(NNAr)_2\text{-}\{PPh(OEt)_2\}_3]^+$.[901] Reaction of the methylhydrazine complex $[Re(NNMe)Cl(H_2NNHMe)\text{-}\{PPh(OEt)_2\}_3][BPh_4]$ with lead(IV) acetate at −30 °C results in selective oxidation of the hydrazine, affording the corresponding methyldiazene derivative $[Re(NNMe)Cl(HNNMe)\{PPh(OEt)_2\}_3][BPh_4]$. In contrast, treatment of the related arylhydrazine derivatives gives bis(aryldiazenido) complexes. Protonation reactions of the diazenides with HCl only proceeds with bis(aryldiazenido) complexes affording the octahedral compounds $[Re(NNAr)Cl(HNNAr)\{PPh(OEt)_2\}_3][BPh_4]$ and $[Re(NNAr)Cl(NNHAr)\{PPh(OEt)_2\}_3][BPh_4]$.[901]

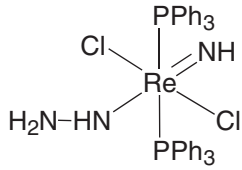
Insertion of mono- or bis(aryldiazonium) cations into the Re—H bonds of the hydride complexes $[ReH(CO)_{5-n}(PR_3)_n]$ ($PR_3 = P(OEt)_3$, $PPh(OEt)_2$, $PPh_2(OEt)$; $n = 1$–4) results in the formation of cationic aryldiazene complexes of the compositions $[Re(HNNAr)(CO)_{5-n}(PR_3)_n]^+$ or $[\{Re(CO)_{5-n}(PR_3)_n\}_2(\mu\text{-}HNNArNNH)]^{2+}$.[1048] Bifunctional diazene/diazonium derivatives which can be prepared in this way are excellent building blocks for heterobinuclear and heterotrinuclear compounds with bis(aryldiazene) bridging ligands as has been demonstrated for Re–Ru, Re–Os,

Re–Mn, and Re–Ru–Mn combinations. Related compounds such as the diazene/diazenido species $[Re(CO)_3\{PPh_2(OEt)\}_2(\mu\text{-}HNArArNNFe(CO)_2\{P(OPh)_3\}]^{2+}$ have been isolated during this type of reactions.[1048]

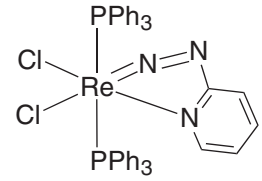
Complexes with chelating diazenido ligands have been obtained from reactions of common rhenium starting materials such as $[ReOCl_3(PPh_3)_2]$, $[ReCl_3(NCCH_3)(PPh_3)_2]$, $[ReNCl_2(PPh_3)_2]$, or perrhenate with 2-hydrazinopyridine (H_2NNHpy) or 2-hydrazino-4-(trifluoromethyl)pyrimidine ($H_2NNHC_4H_2N_2CF_3$). The resulting complexes $[Re(NNpy)Cl_2(PPh_3)_2]$ (**315**) and $[Re(NNC_4H_2N_2CF_3)Cl_2(PPh_3)_2]$ possess octahedral geometry with an almost planar chelating ligand indicating a delocalized π-system.[1049,1050]



(**313**)



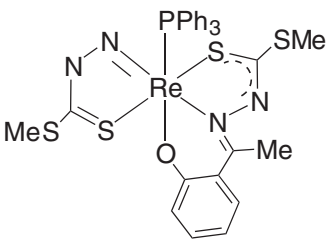
(**314**)



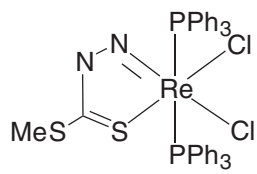
(**315**)

Neutral complexes of the type $[Re\{\eta^2\text{-}NNC(SMe)S\}(PPh_3)(O^{\frown}N^{\frown}S)]$ (**316**) ($O^{\frown}N^{\frown}S$ = tridentate, dianionic Schiff base ligand such as *S*-methyl β-*N*-((2-hydroxyphenyl)ethylidene)dithiocarbazate or *S*-methyl β-*N*-((2-hydroxyphenyl)methylidene)dithiocarbazate) have been prepared via ligand exchange reactions starting from $[ReOCl_4]^-$ or $[ReOCl_3(PPh_3)_2]$. The coordination sphere of the metal contains a chelated hydrazido group, a facially coordinated Schiff base, and PPh_3. Similar reactions starting from perrhenate in acidic ethanolic solution in the presence of $H_2NNHC(SMe)S$ and PPh_3 result in the formation of the complex $[Re(\eta^2\text{-}NNC(SMe)S)Cl_2(PPh_3)_2]$ (**317**) whereas the rhenium(V) nitrido complex is formed when *N*-methyl-substituted dithiocarbazic acid is applied. A similar compound, the black [ReO(NHNC-(SMe)S)(Et_2dtc)], has been prepared from the dimeric, oxo-bridged rhenium(V) complex $[Re_2O_3(Et_2dtc)_4]$ and $H_2NNHC(S)SMe$ in good yields.[616]

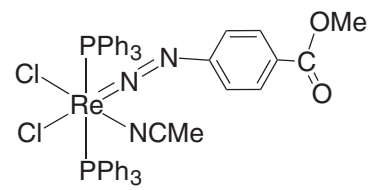
A facile approach to mono-diazenido complexes is the direct synthesis from perrhenate with an excess of phenylhydrazines in the presence of PPh_3. When this reaction is performed in acetonitrile, complexes of the type $[Re(NNC_6H_4\text{-}R\text{-}4)Cl_2(NCCH_3)(PPh_3)_2]$ (**318**) (R = Cl, OMe, CO_2Me) are formed in high yield and purity.[865,1051] This approach is particularly attractive for potential nuclear-medical applications since the substituent R can be varied over a wide range and allows the introduction of reactive sites for the coupling of biomolecules as has been demonstrated by the isolation and structural characterization of an ester-substituted derivative.[1051]



(**316**)



(**317**)



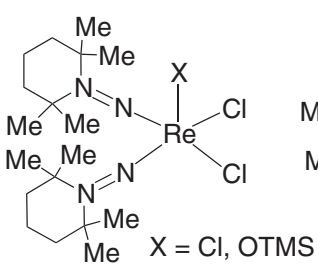
(**318**)

5.3.2.10.3 *Complexes with two and more hydrazide ligands*

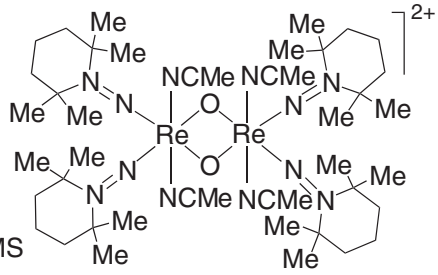
Complexes with two hydrazide ligands such as $[Re(NNPh)(NNHPh)X_2(PPh_3)_2]$ (X = Cl, Br) can be prepared by protonation of $[Re(NNPh)Cl(PPh_3)_2]$ with HCl and subsequent halide exchange with HBr to obtain the bromo analogue. The structural analysis of $[Re(NNPh)(NNHPh)Br_2(PPh_3)_2]$ clearly shows one almost linear diazenido ligand (corresponding to (**309a**)) and one bent hydrazide ligand (probably corresponding to type (**309g**)).[1052] Similar, unequal bonding modes of two hydrazide ligands which can be assigned to mixtures of the ligand types (**309a**), (**309c**), and (**309f**) have been found in the complexes $[Re(NNHCOPh)(NHNHCOPh)Cl_2(PPh_3)_2]$,[1053,1054] $[Re(NNHCOPh)(NHNHCO_2\text{-}Me)Cl_2(PPh_3)_2]$,[1036] or $[Re(NNPh)(NNHPh)(SC_5H_4N\text{-}2\text{-}TMS)(PPh_3)_2][BPh_4]$.[1055]

Reaction of $[Re(NNC_6H_4\text{-}X\text{-}4)_2Cl(PPh_3)_2]$ (X = Cl, Me) with excess dppe in methanol/toluene gives the orange–brown cations $[Re(NNC_6H_4\text{-}X\text{-}4)_2(dppe)_2]^+$ in good yields. An analogous cation with the less bulky bis(phosphine) dmpe has only been obtained with X = Cl, whereas with X = Me the monosubstitution product $[Re(NNC_6H_4\text{-}Me\text{-}4)Cl(dppe)_2]^+$ is formed.[1043] The Re–N–N angles are dependent on the steric requirements of the phosphine ligands.

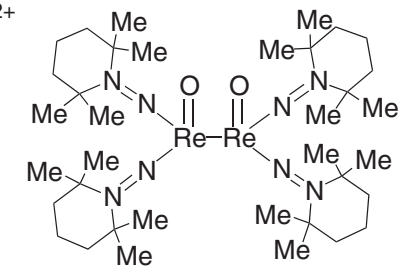
A series of isodiazene complexes has been derived from 1-amino-2,2,6,6-tetramethylpiperidine ($H_2NNC_9H_{18}$).[1056] Interaction of this ligand with $[ReO_3(OTMS)]$ in a mixture of TMSCl and Et_3N gives yellow crystals of $[Re(NNC_9H_{18})Cl_2(OTMS)]$ which can be treated with HCl to afford $[Re(NNC_9H_{18})Cl_3]$ (**319**). The nucleophilicity of the diazene nitrogen atoms is low and, thus protonation occurs at the OTMS group. The chloro ligands in $[Re(NNC_9H_{18})Cl_3]$ are labile and can be replaced by a reaction with $Ag[F_3CSO_3]$ in acetonitrile. The product of this reaction, $[\{Re(\mu\text{-}O)(NNC_8H_{19})_2(NCCH_3)\}_2][F_3CSO_3]_2$ (**320**), which has been isolated as orange–red crystals in moderate yields, contains linear isodiazene ligands. The transannular O···O distance in the central $\{Re_2O_2\}$ ring is short at 2.40 Å. The diamagnetism of the complex, which should contain rhenium in the formal oxidation state "+4", suggests spin-coupling across the $Re(O)_2Re$ bridge since the Re—Re distance of 3.45 Å is too long to assign a metal–metal bond. A third isodiazene complex, the dimeric $[\{ReO(NNC_8H_{19})_2\}_2]$ (**321**) with a rhenium–rhenium single bond has been isolated from reactions of $[Re(NNC_9H_{18})Cl_3]$ with $LiNNC_9H_{18}$ in low yields. The geometry around each rhenium atom can be described as distorted tetrahedral and is "ethane-like" with almost eclipsed conformation of the ligands.[1056]



(**319**)



(**320**)



(**321**)

Reduction of $[Re(NNPh)_2Br_2(PPh_3)_2]Br$, which can be prepared by bromination of $[Re(NNPh)_2Cl(PPh_3)_2]$, gives the paramagnetic diazenido complex $[Re(NNPh)_2Br_2(PPh_3)]$ in which one of the diazenide ligands has a linear Re—N—N bond and the other a bent one. Both are in *trans*-positions to bromo ligands and show a considerable *trans*-influence.[1057] The monodiazenido complex $[Re(NNPh)_2Br_3(PPh_3)_2]$ is produced on standing of $[Re(NNPh)_2Br_2(PPh_3)_2]Br$ in THF. The green crystals are obtained in 85% yield following this route, but are also produced during recrystallization of $[Re(NNPh)_2Br_2(PPh_3)_2]Br$ from acetone as a side-product of the synthesis of the red acetone solvate $[Re(NNPh)_2Br_2(PPh_3)_2]\cdot Me_2CO$. $[Re(NNPh)_2Br_2(PPh_3)_2]Br$, $[Re(NNPh)_2Br_2(PPh_3)_2]$, and $[Re(NNPh)Br_3(PPh_3)_2]$ react with isocyanides to give mixed diazenido/isocyanide complexes of various composition.[1057]

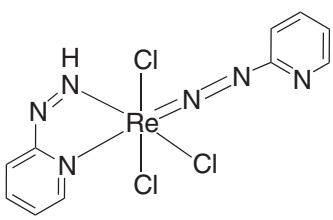
Phosphite/diazenido complexes can be prepared from $[ReCl_3\{P(OR)_3\}_3]$ complexes which are formed from $[ReOCl_3(AsPh_3)_2]$ and phosphites as oily intermediates. They readily react with hydrazines to give dinitrogen or diazenido complexes depending on the phosphites and hydrazines used. Whereas reactions with *t*-butylhydrazine give cationic dinitrogen complexes of the composition $[Re(N_2)_2(PR_3)_4]^+$ ($PR_3 = P(OEt)_3$, $P(OMe)_3$, $PPh(OEt)_2$), reactions with phenylhydrazine yield $[Re(NNPh)Cl\{P(OEt)_3\}_4]^+$ or $[Re(NNPh(H_2NNHPh)\{P(OMe)_3\}_4]^{2+}$ depending on the alkyl substitution of the phosphite. Treatment of $[ReCl_3\{P(OMe)_3\}_3]$ with methylhydrazine gives a mixture of the dinitrogen complex $[Re(N_2)_2\{P(OMe)_3\}_4]^+$ and the methyldiazenido derivative $[Re(NNMe)(H_2NNHMe)Cl\{P(OMe)_3\}_3]^+$, which can be separated by fractional crystallization of their $[BPh_4]^-$ salts.[902]

Chelating diazene coordination has been observed for hydralazine, thiobenzoylhydrazine, 2-hydrazinopyridine, and 2-hydrazinopyrimidines. A cationic tris-chelate of the composition $[Re(HNNN_2C_8H_5)_3]^+$ has been reported as the product of the reduction of perrhenate with excess of hydralazine in methanol. It can be isolated as a green solid by precipitation with $Na[BPh_4]$.[1058]

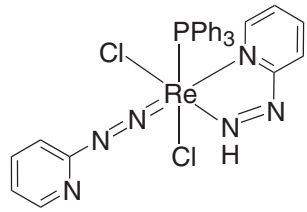
A series of compounds has been isolated with thiobenzoylhydrazine. The reaction with perrhenate in acidic solution yields after recrystallization from DMF the neutral tris-chelate $[Re(NHNC(S)Ph)_3]\cdot DMF$, which is also formed from $[ReOCl_3(PPh_3)_2]$ in neutral ethanol/benzene

mixtures. Acidification with HCl, however, gives [Re(NHNC(S)Ph){NHNHC(S)Ph}$_2$]Cl in which two different bonding modes for the hydrazide are established which can be assigned to the cases (**309d**) and (**309h**).[243] More complexes with chelating thiobenzoylhydrazides have been prepared from [$ReO_2I(PPh_3)_2$] and [$Re_2O_3(Et_2dtc)_4$].[617] The products are [Re{HNNC(S)Ph}{HNNHC(S)Ph}$_2$]I, [ReO{HNC(S)Ph}{HNNHC(S)Ph}], and [Re{HNNC(S)Ph}$_2$(Et_2dtc)]. The related compound [Re{NNC(S)OMe}(Et_2dtc)$_2$] is obtained from *O*-methylthiocarbazate and [$Re_2O_3(Et_2dtc)_4$], and a series of complexes containing diazenido-hydrazino ligands together with benzoyldiazenido ligands has been prepared from [Re{NNC(Ph)O}$Cl_2(PPh_3)_2$] and the functionalized hydrazines H_2NNHR (R = C(S)Ph, CS(O)Me, C(O)SMe, C(S)SMe).[617] The chelating hydrazides show various structural types in which they act as two-electron donors, while mixed diazenido (**309a**) and hydrazine coordination (**309e**) has been detected for the mono-dentate ligands.

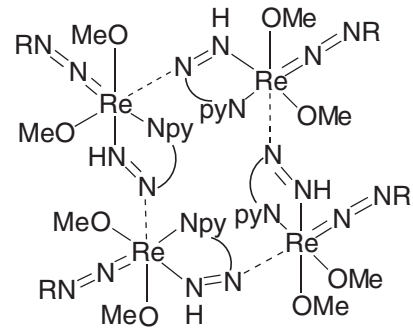
The coordination of 2-pyridinohydrazine and related compounds has attracted considerable attention since they represent a promising class of ligands for the coupling of peptides or other biologically interesting molecules to the metals. The reduction of $[ReO_4]^-$ by 2-pyridinohydrazine in acidic methanolic solution yields the mixed diazenido/diazene complex [Re(NNC_5H_4NH)($HNNC_5H_4N$)Cl_3] (**322**) in excellent yields. The neutral complex contains a bidentate organodiazene ligand and a monodentate pyridinium-diazenido ligand.[1059] The reaction of the red–purple [Re(NNC_5H_4NH)($HNNC_5H_4N$)Cl_3] with triphenylphosphine and a proton scavenger in methanol gives the red–brown, neutral complex [Re(NNC_5H_4N)-($HNNC_5H_4N$)$Cl_2(PPh_3)$] (**323**).[1060] Two chloro ligands can be replaced when the more basic PMe_2Ph is used and the cationic complex [Re(NNC_5H_4N)-($HNNC_5H_4N$)Cl(PMe_2Ph)$_2$]Cl precipitates as a red solid from reaction mixtures of [Re(NNC_5H_4NH)($HNNC_5H_4N$)Cl_3] and dimethylphenylphosphine.[1049] A similar coordination behavior has been established for 2-pyrimidinohydrazines. They also show the coordination types (**309a**) and (**309d**) at the same metal center.[1050] An exceptional compound has been isolated as a side-product of the synthesis of [Re(η^1-$NNC_4H_3N_2H$)(η^2-$HNNC_4H_3N_2$)Cl_3]. The black tetrameric compound [{Re($NNC_4H_3N_2$)($HNNC_4H_3N_2$)($OMe)_{24}$}] is formed during slow diffusion of methanol into a DMF solution of the chloro complex and has been structurally characterized. The structure consists of isolated tetranuclear units, constructed from [Re($NNC_4H_3N_2$)($HNNC_4H_3N_2$)($OMe)_2$] units linked through the β-nitrogen of the chelating organodiazene ligand into a box-like aggregate (**324**).[1061]



(**322**)



(**323**)



(**324**)

The {Re(NNC_5H_4N)($HNNC_5H_4N$)} core has been used for the synthesis of mixed ligand compounds containing phosphine and phosphinophenolato ligands,[458] pyridine-2-thiol, or pyrimidine-2-thiol. [Re(NNC_5H_4NH)($HNNC_5H_4N$)Cl_3] serves as model for the binding of rhenium(V) oxo species to hydrazinonicotinamide conjugated chemotactic peptides. The use of pyrimidinethiol co-ligands results in favorable pharmacokinetics and the thiolate derivatives provide models for possible modes of interaction of metal–hydrazine cores with co-ligands in the radiopharmaceutical agents.[1062]

5.3.2.11 Hydrido complexes

Although some hydride complexes have been included in the chemistry of rhenium already described the main discussion of their chemistry is referred to this point due to the ambiguities

that exist between classical and nonclassical hydrido complexes. There are relatively few neutron diffraction studies and X-ray diffraction or solution NMR are not unequivocal.

Perhaps the best known hydrido complex of rhenium is the hydrido anion $[ReH_9]^{2-}$ which was the first polyhydride to be prepared. Its structure was determined early on,[1063,1064] and all the main structural features have since been confirmed by neutron diffraction.[1065] The results confirm the geometry of the complex anion $[ReH_9]^{2-}$ as a tricapped square antiprism and all proposed structures with a lower hydrogen content and statistically occupied hydrogen positions can be ruled out. The $[ReH_9]^{2-}$ building block is also found in the ternary hydride $[Rb_3ReH_{10}]$, which is better formulated as $[Rb_3H][ReH_9]$ again with tricapped square antiprismatic geometry around Re.[1066] Low-valent rhenium hydrides $[Mg_3H][ReH_6]$ and $K_3[ReH_6]$ have been prepared by high pressure syntheses from rhenium, hydrogen and elemental magnesium or potassium.[1067,1068]

5.3.2.11.1 Phosphorus and arsenic donor ligands

Complexes of the types $[ReH_7(PR_3)_2]$ and $[ReH_5(PR_3)_3]$ (PR_3 = tertiary phosphine or phosphite) have been subject of many studies. They have been identified as classical hydrido species by neutron diffraction.[1069,1070] This shows a tricapped trigonal prismatic geometry for $[ReH_7(PR_3)_2]$ complexes ($PR_3 = PPh_3$, PPr^i_3, PMe_2Ph, PMe_3, P(cyclohexyl)$_3$) with the phosphine ligands in opposing axial and equatorial positions (**325**),[1071–1075] and a dodecahedral core for the $[ReH_5(PR_3)_3]$ complexes with the three phosphine and one hydrido ligands having five neighbors (**326**).[1070,1071,1076,1077] Information about the bonding mode of the hydrogen atoms is derived from NMR data on the basis of ^{1}H-NMR longitudinal relaxation times (T_1) which are normally useful to evaluate the bonding mode of coordinated hydrogen atoms.[1077,1078] Another criterion for the bonding mode of hydrides is provided by the electrochemical behavior of the complexes as has been demonstrated for $[ReH_7(PPh_3)_2]$.[1079] Reduction of $ReCl_5$ with sodium metal in the presence of $PMePh_2$ results in the formation of $[ReCl(\eta^2\text{-}H_2)(PMePh_2)_4]$ or $[ReH_3(PMePh_2)_4]$ depending on the reaction conditions.[807] Whereas ^{1}H-NMR studies strongly suggest dihydrogen coordination in the former complex, an X-ray crystal structure of $[ReH_3(PMePh_2)_4]$ indicates long H—H distances suggesting a "classical" polyhydride. Shorter H—H distances of 1.36 Å (derived from neutron diffraction data) have been found in $[ReH_7\{P(C_6H_4\text{-}Me\text{-}4)_3\}_2]$,[1072] which suggest the formulation $[ReH_5(H_2)\{P(C_6H_4\text{-}Me\text{-}4)_3\}_2]$ despite a T_1 relaxation time value of 66 ms which falls into the range found for "classical" hydrides.[1080] Theoretical studies on $[MH_7L_2]$ species (M = Re, Tc) using *ab initio* techniques including relativistic effective core potentials of rhenium and technetium result in a somewhat higher stability for hydrido-bonded forms.[1081] A dependence of the structural type on electronic ligand effects is suggested by a systematic NMR study on a series of $[ReH_7\{P(C_6H_4\text{-}X\text{-}4)_3\}_2]$ complexes (R = Me, H, F, CF_3, OMe), where a dependence of the T_1 NMR parameter on the Hammet σ_p constants of the substituents was found.[287] The results also fit with the known H—H distances from diffraction studies and allow the description of the bonding situation in some derivatives as "stretched H_2" coordination.

Protonation of $[ReH_5(PPh_3)_3]$ with HBF_4 in CH_2Cl_2 gives yellow $[ReH_6(PPh_3)_3][BF_4]$, whereas treatment with $[C_7H_7][PF_6]$ in the presence of various ligands leads to the formation of the compounds $[ReH_4(PPh_3)_2(L)][PF_6]$ (L = $NCCH_3$, $CNBu^t$, or $CNC_6H_3\text{-}Me_2\text{-}2,6$).[287] Deprotonation of the latter compounds with NEt_3 gives access to the neutral trihydrides $[ReH_3(PPh_3)_3(L)]$. Protonation of the complex $[ReH_3(PPh_3)_3(NCCH_3)]$ with HBF_4 in acetonitrile reforms $[ReH_4(PPh_3)_3(NCCH_3)]^+$, whereas with the hydride abstracting agent $[C_7H_7][PF_6]$ in acetonitrile the dihydride $[ReH_2(PPh_3)_3(NCCH_3)_2][PF_6]$ is produced. Addition of a second equivalent of $[C_7H_7][PF_6]$ in $NCCH_3$ gives $[ReH(PPh_3)_3(NCCH_3)_3][PF_6]_2$.[287] The anionic polyhydride $[ReH_6(PMe_2Ph)_2]^-$ undergoes facile one-electron oxidation when treated with either the ferrocenium ion or $[Fe(bipy)_3]^{3+}$. The products are $[ReH_7(PMe_2Ph)_2]$ and the dimer $[Re_2H_8(PMe_2Ph)_4]$.[1083]

Deprotonation of $[ReH_7(PR_3)_2]$ complexes ($PR_3 = PPh_3$, PMe_2Ph, $PMePh_2$) and $[ReH_5(PMe_2Ph)_3]$ with KH in THF results in anionic polyhydrides. A structural analysis of $K[ReH_6(PPh_3)_2(THF)_2]$ shows a dimeric, hydrogen-bonded compound.[1084] Similar complexes such as $[ReH_6(PR_3)_2]^{2-}$ (R = Me, Ph, Pr^i), have been isolated with crown ether coordinated potassium cations as monomeric units.[1085]

Protonation of $[ReH_3(PMe_2Ph)_4]$ with HBF_4 in diethylether gives the $[ReH_4(PMe_2Ph)_4]^+$ cation. The X-ray crystal structure shows an arrangement of the phosphines which is intermediate between tetrahedral and planar, and lack of exchange with D_2 or ligands such as PhC≡CPh, CO,

or $NCCH_3$, is consistent with a "classical" hydrido complex.[1086] Triethylamine does not deprotonate $[ReH_4(PMe_2Ph)_4]^+$ since it is a weaker base. A quantitative determination of the thermodynamic and kinetic acidity of the tetrahydrido cation has been carried out in acetonitrile solutions giving a pK_a value of 25.5(1). The rate constant for the removal of a proton from $[ReH_4(PMe_2Ph)_4]^+$ with dibutylamine in acetonitrile at 82 °C is 6×10^{-4} $M^{-1}s^{-1}$.[1087]

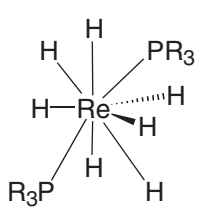
Reduction of $ReCl_5$ in neat trimethylphosphine gives $[ReH(PMe_3)_5]$ in moderate yields.[1088,1089] An improved synthesis giving yields of about 60% uses sodium metal as additional reducing agent. $[ReH_3(PMe_3)_4]$ was isolated with lower yields during the same reaction.[914] Treatment of $[ReH(PMe_3)_5]$ with CO_2 at 70 °C gives white crystals of $[Re(CO)(PMe_3)_4(O_2CH)]$ containing a monodentate formato ligand, whilst the reaction with carbon monoxide gives *cis*-$[ReH(CO)(PMe_3)_4]$. This product undergoes a further reaction with CO_2 to yield $[Re(CO)(PMe_3)_4(O_2CH)]$.[914]

The trihydrido complex $[ReH_3(CO)(PMe_2Ph)_3]$ is formed by treatment of $[ReCl_3(CO)(PMe_2Ph)_3]$ with $LiAlH_4$ in boiling diethylether. Protonation of the product with HBF_4 in $CDCl_3$ at −78 °C results in an equilibrium mixture of $[ReH_4(CO)(PMe_2Ph)_3]^+$ and its "nonclassical" tautomer $[ReH_2(H_2)(CO)(PMe_2PhP)_3]^+$. NMR studies suggest site exchange of dihydrogen and hydride and the interconversion of the two isomers that lead to an unusual temperature dependence of the T_1 values. An isotope effect has been derived for the interconversion and deuteration shifts the equilibrium towards the dihydrogen form.[1090,1091] Dihydrogen coordination is also suggested for $[ReX(H_2)(PMe_2Ph)_4]$ complexes from their NMR spectra and the X-ray structure of the bromo derivative showing the dihydrogen ligand *trans* to Br^-.[1092]

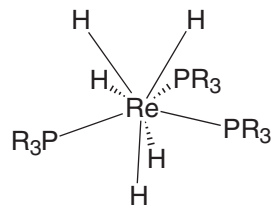
Complexes of the general structure $[Re(L)_5H_2]^+$ adopt either a rhenium(III) dihydrido structure or a rhenium(I) dihydrogen structure dependent on the ligands L. More basic ligands such as PMe_3 favor the dihydride tautomer, while π-acid ligands such as CO or $CNBu^t$ favor the dihydrogen structure. In mixed-ligand phosphine/isocyanide complexes, at least three CNR ligands must be present for the formation of the dihydrogen structure.[909] The Lewis-acidic fragment $\{Re(CNBu^t)_3\{P(cyclohexyl)_3\}_2\}^+$ fragment strongly binds dihydrogen in preference to Cl^-, which has been attributed to the weak Re—Cl bond in the neutral rhenium(I) complex.[909]

In analogy to the synthesis of $[ReH_7(PPh_3)_2]$ from $[ReOCl_3(PPh_3)_2]$ and $LiAlH_4$,[1093] the corresponding triphenylarsine complex can be prepared from $[ReOCl_3(AsPh_3)_2]$.[1094] $[ReH_7(AsPh_3)_2]$ is a "classical" hydride and possesses remarkable stability. It does not undergo substitution with phosphines or nitrogen donor ligands, nor does it react with chelating disilyl ligands. With triphenylsilane and triphenylstannane, however, hexahydrido complexes of the composition $[ReH_6(EPh_3)(AsPh_3)_2]$ (E = Si, Sn) are formed. The arsine complex $[ReH_2Cl(AsMePh_2)_4]$ was prepared analogous to the phosphine analogue from $ReCl_5$, $AsMePh_2$, and sodium amalgam in THF. The arsine derivative, however, is unstable and decomposes in solution. From NMR data a "classical" hydrido structure was suggested with a H—H distance of 1.6 Å which is longer than that derived for the analogous phosphine complex (1.39 Å).[1095]

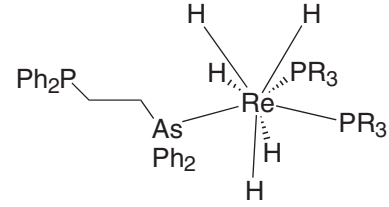
Reactions of $[ReH_7(PPh_3)_2]$ with potentially bidentate phosphines such as dppe and dppm,[1096] or their mixed phosphine/arsine or arsine analogues 1-(diphenylphosphino)-2-(diphenylarsino) ethane (arphos) or bis(diphenylarsino)ethane (DPAE) give the products $[ReH_5(PPh_3)_2(X^{\frown}Y)]$ ($X^{\frown}Y$ = monodentately bonded bis(phosphine/arsine)). The reaction with arphos gives an approximate 50:50 mixture of the P- and As-bound isomers. The As-coordinated compound (**327**) crystallizes as large blocks and can be mechanically separated from its P-bonded isomer.[1097]



(**325**)



(**326**)



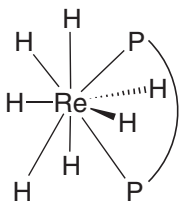
(**327**)

$[ReH_7(P^{\frown}P)]$ complexes ($P^{\frown}P$ = chelating bis(phosphines)) cannot adopt the structure (**325**). A neutron diffraction study on $[ReH_7(dppe)]$ shows that the phosphorus atoms occupy two eclipsed prism positions in a tricapped trigonal prism (**328**). No intramolecular H···H separations less than 1.77 Å are observed confirming the "hydrido character" of the hydrogen atoms in this compound.[1098] Similar bonding situations have also been reported for other representatives including

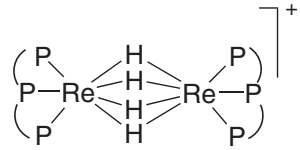
1,1′-bis(diphenylphosphino)ferrocene, 1,4-bis(diphenylphosphino)butane, (4S,5S)-4,5-bis{(diphenylphosphino)methyl}2,2-dimethyl-1,3-dioxolane or the mixed phosphine/arsine $Ph_2AsCH_2CH_2PPh_2$.[1099,1100] Treatment of oxorhenium(V) complexes of the composition $[ReOCl_3(P^{\frown}P)]$ ($P^{\frown}P$ = bis(phosphine)) with $Na[BH_4]$ give complexes of the composition $[ReH_7(P^{\frown}P)]$, which has also been observed when a $P^{\frown}P$ possesses an inflexible skeleton such as *cis*-1,2-bis(diphenylphosphino)ethene (dppeN).[1101] The reaction of $[ReH_7(dppeN\text{-}P^1,P^2)]$ with triphenylphosphine gives a mixture of the pentahydride $[ReH_5(dppeN\text{-}P^1,P^2)(PPh_3)]$ and the trihydride $[ReH_3(dppeN\text{-}P^1,P^2)(PPh_3)_2]$. A similar reaction of $[ReH_7(dppeN\text{-}P^1,P^2)]$ with the potentially chelating phosphine dppm in refluxing toluene leads to the formation of $[ReH_5(dppeN\text{-}P^1,P^2)(dppm\text{-}P^1)]$, whereas the trihydrido compound $[ReH_3(dppeN\text{-}P^1,P^2)(dppm\text{-}P^1,P^2)]$ can be isolated from the same reaction mixtures after prolonged heating. The complex has a fluxional structure as has been shown by NMR spectroscopy. Protonation of $[ReH_7(dppeN\text{-}P^1,P^2)]$ yields $[ReH_6(\eta^2\text{-}H_2)(dppeN\text{-}P^1,P^2)]$ which, on warming to ambient temperatures, is cleanly converted to a dirhenium multihydride species.[1101] The NMR behavior of the asymmetric $[ReH_3(dppeN\text{-}P^1,P^2)(dppm\text{-}P^1,P^2)]$ is similar to that of the bis-dppe compound $[ReH_3(dppe\text{-}P^1,P^2)_2]$.[1102] The latter complex reacts with the hydride abstracting agent $[C_7H_7][PF_6]$ in presence of acetonitrile, $CNBu^t$ or $CNC_6H_3\text{-}Me_2\text{-}2,6$ to produce cationic complexes of the type $[ReH_2(dppe)_2(L)][PF_6]$.[287]

Reduction of $ReCl_5$ by sodium in the presence of bis(phosphines) such as dppe or dppeN gives products of the composition $[ReCl(\eta^2\text{-}H_2)(P^{\frown}P)_2]$, whereas a mixture of $[ReH_3(PMe_2Ph)_4]$ and $[ReH_4(PMe_2Ph)_4]^+$ is formed in the presence of dimethylphenylphosphine. The bonding modes of the hydrogen atoms are derived from the NMR spectra of the compounds.[1103,1104]

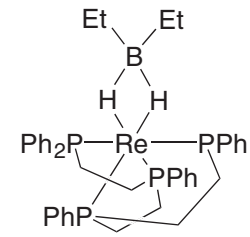
Tridentate phosphine derivatives such as $PhP(CH_2CH_2PPh_2)_2$ or $MeC(CH_2PPh_2)_3$ react with $[ReCl_3(PMe_2Ph)_3]$ or $[ReCl_3(NCCH_3)(PPh_3)_2]$ to give $[ReCl_3(triphos\text{-}P^1,P^2,P^3)]$ complexes which than react with $Na[BH_4]$ to give $[ReH_5(triphos\text{-}P^1,P^2,P^3)]$. The products undergo the usual reactions of $[ReH_5(PR_3)_3]$ derivatives, i.e., protonation by HBF_4 to give $[ReH_6(triphos)]^+$ cations or reductive H_2 elimination with monodentate ligands such as PPh_3 or CO to afford products of the formula $[ReH_3(triphos)(L)]$.[1105–1108] Treatment of $[ReH_5(triphos)]$ with HBF_4 in NCR (R = Me, Et) gives $[ReH(NCR)_3(triphos)]^{2+}$. The trihydrido complexes $[ReH_3(triphos)(L)]$ (L = PPh_3, $AsPh_3$, dppe-P, η^1-arphos) can be protonated by $HBF_4 \cdot Et_2O$ to produce $[ReH_4(triphos)(L)]^+$ which are in turn are readily deprotonated by NEt_3. In absence of the ligand L, solutions of $[ReH_5(triphos)]$ evolve H_2 and the dinuclear dark-red complex $[Re_2H_4(triphos)_2]$ which can readily be oxidized to give $[Re_2H_4(triphos)_2]^+$ (**329**).[1107] Similar results have been obtained with the tridentate phosphine $PhP\{CH_2CH_2CH_2P(cyclohexyl)_2\}_2$ (Cyttp). The complex $[ReH_5(Cyttp)]$, which has the usual triangulated dodecahedral structure with "classical" hydrido ligands, is protonated to give $[ReH_4(\eta^2\text{-}H_2)(Cyttp)]^+$ containing one "nonclassical" dihydrogen ligand with a short H—H distance of 1.08 Å.[1109,1110] The cationic compound is resistant to H_2 loss and unaffected by CO or $CNBu^t$ at room temperature. In contrast, $[ReH_5(Cyttp)]$ reacts with a number of reagents as is expected for a "classical" hydride.[1109] Hydrido complexes of the composition $[ReH_3(tetraphos\text{-}P_4)]$ are produced with various tetradentate phosphine ligands and the structure of the unusual compound $[Re(tetraphos)(H_2BEt_2)]$ has been solved. The $\{H_2BEt_2\}^-$ unit is bound to rhenium via two bridging hydrides (**330**).[1111] Similar coordination has been established for $[ReH_4(PMePh_2)_2(H_2AlMe_2)]$.[1112] Rhenium(III) complexes with the tetradentate ligand $HN(CH_2CH_2PPh_2)_3$ react with $LiAlH_4$ to give $[ReH_3(L)]$ which can be protonated to the tetrahydrido species $[ReH_4(L)]^+$. The BPh_4^- salt of the latter complex has been studied by X-ray crystallography confirming the coordination number eight and a distorted dodecahedral geometry for the complex cation.[1113]



(**328**)



(**329**)



(**330**)

A number of mixed hydrido/nitrosyl complexes and their reactions have been studied. Typical compounds are $[ReH_2(NO)(PPh_3)_3]$ which reacts with perchloric acid in the presence of CO with the loss of only one hydride ligand and carbonyl and alkoxy products have been isolated.[1114–1117] Complexes containing "classical" and "nonclassical" hydrido ligands have been prepared from $[NEt_4][Re(NO)Br_5]$: $[Re(NO)Br_2(\eta^2\text{-}H_2)(PR_3)_2]$ and $[Re(NO)H(BH_4)(PR_3)_2]$ ($R = Pr^i$, cyclohexyl). The compounds show an interesting coordination chemistry which includes ligand exchange reactions and the formation of dinitrosyl species.[994,1014]

The coordination chemistry of the hydrido/phosphine rhenium complexes can be extended to phosphonite and phosphite complexes. This has been demonstrated for monodentate ligands such as $P(OEt)_3$, $P(OCH_2)_3CEt$ and $PPh(OR)_2$ ($R = Me$, Et, Pr^i),[288,779,809,1118] or the chelating phosphinite ligand $Ph_2OCH_2CH_2OPPh_2$.[1119,1120]

5.3.2.11.2 Nitrogen donor ligands

Mixed-ligand hydrido complexes of the composition $[ReH_5(PPh_3)_2(L)]$ ($L =$ pyridine and related donor ligands) have been known for a long time and can be synthesized from $[ReH_7(PPh_3)_2]$ with the appropriate ligand.[1121] The colors of the crystalline solids are strongly dependent on the electronic properties of the ligand L and these vary from bright yellow (4-methylpyridine) to deep-purple (4-carbomethoxypyridine). The structures of the eight-coordinate complexes are fluxional. Two coalescence events have been observed during NMR studies and pseudorotation and turnstile mechanisms have been proposed for the two processes.[1122] The hydride fluxionality can be controlled by interactions in the second coordination sphere of the complexes such as hydrogen bonding. This has been demonstrated in extensive NMR studies on $[ReH_5(PPh_3)_2(L)]$ complexes where L is imidazole or substituted pyridines,[1123–1125] and results in a remarkable solvatochromism.[1076,1126–1128] Reactions of $[ReH_5(PPh_3)_3]$ with typical charge-transfer acceptors such as 4-chloroanil or tetrachloro-4-hydroquinone gave charge-transfer complexes which allowed the characterization of outer-sphere interactions and indicate strong complexation with tetrachloro-4-hydroquinone.[1129]

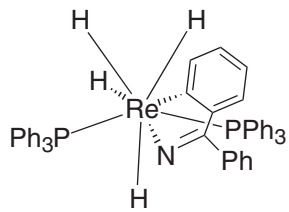
Reactions between $[ReH_7(PPh_3)_2]$ and a series of benzylic imines, PhCHNR ($R = Me$, Ph, CH_2Ph), afford a new type of rhenium hydrido complex with orthometallated ligands, $[ReH_4\{\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR\}(PPh_3)_2]$.[1130] The crystal structure of one representative, $[ReH_4\{\eta^2\text{-}(1,2\text{-}C_6H_4)CHNPh\}(PPh_3)_2]$ (**331**) indicates that the imine ligand binds to rhenium through the nitrogen and an *ortho*-carbon atom of the phenyl ring establishing a five-membered chelate ring. The overall structure of the eight-coordinate complex can be described as a distorted dodecahedron about the central rhenium atom. The hydrogen binding in the molecule can be regarded as "classical" hydrido ligands as has been derived from NMR studies. Acidolysis of $[ReH_4\{\eta^2\text{-}(1,2\text{-}C_6H_4)CHNR\}(PPh_3)_2]$ in acetonitrile results in loss of the orthometallated imine ligand and the reduction of the imine functional group to a secondary ammonium cation. One hydride ligand is transferred to the imine carbon atom and H_2 evolution occurs. The rhenium containing product is $[ReH(NCCH_3)_4(PPh_3)_2]^{2+}$.[1130] Similar products of the composition $[ReH(NCR)_3(PPh_3)_2(L)]^{2+}$ ($R = Me$, Et; $L =$ NCR, py, $NH_2C_6H_{11}$, NH_2Bu^t, PPh_3) have been isolated as products of reactions of $[ReH_5(PPh_3)_2(L)]$ with HBF_4.[1131]

Mixed-ligand species containing phosphine and heterocyclic bidentate amines such as bipy or phen of remarkable stability are formed from reactions of $[ReH_7(PPh_3)_2]$ and an excess of the ligands. The initially formed seven-coordinate trihydrido complexes $[ReH_3(PPh_3)_2(N^{\frown}N)]$ can be protonated by HBF_4 to give $[ReH_4(PPh_3)_2(N^{\frown}N)][BF_4]$, while reactions with $[C_7H_7][PF_6]$ in acetonitrile afford the dihydrides $[ReH_2(PPh_3)_2(N^{\frown}N)(NCCH_3)][PF_6]$.[1132] Unusual nine-coordinate rhenium hydrides result from reactions of $[ReOCl_2\{HB(pz)_3\}]$ or $[ReOCl_3\{H_2C(pz)_2\}]$ with $LiAlH_4$ in THF ($\{HB(pz)_3\}^- =$ hydrotris(pyrazolyl)borate; $\{H_2C(pz)_2\}$ bis(pyrazolyl)methane). "Classical" hydride coordination is suggested for $[ReH_6\{HB(pz)_3\}]$ and $[ReH_7\{H_2C(pz)_2\}]$ despite the fact that the high coordination number requires relatively short H—H contacts. The yellow mixed-ligand tetrahydride $[ReH_4(PPh_3)\{HB(pz)_3\}]$ is derived from reaction of $[ReCl_2(PPh_3)\{HB(pz)_2\}]$ with $LiAlH_4$ in THF.[1133] Rare examples of oxo/hydrido complexes have been isolated by treatment of rhenium(V) oxo-alkoxide complexes containing $\{HB(pz)_3\}^-$ or the more bulky $\{HB(pz\text{-}Me_2\text{-}3,5)_3\}^-$ with $BH_3{\cdot}THF$. Thus, the complexes $[ReO(H)\{HB(pz\text{-}Me_2\text{-}3,5)_3\}Cl]$ and $[ReO(H)_2\{HB(pz\text{-}Me_2\text{-}3,5)_3\}]$ are formed from $[ReO(OMe)_2\{HB(pz\text{-}Me_2\text{-}3,5)_3\}]$ as blue solids in excellent yields.[1134] The analogous compound $[ReO(H)\{HB(pz)_3\}Cl]$ can be prepared in a similar way. The chloro ligands are readily exchanged by triflate using a

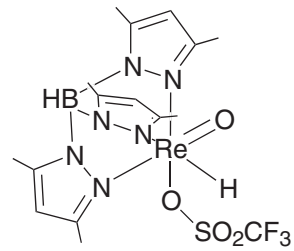
metathesis reaction with $Ag(F_3CSO_3)$ giving complexes of the composition $[ReO(H)(N^{\frown}N^{\frown}N)(F_3CSO_3)]$ (**332**). The use of modified poly(pyrazolyl)borates gives access to a whole family of rhenium hydrido complexes with mixed phosphorus/nitrogen coordination. Treatment of $[ReOCl_3(PPh_3)_2]$ with $Na[H_2B(pz)_2]$ or $Na[H_2B(pz\text{-}Me_2\text{-}3,5)_2]$ in alcohols ROH (R = Me, Et) at room temperature gives yellow products of the compositions $[ReH_2\{\kappa^3\text{-}(OR)(\mu\text{-}OR)B(pz)_2\}(PPh_3)_2]$ and $[ReH_4\{\kappa^3\text{-}(H)(\mu\text{-}OR)B(pz\text{-}Me_2\text{-}3,5)_2\}(PPh_3)]$ (R = Me, Et). The same type of reaction with $Na[Ph_2B(pz)_2]$ in MeOH gives $[ReO(OMe)\{\kappa^2\text{-}Ph_2B(OMe)(pz)\}]$. The presence of B—H bonds is essential for the formation of hydrido complexes, whose oxidation states depend on the number of B—H bonds which are activated.[1135]

Protonation of the red rhenium(III) complex $[Re\{(C_6F_5NCH_2CH_2)_3N\}(PMe_3)]$ containing the trianionic ligand $\{(C_6F_5NCH_2CH_2)_3N\}^{3-}$ (**115**) leads to a green solid which has been characterized as $[Re\{(C_6F_5NCH_2CH_2)_3N\}(H)(PMe_3)]^+$. The structural assignment as an authentic hydrido phosphine complex was based on NMR data. Protonation of other phosphine complexes, however, results in compounds of the composition $[Re\{(C_6F_5NCH_2CH_2)_3N\}(\eta^2\text{-}HPR_nH_{3-n})]^+$ showing NMR spectra with relatively large P—H couplings of about 60 Hz.[432]

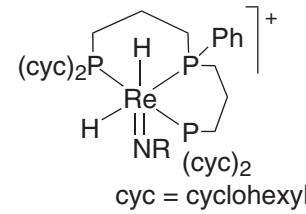
The cationic organoimido/hydrido complexes $[ReH_2(NR)(Cyttp)]^+$ (**333**) (R = Ph, C_6H_4-Me-4, cyclohexyl); Cyttp = $PhP\{CH_2CH_2CH_2P(cyclohexyl)_2\}_2$) can be prepared from the oxo/hydrido complex $[ReH_2(O)(Cyttp)][F_3CSO_3]$[1136] and a primary amine. Unlike their oxo/hydrido analogues, the imido complexes do not react with CO under mild conditions. Hydrogen cleavage and the formation of $[ReCl_3(Cyttp)]$, however, was observed during the reaction with anhydrous HCl, whereas reactions with $Na[BH_4]$ afford the pentahydrido complex $[ReH_5(Cyttp)]$.[1137]



(**331**)



(**332**)



(**333**)

5.3.2.11.3 Sulfur donor ligands and miscellaneous

The hydrido complexes $[ReH_7(PPh_3)_2]$ and $[ReH_5(PPh_3)_3]$ have been used as precursors for reactions with sterically hindered monodentate thiols, but no mixed hydrido/thiolato products have been formed,[294,829] despite the isolation of the cation $[ReH_4(PPh_3)_4]^+$ as counterion in the synthesis of $[ReO(SC_6H_2Pr^i\text{-}2,4,6)_4]$ in such reactions. The cationic complex $[ReH_4(PPh_3)_4]^+$ is conveniently obtained as $[BF_4]^-$ salt from the reaction of $[ReH_7(PPh_3)_2]$ with PPh_3 and $[PPh_3H][BF_4]$.[830] A tetrahydrido/thiolato complex is formed when $[ReOCl_3(PPh_3)_3]$ is treated with 2-triphenylsilylbenzenethiol in MeOH in the presence of $Na[BH_4]$. The blue product has been characterized as $[ReH_4(PPh_3)_3\{SC_6H_4(SiPh_2)\text{-}2\}]$ with the phosphorus and sulfur atoms in a tetrahedral array and the hydrido ligand in capping sites on the tetrahedral faces.[295]

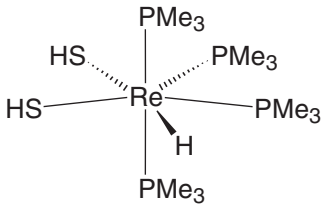
When acetonitrile solutions of $[NEt_4][ReS_4]$ react with excess of PMe_3 under an atmosphere of H_2S, beige crystals of $[ReH(SH)_2(PMe_3)_4]$ are obtained in good yields. The compound has a pentagonal bipyramidal structure with two PMe_3 ligands in axial positions (**334**). The compound reacts with dmpe with exchange of two phosphine ligands and the formation a tan complex $[ReH(SH)_2(dmpe)(PMe_3)_2]$.[1138]

Reactions of $[ReH_7(PPh_3)_2]$ with 2-hydroxypyridine (HOpy), 2-mercaptopyridine (HSpy), or 2-hydroxy-6-methylpyridine (HOpyMe) in acetone afford the diamagnetic seven-coordinate complexes $[ReH(L)_2(PPh_3)_2]$ (L = Spy-, Opy-, OpyMe-) which can be oxidized by $[(\eta^5\text{-}C_5H_5)_2Fe][PF_6]$ to give paramagnetic products of the composition $[ReH(L)_2(PPh_3)_3][PF_6]$. Protonation of $[ReH(L)_2(PPh_3)_2]$ complexes by treatment with HPF_6 gives the dihydrido species $[ReH_2(L)_2(PPh_3)_2][PF_6]$, which are stable for the hydroxypyridine species whereas $[ReH_2(Spy)_2(PPh_3)_2]^+$ readily converts to $[ReH(Spy)_2(PPh_3)_2]^+$ with loss of H_2. Two similar geometric isomers have been isolated and structurally characterized for $[ReH_2(OpyMe)_2(PPh_3)_2][PF_6]$.[1139,1140] This isomerism has been found in the solid state and in solution, where the *trans* isomer converts slowly to *cis*. In contrast to the situation with hydroxy- and

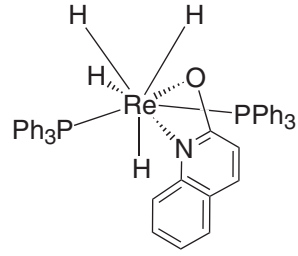
mercaptopyridines, thermal reactions of $[ReH_7(PPh_3)_2]$ with hydroxyquinoline (Hoxine) or mercaptoquinoline (HSqu) only introduce one chelating ligand and the products $[ReH_4(oxine)(PPh_3)_2]$ and $[ReH_4(Squ)(PPh_3)_2]$ are formed in good yields. They possess fluxional structures in solution at room temperature. The crystal structure of $[ReH_4(oxine)(PPh_3)_2]$ confirms a dodecahedral geometry in the solid state (**335**).[863] The mercaptoquinoline derivative exhibits remarkable reactivity. Reactions with terminal alkynes in the presence of electrophiles provide a facile approach to alkylidene complexes and a series of subsequent organometallic reactions.[1141] When $[ReH_4(Squ)(PPh_3)_2]$ is treated with an electrophile such as H^+ or Ph_3C^+ in the absence of alkyne, the dirhenium(V) complex $[Re_2H_6(\mu\text{-S-Squ})_2(PPh_3)_4][PF_6]_2$ is formed. The dirhenium cation contains two eight coordinate metal centers linked through a almost symmetrical $\{Re_2(\mu\text{-S})_2\}$ unit.[1141] Deprotonation of the compound can be carried out in two steps to give the diamagnetic compounds $[Re_2H_5(\mu\text{S-Spy})_2(PPh_3)_4]^+$ and $[Re_2H_4(\mu\text{S-Spy})_2(PPh_3)_4]$.[1142]

The hydride complex $[ReH_5(PMe_2Ph)_3]$ reacts with HSpy in the presence of HBF_4 to give the cationic complexes $[ReH(Spy)(PMe_2Ph)_4][BF_4]$ and $[ReHF(Spy)_2(PMe_2Ph)_2][BF_4]$.[1143] Treatment of $[ReOCl_3(dppe)]$ with $NaBH_4$ in the presence of HSpy results in the formation of the tetrahydrido mixed-ligand complex $[ReH_4(Spy)(dppe)]$,[1143] whereas reactions of $[ReH_7(dppe)]$ with HSqu and related ligands afford monohydrido species of the composition $[ReH(Squ)_2(dppe)]$.[1144]

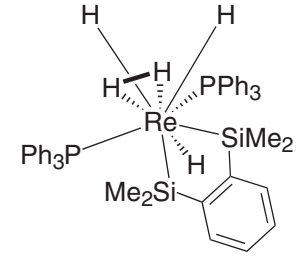
Rhenium hydrido complexes with silyl ligands have been isolated from reactions of various hydrido starting materials with silanes as has been demonstrated for reactions of $[ReH_3(CO)(PMe_2Ph)_3]$ with $HSiPh_3$. The resulting seven-coordinate complex $[ReH_2(CO)(SiPh_3)(PMe_2Ph)_3]$ contain only one triphenylsilyl ligand.[1145] The product has been the subject of *ab initio* MO calculations to understand the bonding mode of the hydride and these suggest weak Si···H interactions.[1146] An isostructural complex has also been reported containing $\{Ph_3Sn\}$ instead of $\{Ph_3Si\}$.[1145] More examples of rhenium hydrides with silyl ligands have been reported: these include $[ReH_6(SiPh_3)(P^{\cap}P)]$,[1099] and penta- and hexahydrides of the compositions $[ReH_5(PR_3)(SiR_3)_2]$ or $[ReH_6(PR_3)_2(SiPh_3)]$.[1147–1149] The chelating disilyl ligands 1,2-bis(dimethylsilyl)benzene (H_2dmsb) and 1,2-bis(dimethylsilyl)ethane (H_2dmse) react with $[ReH_7(PPh_3)_2]$ to give the chelating bis(silyl) polyhydride complexes $[ReH_5(dmsb)(PPh_3)_2]$ and $[ReH_5(dmse)(PPh_3)_2]$.[1150] The X-ray structure of $[ReH_5(dmsb)(PPh_3)_2]$ (**336**) suggests a dodecahedral ligand arrangement typical for eight-coordinate compounds and the presence of a "stretched" η^2-H_2 ligand has been proposed.



(**334**)



(**335**)



(**336**)

The reaction of $[ReH_5(PMe_2Ph)_3]$ with $B_{20}H_{16}$ yields a 21-vertex metallaborane of the composition $[H(PMe_2Ph)_3ReB_{20}H_{15}Ph(PMe_2Ph)]$ which consists of a *closo* 12-vertex unit and a *nido* 11-vertex unit fused with a common triangular face, with the $\{(PMe_2Ph)_3HRe\}$ unit capping exo to the *nido* unit with three Re—H—B bonds.[1151]

5.3.2.11.4 Bi- and multinuclear hydrides

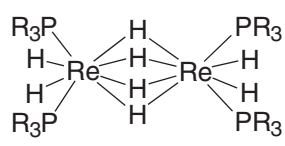
The dimeric octahydrido complexes $[Re_2(\mu\text{-H})_4H_4(PR_3)_4]$ ($PR_3 = PPh_3$, $PEtPh_2$, PEt_2Ph, and others) (**337**) are key compounds in the chemistry of hydrido bridged complexes.[1152,1153] The triphenylphosphine complex is readily prepared by the reaction of $[Re_2Cl_6(PPh_3)_2]$ with $Na[BPh_4]$ in the presence of PPh_3 or alternatively by the heating of $[ReH_7(PPh_3)_2]$.[1093] Treatment of $[Re_2Cl_4(PEt_3)_4]$ with H_2 under a pressure of 120 atm and at a temperature of 60 °C gives a mixture of dimeric compounds which contains the monohydrido bridged complex $[Re_2HCl_6(PEt_3)_2]$ as the main product.[1154] $[Re_2(\mu\text{-H})_4H_4(PR_3)_4]$ complexes are electrochemically oxidized at potentials between −0.15 V and −0.40 V to produce the corresponding paramagnetic ESR-active monocations.

The oxidation has been accomplished chemically in the case of the PPh_3 complex using $[Ph_3C][PF_6]$ or $[C_7H_7][PF_6]$ as oxidants. When the reaction is performed in nitriles, hydride abstraction occurs in preference to oxidation and diamagnetic compounds of the composition $[Re_2(\mu\text{-}H)_4H_3(PPh_3)_4(NCR)]^+$ are formed. Both products are useful precursors for the synthesis of other polyhydride complexes of rhenium.[1155] $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4][PF_6]$ reacts rapidly with *t*-butylisocyanide with formation of the dirhenium pentahydride $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CNBu^t)_2][PF_6]$ having a $\{\mu\text{-}uH\}_3$ bridge.[1156] Another route to triply hydrogen-bridged compounds starts from the $[ReH_9]^{2-}$ anion. $[NEt_4]_2[ReH_9]$ reacts with $CH_3C(CH_2PPh_2)_3$ to produce $[NEt_4][Re_2(\mu\text{-}uH)_3H_6\{CH_3C(CH_2PPh_2)_3\}]$ (**338**) containing 10-coordinate rhenium including an Re—Re bond.[1157] A previous report, which assigned the product to have the structure of $[Re_2(\mu\text{-}H)_3H_4\{CH_3C(CH_2PPh_2)_3\}]$,[1158] has been corrected by the authors.

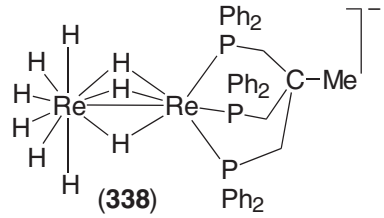
For the synthesis of mixed phosphine/phosphine or phosphine/arsine complexes of the types $[Re_2H_8(PR_2Ph)_2(EPh_3)_2]$ and $[Re_2H_8(PRPh_2)(EPh_3)]$ (R = Me, Et; E = P, As, Sb), a number of routes have been established which all involve the treatment of dimeric rhenium precursors such as $[Re_2Cl_8]^{2-}$, $[Re_2Cl_6(PR_2Ph)_2]$ or $[Re_2Cl_5(PRPh_2)_3]$ with $Na[BH_4]$ in the presence of EPh_3 in ethanol.[1159] Most of the procedures give mixtures and the reaction conditions and the basicity of the ligands must be controlled carefully to get pure products.

Unsymmetrical polyhydrides of the composition $[(L)_3HRe(\mu\text{-}H)_3ReH_2(L)_2]$ (L = PMe_3) have been isolated from reaction mixtures of $[Re_2H_8(PMe_3)_4]$ and PMe_3 in methanol, but the final product is $[Re_2H_5(PMe_3)_6]^+$.[1160] A similar type of structure has been found in the solid state for $[Re_2H_6(SbPh_3)_5]$ which is formed from $[NBu_4][Re_2Cl_8]$, excess of $SbPh_3$ and $Na[BH_4]$ in ethanol,[1160] or the PMe_2Ph derivative $[Re_2H_6(PMe_2Ph)_5]$.[1161] Anionic polyhydride dimers of the composition $[(PMe_2Ph)_2H_2Re(\mu\text{-}H)_3ReH_2(PMe_2Ph)_2]^-$ have been isolated from the reaction of $[(PMe_2Ph)_2H_2Re(\mu\text{-}H)_4ReH_2(PMe_2Ph)_2]$ with KH in the presence of a crown ether which coordinates the potassium ion to form the counterion for the hydrido anion. The reaction proceeds with release of H_2.[1162]

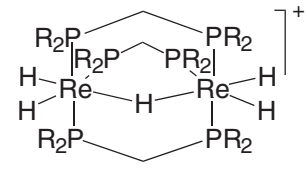
Dimeric rhenium hydrides which contain additional chelating phosphines such as bis(dimethylphosphino)methane (DMPM), dppm, or dppe in their bridging units have been prepared from reactions of multiply bonded starting materials such as $[Re_2Cl_4(\mu\text{-dppm})_2]$, $[Re_2Cl_4(\mu\text{-DMPM})_3]$ or related complexes under various conditions and products of the compositions $[Re_2H_6(\mu\text{-}H)_2(\mu\text{-dppm})_2]$,[1163] $[Re_2H_4(\mu\text{-}H)(\mu\text{-DMPM})_3]$ (**339**),[1164] or $[Re_2H_2(\mu\text{-}H)_3(\mu\text{-dppe})(dppe)_2]^+$ have been isolated and structurally characterized.[1165] The degree of rhenium–rhenium bonding is dependent on the number of the bridging hydrogen atoms and short Re—Re contacts in the range of 2.5–2.6 Å have been observed for compounds with three or four bridging hydrogen atoms, whereas a long bond of about 2.93 Å has been observed for the $\{(\mu\text{-}H)_2\}$ bridge and no direct Re—Re bonding has been derived for $[Re_2H_4(\mu\text{-}H)(\mu\text{-DMPM})_3]$ (Re—Re distance of 3.5 Å) containing only one bridging hydride. $[Re_2H_4(\mu\text{-}H)(\mu\text{-DMPM})_3]$ reacts with CO or isocyanides to give $[Re_2H_3(L)_3(\mu\text{-dppm})_3]^+$ and $[Re_2H(L)_4(\mu\text{-DMPM})_3]^+$ cations in which the electronic unsaturation of the central unit is eliminated in two two-electron reduction steps.[1166]



(**337**)



(**338**)



(**339**)

Many compounds with related structures have been reported containing additional carbonyl ligands. Here a few examples with low (less than three CO ligands per rhenium atom) numbers of CO ligands are listed: $[Re_3(CO)_6(\mu_2\text{-}PPh_2)_3(\mu_3\text{-}H)_2]$,[1167] $[Re_4(CO)_8(\mu_2\text{-}PPh_2)_4(\mu_4\text{-}PPh)(\mu_2\text{-}H)_2]$,[1168] $[Re_3(CO)_6(\mu_3\text{-}I)(\mu_2\text{-}I)_2(\mu_3\text{-}H)(\mu_2\text{-}PPh_2)_2]$,[1169] $[Re_2(CO)_2(\mu_2\text{-}H)(\mu_2\text{-}Cl)Cl_2(\mu_2\text{-dppm})_2]$,[1170] $[Re_3(CO)_6(\mu_3\text{-}Cl)(\mu_3\text{-}H)(\mu_2\text{-}PPh_2)_3]$,[1171] $[Re_3(CO)_6(\mu_2\text{-}PPh_2)_4(\mu_4\text{-}PPh)(\mu_2\text{-}H)(\mu_2\text{-}Br)]$,[1171] $[Re_3(CO)_6(\mu_3\text{-}H)_2\{\mu_2\text{-}P(C_6H_4\text{-}F\text{-}4)_2\}_3]$,[1172] $[Re_3(CO)_5(PPh_3)(\mu_2\text{-}PPh_2)_3(\mu_3\text{-}H)(\mu_3\text{-}I)]$,[1173] $[Re_4(CO)_8(\mu_2\text{-}H)(\mu_2\text{-}PPh_2)_3(\mu_4\text{-}PPh)_2]$,[117] $[Re_4(CO)_8(\mu_2\text{-}H)(\mu_2\text{-}I)(\mu_2\text{-}O)(\mu_2\text{-}PPh_2)_3(\mu_4\text{-}PPh)]$,[1175] $[Re_3(CO)_6(\mu_3\text{-}H)(\mu_3\text{-}I)(\mu_2\text{-}PPh_2)_3]$ (X = I, Br),[1176,1177] $[Re_4(CO)_8(\mu_2\text{-}H)(\mu_2\text{-}I)(\mu_2\text{-}PPh_2)(\mu_4\text{-}PPh)]$,[1178] $[Re_2(CO)_6(\mu_3\text{-}H)_2\{\mu_2\text{-}P(cyclohexyl)_2\}_3]$,[1179] $[Re_2(CO)_6(\mu_3\text{-}H)\{\mu_2\text{-}P(cyclohexyl)_2\}_3]$,[1179] and $[Re_3(CO)_6(\mu_3\text{-}H)(\mu_3\text{-}P)(\mu_2\text{-}PMePh)_3]$.[1179] A mixed hydrido/hydrogensulfido bridge between two rheniums is known $[Re_2Br_4(\mu\text{-}H)(\mu\text{-}SH)(\mu\text{-dppm})_2]$,[1180] and a rare η^4-coordination of a fullerene has been found in the hydrido-bridged dirhenium complex $[Re_2H_8(PMe_3)_4(\eta^2,\eta^{2'}\text{-}C_{60})]$.[1181]

There are also numerous examples of hydrogens bridging between rhenium and other metals such as aluminum,[1182] tin,[1183] gold,[1184–1186] silver,[1187] zirconium,[1188] rhodium,[1189–1191] ruthenium,[1192–1196] iridium,[1197–1199] osmium,[1199] platinum,[1200] chromium,[1201] molybdenum,[1201] tungsten,[1201] lanthanides,[1202,1203] and actinides.[1204]

5.3.3 RHENIUM COMPOUNDS AND NUCLEAR MEDICINE

The "nuclear medicinal chemistry" of technetium, the lighter homologue of rhenium, has been studied for some decades, and the metastable nuclear isomer, γ-emitting ^{99m}Tc, has been established as the "work horse" of diagnostic nuclear medicine. Thus, a considerable knowledge about the formation of technetium complexes in aqueous solutions has been accumulated. A comprehensive summary of the present status and perspectives of technetium radiopharmaceuticals is given in the preceding Chapter of this Volume. Most of the Tc complexes described there are also available with rhenium and, therefore, will not be treated separately here. The successful and widespread application of ^{99m}Tc (more than 80% of the diagnostic studies in routine nuclear medicine are done with this nuclide) and the chemical similarities between the two elements focused attention to the radioactive rhenium isotopes, ^{186}Re and ^{188}Re, which possess physical properties that make them attractive candidates for therapeutic applications. Both isotopes are β^--emitters (^{186}Re: $\beta^-_{max} = 2.1$ MeV, $t_{1/2} = 17$ h, $E_\gamma = 155$ keV; ^{188}Re: $\beta^-_{max} = 1.07$ MeV, $t_{1/2} = 3.8$ d, $E_\gamma = 137$ keV). The accompanying emission of γ-radiation can be used for scintigraphic imaging but also makes patient isolation necessary. The different half-lifes and β^--energies allow individual therapeutic demands such as the pharmacokinetics of the tracer molecule, the linear energy transfer of the nuclides or the biodistribution and clearance of the radiolabeled drug to be met. The principles of the application of radioactive materials for therapy are summarized in an excellent review.[19]

Special attention has been paid to ^{188}Re, since this isotope can readily be obtained from isotope generators which are based on the decay of ^{188}W (physical $t_{1/2} = 69.4$ d) in a matrix from which the daughter nuclide ^{188}Re can readily be separated. This permits continuous availability of the radioisotope at the clinic and allows the preparation of Re-radiopharmaceuticals in a "kit procedure" as has been established for technetium radiopharmaceuticals. ^{188}W/^{188}Re generators commonly contain $^{188}WO_4^{2-}$ on a stationary phase such as alumina, zirconium oxide, gels, or ion exchange resins, where it disintegrates and forms perrhenate or perrhenic acid which can be eluted with saline. This requires, that all radiopharmaceutical preparations start from perrhenate and reduction/complexation procedures should proceed in one-pot reactions giving the complex of the radioisotope in almost quantitative yields.

The general pathways for the preparation of rhenium radiopharmaceuticals follow those of the preparations of ^{99m}Tc diagnostic radiopharmaceuticals and can broadly be classified as follows: (i) The synthesis of complexes with the desired biological properties which are mainly controlled by charge, size and lipophilicity of the molecule, (ii) The development of rhenium complexes which resemble the shape and polarity of receptor-binding organic molecules, (iii) the direct labeling of peptides or proteins using their intrinsic donor functions, or (iv) the labeling of bioactive molecules by conjugation with an appropriate highly stable rhenium complex. All these routes require detailed knowledge about the coordination chemistry of rhenium and many of the chemical studies described in the previous Sections have been done primarily to obtain rhenium complexes with optimal molecular properties for medical applications.

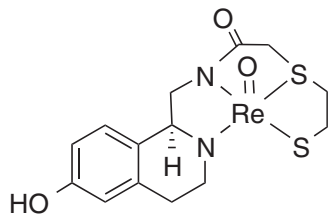
A different route of radiolabeling with rhenium compounds has been suggested by the use of liposomes which contain radioactive rhenium compounds in the bilayer.[20]

5.3.3.1 Small Molecules

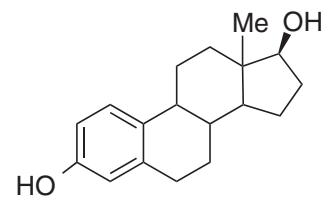
A huge number of rhenium complexes, mainly structural analogues of ^{99m}Tc radiopharmaceuticals have been studied for their potential as therapeutic agents. These include *inter alia* complexes with phosphines,[1206] DMSA,[1207,1208] dithiocarbamates,[662] aminothiolates, and amidothiolates.[1209] But most of these complexes did not satisfy the stronger requirements for a therapeutic radiopharmaceutical to discriminate strongly between target and nontarget tissues. A successful example is ^{186}Re-HEDP (HEDP = hydroxyethylidenediphosphonate) which has been developed in parallel to the ^{99m}Tc-HEDP diagnostic agent and can be used to palliate pain due to

bone metastases.[1210,1211] It is prepared by reduction of perrhenate with $SnCl_2$ in the presence of excess of the ligand. The oxidation state of the metal is assumed to be "+4", although HPLC studies show the presence of an equilibrium between several rhenium-containing species.[1212,1213] This mixture is believed on the basis of EXAFS studies to contain oligomeric and polymeric species in which phosphonato oxygens are coordinated to rhenium.[746] The high affinity of the uncomplexed oxygens of diphosphonate for Ca^{2+} binds the radioactive metal complex to exposed Ca^{2+} ions in hydroxyapatite on bone surfaces. The use of tin compounds as reducing agent is essential since Sn^{IV} is believed to be involved in the coordination of the complexes. Similar results have been obtained for analogous species with methylendiphosphonates.[1214]

A challenging approach to new radiopharmaceuticals is to mimic receptor binding organic molecules with rhenium complexes. To achieve this, the coordination sphere of the metal must match not only the general shape of the receptor ligands but also their size, polarity and lipophilicity. Finally the resulting complexes must also possess a reasonable stability *in vivo* which has been achieved by the use of tetradentate chelating ligands with sulfur and nitrogen donor atoms.[588,1215] Thus, the rhenium(V) oxo complex (**340**) mimics a large number of the molecular parameters of estradiol (**341**) and is more stable than similar complexes using a bis(bidentate) ligand approach exemplified by the progesterone-mimicking complex (**159a**).[563,564,1216,1217]



(**340**)



(**341**)

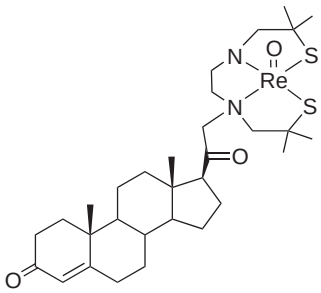
5.3.3.2 Direct Peptide and Protein Labeling and Bioconjugates

There are only a few reports of well-characterized rhenium complexes of amino acids. Oxo complexes with histidine and methionine have been prepared by ligand exchange reactions starting from $[ReOCl_3(PPh_3)_2]$ and the X-ray crystal structures of $[ReO(His\text{-}N,N,O)(His\text{-}N,N)]^+$ and other derivatives have been determined.[1218] The formation of stable complexes of rhenium and technetium with a peptide has been demonstrated by the synthesis and application of the technetium(V) oxo complex $[TcO(MAG_3)]^{2-}$ containing the anion of mercaptoacetyltriglycine (H_5MAG_3) (**165**) as renal imaging agent. The related rhenium complex as well as sulfonate and phosphonate derivatives have been prepared and their biological behavior has been studied.[590,591] Rhenium complexes with peptides which possess a high affinity for the somatostatin receptor have been prepared showing binding affinities which are in some cases higher than those of the free peptides.[1219,1220] Similar results have been obtained for α-melanotropin analogs.[1221]

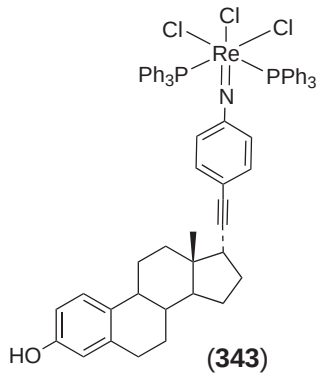
To obtain the high target/nontarget ratio for the biodistribution of a potential radiotherapeutic agent which is required for clinical applications, coupling of the metal to a targeting biomolecule such as a monoclonal antibody, a peptide, or another biologically active molecule is an appropriate strategy. The chelating site of the molecule must not influence the receptor binding site of the molecule and an exactly balanced lipophilicity and polarity is required. A huge number of chelators has been discussed in this context and attention has focused on the relatively inert rhenium(V) oxo and imido cores and rhenium(I) tricarbonyl compounds.

Rhenium(V) oxo bioconjugates have been prepared with chelating *N*/*S* donor ligands such as MAG_3^{5-},[1222] amino/amido/thiolates,[1223] mixed-ligand complexes of tridentate ligands with monodentate thiolates,[376,377,476,558,1224–1228] and dithiabis(phosphines).[1229] Functionalized organoimides, which can be prepared by the reaction of oxorhenium complexes with amines or hydrazines, represent another approach to bioconjugated rhenium compounds.[709–711] Typical examples of rhenium conjugated steroids comprising different coupling modes are shown in structures (**342**)–(**344**).

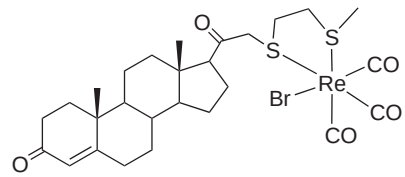
A particularly promising approach is provided by rhenium(I) tricarbonyl compounds, which can readily be prepared from perrhenate and potassium boranocarbonate, $K_2[H_3BCO_2]$ in



(342)



(343)



(344)

aqueous solutions. *In situ* ligand exchange reactions give access to a wide range of coordination environments including bioconjugating ligands of various donor atom combinations,[1230–1232] or direct binding to peptides.[965] More examples of this chemistry can be found in the previous sections which describe the systematic chemistry of rhenium.

Compared to technetium radiopharmaceuticals the development on therapeutic agents based on rhenium is at an early stage. Simple extrapolation of the chemistry of Tc to Re is not always possible due to the differences in redox chemistry and new synthetic approaches are required. Also the high potential radiotoxicity of β^--emitting nuclides such as ^{188}Re requires higher complex stabilities and more specific targeting than is the case for imaging agents. However, the rapid developments made in rhenium chemistry outlined in the above review suggest that these problems will be successfully addressed in the near future.

5.3.4 REFERENCES

1. Noddack, W.; Tacke, I. *Sitzber. Preuss. Akad. Wiss.* **1925**, *19*, 400–405.
2. Wedepohl, K. H. *Met. Their Compd. Environ.* **1991**, 3–17.
3. Coplen, T. B. *Pure Appl. Chem.* **1996**, *68*, 2339–2359.
4. Pfennig, G.; Klewe-Nebenius, H.; Seelmann-Eggebert, W. *Chart of the Nuclides*, 6th ed. 1995, revised reprint 1998, Research Centre Karlsruhe, Germany.
5. Johnson, C. L.; Shirey, S. B.; Barovich, K. M. *Trans. R. Soc. Edinburgh: Earth Sci.* **1996**, *87*, 339–352.
6. Zhi, X *Chin. Sci. Bull.* **2000**, *45*, 193–200.
7. Yang, G.; Xie, Z.; Chen, J.-F. *Dixue Qianyun* **2001**, *8*, 339–344.
8. Fritzberg, A. R. In *Rhenium, Rhenium Alloys*; Proceedings of the International Symposium 1997; Bryskin, B. D., Ed.; Minerals, Metals & Materials Society, Warrendale, U.S.A., 1998.
9. Deutsch, E.; Libson, K.; Vanderheyden, J. L.; Ketring, A. R.; Maxon, H. R. *Nucl. Med. Biol.* **1986**, *13*, 465–477.
10. Knapp, F. F., Jr.; Lisic, E. C.; Mirzadeh, S.; Callahan, A. P. Tungsten-188/carrier-free rhenium-188 perrhenic acid generator system. World Pat. Appl. 219541, 1992.
11. Hsieh, B. T.; Liu, C. J.; Hsieh, H. S.; Tsai, Z. T.; Ting, G.; Knapp, F. F., Jr. *Nucl. Sci. J.* **1996**, *33*, 26–38.
12. Knapp, F. F., Jr.; Beets, A. L.; Guhlke, S.; Zamora, P. O.; Bender, H.; Palmedo, H.; Biersack, H.-J. *Anticancer Res.* **1997**, *17*, 1783–1795.
13. Bläuenstein, P. *New. J. Chem.* **1990**, *14*, 405–407.
14. Hashimoto, K.; Yoshihara, K. *Top. Curr. Chem.* **1996**, *176*, 275–291.
15. Dilworth, J. R.; Parrot, S. J. *Chem. Soc. Rev.* **1998**, *27*, 43–55.
16. Alberto, R.; Schubiger, P. A. *Recent Res. Dev. Inorg. Chem.* **1998**, *1*, 73–89.
17. Blower, P. J.; Prakash, S. *Persp. Bioinorg. Chem.* **1999**, *4*, 91–143.
18. Kohlickova, M.; Jedinakova-Krizova, V.; Melichar, F. *Chemicke Listy* **2000**, *94*, 151–158.
19. Volkert, W. A.; Hoffman, T. J. *Chem. Rev.* **1999**, *99*, 2269–2292.
20. Heeg, M. J.; Jurisson, S. S. *Acc. Chem. Res.* **1999**, *32*, 1053–1060.
21. Connor, K. A.; Walton, R. A. Rhenium. In *Comprehensive Coordination Chemistry*, Wilkinson, G., Gillard, R. D., McCleverty, J.A. Eds.; Elsevier: Oxford, 1985.
22. Abel, E.W., Stone, F.G.A., Wilkinson, G. Eds. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K, 1995.
23. Crane, J. D. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **1993**, *88*, 147–152.
24. Crane, J. D. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **1995**, *91*, 205–218.
25. Crane, J. D. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **1996**, *92*, 195–205.
26. Thompson, A. M. W. Cargill *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **1997**, *93*, 189–198.
27. Thompson, A. M. W. Cargill *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **1998**, *94*, 201–210.
28. Thompson, A. M. W. Cargill *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **1999**, *95*, 153–164.
29. Thornton, P. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2000**, *96*, 215–228.
30. Thornton, P. *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **2001**, *97*, 183–192.
31. Vites, J. C.; Lynam, M. M. *Coord. Chem. Rev.* **1994**, *131*, 127–152.

32. Vites, J. C.; Lynam, M. M. *Coord. Chem. Rev.* **1995**, *142*, 1–20.
33. Vites, J. C.; Lynam, M. M. *Coord. Chem. Rev.* **1995**, *146*, 207–224.
34. Lynam, M. M.; Vites, J. C. *Coord. Chem. Rev.* **1997**, *162*, 319–344.
35. Vites, J. C.; Lynam, M. M. *Coord. Chem. Rev.* **1998**, *169*, 201–235.
36. Vites, J. C.; Lynam, M. M. *Coord. Chem. Rev.* **1998**, *172*, 357–388.
37. Romao, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197–3246.
38. Kühn, F. E.; Herrmann, W. A. *Struct. Bond.* **2000**, *97*, 213–236.
39. Owens, G. S.; Arias, J.; Abu-Omar, M. M. *Catal. Today* **2000**, *55*, 317–363.
40. Mol, J. C. *Catal. Today* **1999**, *51*, 289–299.
41. Fischer, R. W.; Herrmann, W. A. *Transition Met. Organ. Synth.* **1998**, *2*, 341–349.
42. Herrmann, W. A. *J. Organomet. Chem.* **1990**, *382*, 1–18.
43. Bandoli, G.; Tisato, F.; Refosco, F.; Gerber, T. I. A. *Rev. Inorg. Chem.* **1999**, *19*, 187–210.
44. Holloway, C. E.; Melnik, M. *Rev. Inorg. Chem.* **1989**, *10*, 235.
45. Che, C.-M.; Yam, V. W. W. *Adv. Transition Met. Coord. Chem.* **1996**, *1*, 209–237.
46. Gabriel, J.-C. P.; Boubekeur, K.; Uriel, S.; Batail, P. *Chem. Rev.* **2001**, *101*, 2037–2066.
47. Naumov, N. G.; Virovets, A. V.; Fedorov, V. E. *J. Struct. Chem.* **2000**, *41*, 499–520.
48. Bronger, W. *Met. Clusters Chem.* **1999**, *3*, 1591–1611.
49. Saito, T. *J. Chem. Soc., Dalton Trans.* **1999**, 97–106.
50. Perrin, A.; Sergent, M. *New J. Chem.* **1988**, *12*, 337–356.
51. Perrin, A.; Perrin, C.; Sergent, M. *Less-Common Met.* **1988**, *137*, 241–265.
52. Xiao, J.; Puddephatt, R. J. *Coord. Chem. Rev.* **1995**, *143*, 457–500.
53. Stiefel, E. I.; Halbert, T. R.; Coyle, C. L.; Wei, L.; Pan, W. H.; Ho, T. C.; Chianelli, R. R.; Daage, M. *Polyhedron* **1989**, *8*, 1625–1629.
54. Henly, T. J. *Coord. Chem. Rev.* **1989**, *93*, 269–295.
55. Paulo, A.; Correia, J. D. G.; Santos, I. *Trends Inorg. Chem.* **1998**, *5*, 57–87.
56. Roodt, A.; Abou-Hamdan, A.; Engelbrecht, H. P.; Merbach, A. E. *Adv. Inorg. Chem.* **2000**, *49*, 59–126.
57. Walton, R. A. *J. Cluster Sci.* **1994**, *5*, 173–184.
58. Walton, R. A. *Polyhedron* **1989**, *8*, 1689–1693.
59. Chakravorti, M. C. *Coord. Chem. Rev.* **1990**, *106*, 205–225.
60. Jurisson, S. S; Murmann, R. K. *Inorg. Chem.* **1999**, *38*, 3919–3921.
61. Ohlhausen, L.; Cockrum, D.; Register, J.; Roberts, K.; Long, G. J.; Powell, G. L.; Hutchinson, B. B. *Inorg. Chem.* **1990**, *29*, 4886–4891.
62. Bryan, J. C.; Sachleben, R. A. *J. Chem. Cryst.* **1999**, *29*, 1255–1259.
63. Steed, J. W.; Junk, P. C. *J. Chem. Soc., Dalton Trans.* **1999**, 2141–2146.
64. Bryan, J. C.; Sachleben, R. A.; Lavis, J. M.; Davis, M. C.; Burns, J. H.; Hay, B. P. *Inorg. Chem.* **1998**, *37*, 2749–2755.
65. Bryan, J. C. *Acta Crystallogr.* **1998**, *54C*, 1569–1571.
66. Weller, F.; Borgholte, H.; Vogler, S.; Dehnicke, K. *Z. Naturforsch.* **1989**, *44B*, 1524–1530.
67. Thuery, P.; Nierlich, M.; Asfari, Z.; Vicens, J.; Dozol, J.-F. *Polyhedron* **2000**, *19*, 1749–1756.
68. Petrova, R.; Todorov, T.; Bakardjieva, S.; Mihailova, B.; Angelova, O. *Z. Kristallogr.* **2000**, *215*, 309–316.
69. Petrova, R.; Angelova, O.; Maciček, J. *Acta Crystallogr.* **1996**, *52C*, 1935–1939.
70. Petrova, R.; Angelova, O.; Bakardjieva, S.; Maciček, J. *Acta Crystallogr.* **1996**, *52C*, 2432–2434.
71. Maciček, J.; Angelova, O.; Petrova, R. *Z. Kristallogr.* **1995**, *210*, 24–30.
72. Maciček, J.; Angelova, O.; Petrova, R. *Z. Kristallogr.* **1995**, *210*, 319–322.
73. Maciček, J.; Angelova, O. *Acta Crystallogr.* **1995**, *51C*, 2539–2542.
74. Angelova, O.; Maciček, J.; Petrova, R.; Todorov, T.; Mihailova, B. *Z. Kristallogr.* **1996**, *211*, 163–169.
75. Grigoriev, M. S.; Kryuchkov, S. V.; Lapitskaya, T. S.; Makarenkov, V. I.; Maksimov, V. G.; Stuchkov, Yu. T.; Yanovsky, A. I. *Koord. Khim.* **1998**, *24*, 750–755.
76. Mujica, C.; Peters, K.; Peters, E.-M.; Carrillo, W.; von Schnering, H. G. *Bol. Soc. Chil. Quim.* **1999**, *44*, 161–166.
77. Gardberg, A. S.; Doan, P. E.; Hoffman, B. M.; Ibers, J. A. *Angew. Chem.* **2001**, *113*, 250–252.
78. Gardberg, A. S.; Doan, P. E.; Hoffman, B. M.; Ibers, J. A. *Angew. Chem. Int. Ed. Engl.* **2001**, *40*, 244–246.
79. Zhang, Q.-F.; Lau, K.-K.; Chim, J. L.; Wong, T. K. T.; Wong, W.-T.; Williams, I. D.; Leung, W.-H. *J. Chem. Soc., Dalton Trans.* **2000**, 3027–3033.
80. Seisenbaeva, G. A.; Kessler, V. G. *Inorg. Chem. Commun.* **2001**, *4*, 534–536.
81. Herrmann, W. A.; Marz, D.; Herdtweck, E.; Schäfer, A.; Wagner, W.; Kneuper, H.-J. *Angew. Chem.* **1987**, *99*, 462–464.
82. Manojlovic-Muir, L.; Muir, K. W.; Rennie, M.-A.; Xiao, J.; Puddephatt, R. J. *J. Organometallic Chem.* **1993**, *462*, 235–241.
83. D'Alfonso, G.; Roberto, D.; Ugo, R.; Bianchi, C. L.; Sironi, A. *Organometallics* **2000**, *19*, 2564–2572.
84. Ardizzoia, G. A.; Cenini, S.; D'Alfonso, G.; La Monica, G.; Masciocchi, N.; Moret, M. *Gazz. Chim. Ital.* **1992**, *122*, 515–520.
85. Abram, U.; Voigt, A.; Kirmse, R.; Ortner, K.; Hübener, R.; Carballo, R.; Vazquez-Lopez, E. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1662–1668.
86. Abram, U.; Voigt, A.; Kirmse, R. *Polyhedron* **2000**, *19*, 1741–1748.
87. Göldner, M.; Galich, L.; Cornelissen, U.; Homborg, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 985–995.
88. Perez-Lourido, P.; Romero, J.; Garcia-Vazquez, J.; Sousa, A.; Maresca, K. P.; Rose, D. J.; Zubieta, J. *Inorg. Chem.* **1998**, *37*, 3331–3336.
89. Herrmann, W. A.; Roesky, P. W.; Kühn, F. E.; Elison, M.; Artus, G.; Scherer, W.; Ramão, C. C.; Lopes, A.; Basset, J.-M. *Inorg. Chem.* **1995**, *34*, 4701–4707.
90. Schmid, S.; Strähle, J. *Z. Naturforsch.* **1991**, *46B*, 235–244.
91. Krebs, B.; Müller, A.; Beyer, H. H. *Inorg. Chem.* **1969**, *8*, 436–443.
92. Beyer, H.; Glemser, O.; Krebs, B. *Angew. Chem.* **1968**, *80*, 286–287.
93. Beyer, H.; Glemser, O.; Krebs, B. *Angew. Chem. Intern. Ed. Engl.* **1968**, *7*, 295–296.
94. Krebs, B.; Fischer, D.; Paul, G. *Z. Anorg. Allg. Chem.* **1996**, *622*, 448–454.

95. Herrmann, W. A.; Correia, J. D. G.; Kühn, F. E.; Artus, G. R. J.; Romao, C. C. *Chem. Eur. J.* **1996**, *2*, 168–173.
96. Roesky, H. W.; Hesse, D.; Noltemeyer, M. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 809–814.
97. Herrmann, W. A.; Thiel, W. R.; Kühn, F. E.; Fischer, R. W.; Kleine, M.; Herdtweck, E.; Scherer, W.; Mink, J. *Inorg. Chem.* **1993**, *32*, 5188–5194.
98. Kiprof, P.; Herrmann, W. A.; Kühn, F. E.; Scherer, W.; Kleine, M.; Elison, M.; Rypdal, K.; Volden, H. V.; Gundersen, S.; Haaland, A. *Bull. Soc. Chim. Fr.* **1993**, *129*, 655–662.
99. Johnson, J. W.; Brody, J. F.; Ansell, G. B.; Zentz, S. *Acta Crystallogr.* **1984**, *40C*, 2024–2026.
100. Johnson, J. W.; Brody, J. F.; Ansell, G. B.; Zentz, S. *Inorg. Chem.* **1984**, *23*, 2415–2418.
101. Herrmann, W. A.; Correia, J. D. G.; Kühn, F. E.; Artus, G. R. J.; Romao, C. C. *Chem. Eur. J.* **1996**, *2*, 168–173.
102. Bellemin-Laponnaz, S.; Gisie, H.; Le Ny, J. P.; Osborn, J. A. *Angew. Chem.* **1997**, *109*, 1011–1013.
103. Bellemin-Laponnaz, S.; Gisie, H.; Le Ny, J. P.; Osborn, J. A. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 976–978.
104. Schoop, T.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Organometallics* **1993**, *12*, 571–574.
105. Roesky, H. W.; Mazzah, A.; Hesse, D.; Noltemeyer, M. *Chem. Ber.* **1991**, *124*, 519–521.
106. Gosink, H.-J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Irmer, E.; Herbst-Irmer, R. *Organometallics* **1994**, *13*, 3420–3426.
107. Wirringa, U.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Chem. Ber.* **1992**, *125*, 2359–2361.
108. Winkhofer, N.; Roesky, H. W.; Robinson, W. T. *Angew. Chem.* **1992**, *104*, 670–671.
109. Winkhofer, N.; Roesky, H. W.; Robinson, W. T. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 599–601.
110. Herrmann, W. A.; Kuchler, J. G.; Weichselbaumer, G.; Herdtweck, E.; Kiprof, P. *J. Organomet. Chem.* **1989**, *372*, 351–370.
111. Herdtweck, E.; Kiprof, P.; Herrmann, W. A.; Kuchler, J. G.; Degnan, I. *Z. Naturforsch.* **1990**, *45B*, 937–942.
112. Herrmann, W. A.; Roesky, P. W.; Kühn, F. E.; Scherer, W.; Kleine, M. *Angew. Chem.* **1993**, *105*, 1768–1770.
113. Herrmann, W. A.; Roesky, P. W.; Kühn, F. E.; Scherer, W.; Kleine, M. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1714–1716.
114. Küppers, H.-J.; Nuber, B.; Weiss, J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1990**, 979–980.
115. Wieghardt, K.; Pomp, C.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1986**, *25*, 1659–1661.
116. Pomp, C.; Wieghardt, K. *Polyhedron* **1988**, *7*, 2537–2542.
117. Böhm, G.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem.* **1990**, *102*, 832–834.
118. Böhm, G.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 787–790.
119. Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862–4867.
120. Sugimoto, H.; Sasaki, Y. *Chem. Lett.* **1997**, 541–542.
121. Mosny, K. K.; Crabtree, R. H. *Inorg. Chim. Acta* **1996**, *247*, 93–98.
122. Degnan, I. A.; Herrmann, W. A.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1347–1349.
123. Coe, B. J. *Polyhedron* **1992**, *11*, 1085–1091.
124. Thomas, J. A.; Davison, A. *Inorg. Chim. Acta* **1991**, *190*, 231–235.
125. Pearlstein, R. M.; Davison, A. *Polyhedron* **1988**, *7*, 1981–1989.
126. Domingos, A.; Marcalo, J.; Paulo, A.; Pires de Matos, A.; Santos, I. *Inorg. Chem.* **1993**, *32*, 5114–5118.
127. Paulo, A.; Domingos, A.; Marcalo, J.; Pires de Matos, A.; Santos, I. *Inorg. Chem.* **1995**, *34*, 2113–2120.
128. Dyckhoff, B.; Schulte, H.-J.; Englert, U.; Spaniol, T. P.; Kläui, W.; Schubiger, P. A. *Z. Anorg. Allg. Chem.* **1992**, *614*, 131–141.
129. Banbery, H. J.; Hussain, W.; Evans, I. G.; Hamor, T. A.; Jones, C. J.; Mc Cleverty, J. A.; Schulte, H.-J.; Engels, B.; Kläui, W. *Polyhedron* **1990**, *9*, 2549–2551.
130. Edwards, P.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1984**, 2695–2702.
131. Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Solouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527–6537.
132. Herrmann, W. A.; Wojtczak, W. A.; Artus, G. R. J.; Kühn, F. E.; Mattner, M. R. *Inorg. Chem.* **1997**, *36*, 465–471.
133. Edwards, P. G.; Jokela, J.; Lehtonen, A.; Sillanpää, R. *J. Chem. Soc., Dalton Trans.* **1998**, 3287–3294.
134. Herrmann, W. A.; Thiel, W. R.; Kühn, F. E.; Fischer, R. W.; Kleine, M.; Herdtweck, E.; Scherer, W.; Mink, J. *Inorg. Chem.* **1993**, *32*, 5188–5194.
135. Weber, R.; Dehnicke, K.; Müller, U. *Z. Anorg. Allg. Chem.* **1984**, *516*, 214–222.
136. Lis, T. *Acta Crystallogr.* **1987**, *43C*, 1710–1711.
137. Kühn, F. E.; Haider, J. J.; Herdtweck, E.; Herrmann, W. A.; Lopes, A. D.; Pillinger, M.; Romao, C. C. *Inorg. Chim. Acta* **1998**, *279*, 44–50.
138. Gowda, N. M. M.; Phyu, H. P.; Ackerson, B. E. *Transition Met. Chem.* **1993**, *18*, 64–68.
139. Kunkely, H.; Vogler, A. *J. Photochem. Photobiol. A: Chem.* **2000**, *136*, 175–177.
140. Kunkely, H.; Vogler, A. *Inorg. Chem. Commun.* **2000**, *3*, 645–647.
141. Walter, D.; Gebhardt, P.; Fischer, R.; Kreher, U.; Görls, H. *Inorg. Chim. Acta* **1998**, *281*, 181–189.
142. McGilligan, B. S.; Arnold, J.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1990**, 2465–2475.
143. LeBlond, N.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2000**, *39*, 2473–2487.
144. Casteel, W. J., Jr.; MacLeod, D. M.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **1996**, *35*, 7279–7288.
145. Turowsky, L.; Seppelt, K. *Z. Anorg. Allg. Chem.* **1990**, *590*, 37–47.
146. Dilworth, J. R.; Ibrahim, S. K.; Khan, S. R.; Hursthouse, M. B.; Karaulov, A. A. *Polyhedron* **1990**, *10*, 1323–1329.
147. Reibenspies, J. H.; Draper, J. D.; Darensbourg, D. J. *Z. Kristallogr.* **1996**, *211*, 501–502.
148. Zaidi, S. A. A.; Lutfullah, Siddiqi, Z. A. *Polyhedron* **1988**, *7*, 705–707.
149. Jostes, R.; Müller, A. *Theochem.* **1988**, *41*, 211–247.
150. Záliš, S.; Stoll, H.; Baerends, E.J., Kaim, W. *Inorg. Chem.* **1999**, *38*, 6101–6105.
151. Müller, A.; Krickemeyer, E.; Bögge, H. *Z. Anorg. Allg. Chem.* **1987**, *554*, 61–78.
152. Müller, A.; Krickemeyer, E.; Wittneben, V.; Bögge, H.; Lemke, M. *Angew. Chem.* **1991**, *103*, 1501–1503.
153. Müller, A.; Jostes, R.; Schmitz, K.; Krickemeyer, E.; Bögge, H.; Bill, E.; Trautwein, A. *Inorg. Chim. Acta* **1988**, *149*, 9–12.
154. Müller, A.; Krickemeyer, E., Baumann, F. W.; Jostes, R.; Bögge, H. *Chimia* **1986**, *40*, 310–311.
155. Do, Y.; Simhon, E. D.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 4635–4642.

156. Ciurli, S.; Carney, M. J.; Holm, R. H.; Papaefthymiou, G. C. *Inorg. Chem.* **1989**, *28*, 2696–2698.
157. Schäfer, R.; Kaim, W.; Fiedler, J. *Inorg. Chem.* **1993**, *32*, 3199–3200.
158. Müller, A.; Krickemeyer, E.; Bögge, H.; Penk, M. *Chimia* **1989**, *43*, 319–320.
159. Clegg, W.; Garner, C. D.; Scattergood, C. D. *Acta Crystallogr.* **1988**, *44C*, 753–755.
160. Müller, A.; Hildebrand, A.; Krickemeyer, E.; Khan, M. I.; Penk, M.; Bögge, H.; Secheresse, F. *Chem. Eur. J.* **1998**, *4*, 1932–1937.
161. Müller, A.; Hildebrand, A.; Krickemeyer, E.; Sölter, D.; Bögge, H.; Armatage, A. *Z. Anorg. Allg. Chem.* **1992**, *614*, 115–120.
162. Wei, L.; Halbert, T. R.; Murray, H. H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 6431–6433.
163. Murray, H. H.; Wei, L.; Sherman, S. E.; Greaney, M. A; Eriksen, K. A.; Carstensen, B.; Halbert, T. R.; Stiefel, E. I. *Inorg. Chem.* **1995**, *34*, 841–853.
164. Schwarz, D. E.; Rauchfuss, T. B. *Chem. Commun.* **2000**, 1123–1124.
165. Dopke, J. A.; Wilson, S. R.; Rauchfuss, T. B. *Inorg. Chem.* **2000**, *39*, 5014–5021.
166. Goodman, J. T.; Rauchfuss, T. B. *Inorg. Chem.* **1998**, *37*, 5040–5041.
167. Goodman, J. T.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 5017–5022.
168. Wang, K.; McConnachie, J. M.; Stiefel, E. I. *Inorg. Chem.* **1999**, *38*, 4334–4341.
169. Goodman, J. T.; Rauchfuss, T. B. *Angew. Chem.* **1997**, *109*, 2173–2175.
170. Goodman, J. T.; Rauchfuss, T. B. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2083–2085.
171. Kafitz, W.; Dehnicke, K.; Schweda, E.; Strähle, J. *Z. Naturf.* **1984**, *39b*, 1114–1117.
172. Fawcett, J.; Peacock, R. D.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1987**, 567–571.
173. Dietrich, A., Neumüller, B., Dehnicke, K. *Z. Anorg. Allg. Chem.* **2000**, *626*, 315–317.
174. Chatt, J.; Falk, C. D.; Leigh, G. J.; Paske, R. J. *J. Chem. Soc. A* **1969**, 2288–2293.
175. Dilworth, J. R.; Jobanputra, P.; Parrott, S. J.; Thompson, R. M.; Povey, D.; Zubieta, J. A. *Polyhedron* **1992**, *11*, 147–155.
176. Dilworth, J. R.; Jobanputra, P.; Miller, J.; Parrott, S. J.; Chen, Q.; Zubieta, J. A. *Polyhedron* **1993**, *12*, 513–522.
177. Danopoulos, A. A.; Longley, C. J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1989**, *8*, 2657–2670.
178. Williams, D. S.; Schrock, R. R. *Organometallics* **1993**, *12*, 1148–1160.
179. Danopoulos, A. A.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1989**, 896–897.
180. Lam, H.-W.; Wilkinson, G.; Williams, D. J. *Polyhedron* **1991**, *10*, 2647–2650.
181. Saboonchian, V.; Danopoulos, A. A.; Guttierez, A.; Wilkinson, G.; Williams, D. J. *Polyhedron* **1991**, *10*, 2241–2253.
182. Saboonchian, V.; Guttierez, A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1991**, *10*, 1423–1425.
183. Burrell, A. K.; Clark, D. L.; Gordon, P. L.; Sattelberger, A. P.; Bryan, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 3813–3821.
184. Bryan, J. C.; Burrell, A. K.; Miller, M. M.; Smith, W. H.; Burns, C. L.; Sattelberger, A. P. *Polyhedron* **1993**, *12*, 1769–1777.
185. Burrell, A. K.; Steedman, A. J. *J. Chem. Soc., Dalton Trans.* **2000**, 2501–2503.
186. Choi, N.-S.; Lee, S. W. *Bull. Korean Chem. Soc.* **2000**, *21*, 638–640.
187. Edwards, D. S.; Biondi, L. V.; Zillen, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505–1513.
188. Horton, A. D.; Schrock, R. R.; Freundenberger, J. H. *Organometallics* **1987**, *6*, 893–894.
189. Sundermeyer, J.; Putterlik, J.; Foth, M.; Field, J. S.; Ramesar, N. *Chem. Ber.* **1994**, *127*, 1201–1212.
190. Cheng, J. Y. K.; Cheung, K.-K.; Chan, M. C. W.; Wong, K.-Y.; Che, C.-M. *Inorg. Chim. Acta* **1998**, *272*, 176–187.
191. Herrmann, W. A.; Ding, H.; Kühn, F. E.; Scherer, W. *Organometallics* **1998**, *17*, 2751–2757.
192. Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965–969.
193. Roesky, H. W.; Hesse, D.; Bohra, R.; Noltemeyer, M. *Chem. Ber.* **1991**, *124*, 1913–1915.
194. Roesky, H. W.; Hesse, D.; Rietzel, M.; Noltemeyer, M. *Z. Naturforsch.* **1990**, *45B*, 72–76.
195. Schlecht, S.; Deubel, D. V.; Frenking, G., Geiseler, G.; Harms, K.; Magull, J.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 887–891.
196. Katti, K. V.; Singh, P. R.; Barnes, C. L.; Katti, K. K.; Kopicka, K.; Ketring, A. R.; Volkert, W. A. *Z. Naturforsch.* **1993**, *48B*, 1381–1385.
197. Diefenbach, A.; Bickelhaupt, F. M. *Z. Anorg. Allg. Chem.* **1999**, *625*, 892–900.
198. Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 3033–3036.
199. Roesky, H. W.; Hesse, D.; Noltemeyer, M.; Sheldrick, G. M. *Chem. Ber.* **1991**, *124*, 757–759.
200. Hasselbring, R.; Roesky, H. W.; Noltemeyer, M. *Angew. Chem.* **1992**, 104, 613–615.
201. Hasselbring, R.; Roesky, H. W.; Noltemeyer, M. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 601–603.
202. Mujica, C.; Llanos, J.; Peters, K.; Peters, E.-M. *Bol. Soc. Chil. Quim.* **2000**, *45*, 329–332.
203. Miranda, J. M.; Oliveira, M. A.; Castellano, E. E.; Scoralick, E.; Zinner, L. B.; Vicentini, G. *Inorg. Chim. Acta* **1987**, *139*, 131–133.
204. Oliveira, M. A.; Miranda, J. M.; Castellano, E. E.; Scoralick, E.; Zinner, L. B.; Vicentini, G. *Lanth. Actin. Res.* **1986**, *1*, 205–215.
205. Sharma, C. V. K.; Griffin, S. T.; Rogers, R. D. *Chem. Commun.* **1998**, 215–216.
206. Shapley, J. R.; Whittlesey, B. R.; Wilson, S. R. *Polyhedron* **1989**, *8*, 375–377.
207. Ortega, F.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 3292–3297.
208. Ortega, F.; Pope, M. T.; Evans, H.T., Jr. *Inorg. Chem.* **1997**, *36*, 2166–2169.
209. Venturelli, A.; Nilges, M. J.; Smirnov, A.; Belford, R. L.; Francesconi, L. C. *J. Chem. Soc., Dalton Trans.* **1999**, 301–310.
210. Gable, K. P.; Zhuravlev, F. A.; Yokochi, A. F. T. *Chem. Commun.* **1998**, 799–800.
211. Xiao, J.; Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Torabi, A. A. *J. Am. Chem. Soc.* **1994**, *116*, 1129–1130.
212. Hao, L.; Vittal, J. J.; Puddephatt, R. J.; Manojlovic-Mur, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1995**, 2381–2182.
213. Hao, L.; Vittal, J. J.; Xiao, J.; Puddephatt, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 8035–8036.
214. Hao, L.; Xiao, L.; Vittal, J. J.; Puddephatt, R. J.; Manojlovic-Muir, L.; Muir, K. W.; Torabi, A. A. *Inorg. Chem.* **1996**, *35*, 658–666.

215. Voigt, A.; Abram, U.; Böttcher, R.; Richter, U.; Reinhold, J.; Kirmse, R. *Chem. Phys.* **2000**, *253*, 171–181.
216. Ermakov, A. N.; Borisova, L. V. *Zh. Neorg. Khim.* **1986**, *31*, 2814–2820.
217. Wilgocki, M.; Rybak, W. K. *Port. Electrochim. Acta* **1995**, *13*, 211–218.
218. Edwards, P. G.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 2467–2475.
219. Jacob, E. *Angew. Chem.* **1982**, 94, 146–147.
220. Jacob, E. *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 141–142.
221. Thorp, H. H.; van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889–892.
222. Brewer, J. C.; Thorp, H. H.; Slagle, K. M.; Brudvig, G. W.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 3171–3173.
223. DuMez, D. D.; Mayer, J. M. *Inorg. Chem.* **1998**, *37*, 445–453.
224. Liese, W.; Dehnicke, K.; Walker, I.; Strähle, J. *Z. Naturforsch.* **1979**, *34B*, 693–696.
225. Abram, U.; Braun, M.; Abram, S.; Kirmse, R.; Voigt, A. *J. Chem. Soc., Dalton Trans.* **1998**, 231–238.
226. Voigt, A.; Abram, U.; Strauch, P.; Kirmse, R. *Inorg. Chim. Acta* **1998**, *271*, 199–202.
227. Voigt, A.; Abram, U.; Kirmse, R. *Inorg. Chem. Commun.* **1998**, *1*, 141–142.
228. Voigt, A.; Abram, U.; Kirmse, R. *Z. Naturforsch.* **1998**, *53B*, 1183–1187.
229. Leung, W.-H.; Chan, E. Y. Y.; Lai, T. C. Y.; Wong, W.-T. *J. Chem. Soc., Dalton Trans.* **2000**, 51–56.
230. Abram, U.; Kohl, F.; Öfele, K.; Herrmann, W. A.; Voigt, A., Kirmse, R. *Z. Anorg. Allg. Chem.* **1998**, *624*, 934–936.
231. Abram, U.; Voigt, A.; Kirmse, A. *Inorg. Chem. Commun.* **1998**, *1*, 213–216.
232. Blower, P. J.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1985**, 2305–2309.
233. Voigt, A., Abram, U., Kirmse, R. *Inorg. Chem. Commun.* **1998**, *1*, 203–205.
234. Abram, U., Kirmse, R.; Voigt, U. *Z. Anorg. Allg. Chem.* in press.
235. Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *Polyhedron* **1988**, *7*, 117–128.
236. Lahiri, G. K.; Goswami, S.; Falvello, L. R.; Chakravorty, A. *Inorg. Chem.* **1987**, *26*, 3365–3370.
237. Banerjee, S.; Dirghangi, B. K.; Menon, M.; Pramanik, A.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1997**, 2149–2153.
238. Dirghangi, B. K.; Menon, M.; Banerjee, S.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 3595–3601.
239. Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 2995–3000.
240. Nuβhär, D.; Weller, F., Dehnicke, K. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1121–1126.
241. DeLearie, L. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1986**, *108*, 6393–6394.
242. DeLearie, L. A.; Haltiwanger, R. C.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 817–821.
243. Möhlenkamp, A.; Mattes, R. *Z. Naturforsch.* **1990**, *45B*, 1167–1176.
244. Bukharizoda, R. A.; Temurova, M. T.; Larin, G. M. *Koord. Khim.* **1991**, *17*, 1372–1374.
245. Matsubayashi, G.; Maikawa, T.; Nakano, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2995–2999.
246. Seisenbaeva, G. A.; Shevelkov, A. V.; Tegenfeld, J.; Kloo, L.; Drobot, D. V.; Kessler, V. G. *J. Chem. Soc., Dalton Trans.* **2001**, 2762–2768.
247. Neuhaus, A.; Veldkamp, A.; Frenking, G. *Inorg. Chem.* **1994**, *33*, 5278–5286.
248. Demachy, I.; Jean, Y. *New J. Chem.* **1996**, *20*, 53–63.
249. Newsham, M. D.; Giannelis, E. P.; Pinnavaia, T. J.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 3885–3891.
250. Böhm, G.; Wieghard, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1991**, *30*, 3464–3476.
251. Doerrer, L. H.; Graham, A. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1998**, 3941–3946.
252. Alberto, R.; Schibli, R.; Egli, A.; Schubiger, P. A.; Herrmann, W. A.; Artus, G.; Abram, U.; Kaden, T. A. *J. Organomet. Chem.* **1995**, *493*, 119–127.
253. Rose, D. J.; Maresca, K. P.; Kettler, P. B.; Chang, Y. D.; Soghomomian, V.; Chen, Q.; Abrams, M. J.; Larsen, S. K.; Zubieta, J. *Inorg. Chem.* **1996**, *35*, 3548–3558.
254. Sergienko, V. S.; Minacheva, L. K.; Ashurova, N. K.; Porai-Koshits, M. A.; Yakubov, K. G.; Sakharova, V. G. *Zh. Neorg. Khim.* **1991**, *36*, 381–92.
255. Fenske, D.; Stahl, K.; Hey, E.; Dehnicke, K. *Z. Naturforsch.* **1984**, *39B*, 850–854.
256. Glowiak, T.; Jezowska-Trzebiatowska, B.; Lis, T. *Acta Crystallogr.* **1991**, *47C*, 177–178.
257. Sergienko, V. S.; Ilyukhin, A. B.; Luzikova, A. V.; Porai-Koshits, M. A. *Koord. Khim.* **1991**, *17*, 1489–1496.
258. Hanuza, J.; Baluka, M.; Machner, W.; Jezowska-Trzebiatowska, B. *Acta Phys. Pol.* **1987**, *71 A*, 91–110.
259. Purcell, W.; Roodt, A.; Basson, S. S.; Leipoldt, J. G. *Transition Met. Chem.* **1989**, *14*, 224–226.
260. Purcell, W.; Roodt, A.; Basson, S. S.; Leipoldt, J. G. *Transition Met. Chem.* **1989**, *14*, 369–370.
261. Abou-Hamdan, A.; Roodt, A.; Merbach, A. E. *Inorg. Chem.* **1998**, *37*, 1278–1288.
262. Roodt, A.; Leipoldt, J. G.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1994**, *33*, 140–147.
263. Roodt, A.; Leipoldt, J. G.; Helm, L.; Abou-Hamdan, A.; Merbach, A. E. *Inorg. Chem.* **1995**, *34*, 560–568.
264. Purcell, W.; Roodt, A.; Basson, S. S.; Leipoldt, J. G. *Transition Met. Chem.* **1989**, *14*, 5–6.
265. Purcell, W.; Roodt, A.; Leipoldt, J. G. *Transition Met. Chem.* **1991**, *16*, 339–343.
266. Basson, S. S.; Leipoldt, J. G.; Roodt, A.; Purcell, W. *Transition Met. Chem.* **1987**, *12*, 82–84.
267. Lumme, P. O.; Turpeinen, U.; Stasicka, Z. *Acta Crystallgr.* **1991**, *C47*, 501–503.
268. Amindzhanov, A. A.; Kotegov, K. R. *Neorg. Khim.* **1992**, *37*, 2229–2233.
269. Chakravorti, M. C.; Gangopadhyay, T. *Inorg. Chim Acta* **1989**, *162*, 127–130.
270. Lebuis, A.-M.; Beauchamp, A. L. *Can. J. Chem.* **1993**, *71*, 441–449.
271. Pearson, C.; Dartiguenave, M.; Beauchamp, A. L. *Inorg. Chem.* **1996**, *35*, 7448–7449.
272. Bryan, J. C.; Perry, M. C.; Arterburn, J. B. *Acta Crystallogr.* **1998**, *54C*, 1607–1608.
273. Graziani, R.; Casellato, U.; Rossi, R.; Marchi, A., *J. Crystallogr. Spectrosc. Res.* **1985**, *15*, 573–579.
274. Galdecki, Z.; Galdecka, E.; Kowalski, A. *Pol. J. Chem.* **1999**, *73*, 1391–1403.
275. Abram, S.; Abram, U.; Schulz-Lang, E.; Strähle, J. *Acta Crystallogr.* **1995**, *51C*, 1078–1080.
276. Lebuis, A.-M.; Roux, C.; Beauchamp, A. L. *Acta Crystallogr.* **1993**, *49C*, 33–36.
277. Battistuzzi, R.; Saladini, M. *Inorg. Chim. Acta* **2000**, *304*, 114–117.
278. Sullivan, B. P.; Brewer, J. C.; Gray, H. B.; Linebarrier, D.; Mayer, J. M. *Inorg. Synth.* **1992**, *29*, 146–150.
279. Rossi, S.; Bélanger, S.; Lebuis, A.-M.; Beauchamp, A. L. *Acta Crystallogr.* **1993**, *49C*, 1498–1500.
280. Schmid, S.; Strähle, J. *Z. Kristallogr.* **1991**, *196*, 243–253.
281. Sergienko, V. S.; Porai-Koshits, M. A. *Dokl. Phys. Chem. (Engl.)* **1989**, *12*, 978–981.

282. Ondracek, A. L.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1998**, *267*, 123–126.
283. Arif, A. M.; Bright, T. A.; Jones, R. A. *J. Coord. Chem.* **1987**, *16*, 45–50.
284. Glowiak, T.; Rybak, W. K.; Skarzynska, A. *Polyhedron* **2000**, *19*, 2667–2672.
285. Skarzynska, A.; Rybak, W. K.; Glowiak, T. *Polyhedron* **2001**, *20*, 2667–2674.
286. Fernanda, M.; Carvalho, N. N.; Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1987**, *335*, C23–C26.
287. Michos, D.; Luo, Xiao-Liang; Howard, J. A. K.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 3914–3916.
288. Fontán, S. G.; Marchi, A.; Marvelli, L.; Rossi, R.; Antoniutti, S.; Albertin, G. *J. Chem. Soc., Dalton Trans.* **1996**, 2779–2785.
289. Bryan, J. C.; Stenkamp, R. E.; Tulip, T. H.; Mayer, J. M. *Inorg. Chem.* **1987**, *26*, 2283–2288.
290. Arterburn, J. B.; Perry, M. C. *Tetrahedron Lett.* **1996**, *37*, 7941–7944.
291. Block, E.; Kang, Hyunkyu; Ofori-Okai, G.; Zubieta, J. *Inorg. Chim. Acta* **1989**, *156*, 27–28.
292. Blower, P. J.; Dilworth, J. R.; Hutchinson, J.; Nicholson, T.; Zubieta, J. *Inorg. Chim. Acta* **1984**, *90*, L27–L30.
293. Dilworth, J. R.; Lu, C.; Zheng, Y.; Zubieta, J. *Polyhedron* **1998**, *18*, 501–509.
294. Dilworth, J. R.; Hu, J.; Liu, S.-X.; Howard, J. A. K.; Povey, D. C. *Inorg. Chim. Acta* **1994**, *223*, 63–69.
295. Ahmet, M. T.; Lu, C.; Dilworth, J. R.; Miller, J. R.; Zheng, Y.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1995**, 3143–3152.
296. Morales-Morales, D.; Zheng, Y.; Dilworth, J. A.; Redon, R.; Torrens, H. *Inorg. Chim. Acta* **2001**, *314*, 37–41.
297. Schmidt-Brücken, B.; Abram, U. *Z. Anorg. Allg. Chem.* **2000**, *626*, 951–958.
298. Battistuzzi, G.; Cannio, M.; Saladini, M.; Battistuzzi, R. *Inorg. Chim. Acta* **2001**, *320*, 178–183.
299. Mashaly, M. M.; El-Behairy, M. *Pol. J. Chem.* **1997**, *71*, 705–711.
300. Bandoli, G.; duPreez, J. G. H.; Gerber, T. I. A.; Kemp, H. J. *Inorg. Chem.* **1993**, *32*, 3964–3965.
301. Borisova, L. V.; Ismagulova, A. B.; Ponomareva, E. I. *Kompleksn. Ispolz. Miner. Syrya* **1984**, *12*, 22–25.
302. Gambino, D.; Otero, L.; Kremer, E.; Piro, O. E.; Castellano, E. E. *Polyhedron* **1997**, *16*, 2263–2270.
303. Gambino, D.; Kremer, E.; Baran, E. J.; Mombrú, A.; Suescun, L.; Mariezcurrena, R.; Kieninger, M.; Ventura, O. N. *Z. Anorg. Allg. Chem.* **1999**, *625*, 813–819.
304. Schmid, S.; Strähle, J. *Z. Kristallogr.* **1992**, *198*, 49–59.
305. Connac, F.; Lucchese, Y.; Dartiguenave, M.; Coulais, Y.; Beauchamp, A. L. *Inorg. Chim. Acta* **1999**, *295*, 209–213.
306. Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054–1066.
307. Beard, J. H.; Casey, J.; Murmann, K. R. *Inorg. Chem.* **1965**, *4*, 797–803.
308. Brewer, J. C.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 3334–336.
309. Ram, M. S.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 130–133.
310. Pipes, D. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 7201–7202.
311. Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 3256–3262.
312. Jones-Skeens, L. M.; Zhang, X. L.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 3879–3881.
313. Kashani, F. F.; Murman, R. K. *Int. J. Chem. Kinet.* **1985**, *17*, 1007–1015.
314. Botha, J. M.; Roodt, A.; Leipoldt, J. G. *S. Afr. J. Chem.* **1995**, *48*, 120–126.
315. Ram, M. S.; Skeens-Jones, L. M.; Johnson, C. S.; Zhang, X. L.; Stern, C.; Yoon, D. I.; Selmarten, D.; Hupp, J. T. *J. Am. Chem. Soc.* **1995**, *117*, 1411–1421.
316. Fortin, S.; Beauchamp, A. L. *Inorg. Chim. Acta* **1998**, *279*, 159–164.
317. Graziani, R.; Casellato, U.; Rossi, R.; Marchi, A. *J. Cryst. Spectr. Res.* **1985**, *15*, 573–579.
318. Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1978**, *56*, 179–188.
319. Wittern, U.; Strähle, J.; Abram, U. *Z. Anorg. Allg. Chem.* **1997**, *623*, 218–223.
320. Holder, G. N.; Bottomley, L. A. *Inorg. Chim. Acta* **1992**, *194*, 133–137.
321. Berning, D. E.; Katti, K. V.; Barbour, L. J.; Volkert, W. A. *Inorg. Chem.* **1998**, *37*, 334–339.
322. Bélanger, S.; Beauchamp, A. L. *Inorg. Chem.* **1996**, *35*, 7836–7844.
323. Alessio, E.; Zangrando, E.; Iengo, E.; Macchi, M.; Marzilli, P. A.; Marzilli, L. G. *Inorg. Chem.* **2000**, *39*, 294–303.
324. Hansen, L.; Alessio, E.; Iwamoto, M.; Marzilli, P. A.; Marzilli, L. G. *Inorg. Chim. Acta* **1995**, *240*, 413–417.
325. Gagieva, S. C. *Zh. Neorg. Khim.* **2000**, *45*, 1156–1159.
326. Iengo, E.; Zangrando, E.; Mestroni, S.; Fronzoni, G.; Stener, M.; Alessio, E. *J. Chem. Soc., Dalton Trans.* **2001**, 1338–1346.
327. Hinton, H. A.; Chen, H.; Hamor, T. A.; McQuillan, F. S; Jones, C. J. *Inorg. Chim. Acta* **1999**, *285*, 55–59.
328. Backes-Dahmann, G.; Enemark, J. H. *Inorg. Chem.* **1987**, *26*, 3960–3962.
329. Maresca, K. P.; Rose, D. J.; Zubieta, J. *Inorg. Chim. Acta* **1997**, *260*, 83–88.
330. Savoie, C.; Reber, C.; Bélanger, S.; Beauchamp, A. L. *Inorg. Chem.* **1995**, *34*, 3851–3852.
331. Lebuis, A. M.; Young, J. M. C.; Beauchamp A. L. *Can. J. Chem.* **1993**, *71*, 2070–2078.
332. Bélanger, S.; Beauchamp, A. L. *Inorg. Chem.* **1997**, *36*, 3640–3647.
333. Abe, M.; Mikami, T.; Sugimoto, H.; Nagasawa, A.; Sasaki, Y. *Chem. Lett.* **1997**, 1073–1074.
334. Pearson, C.; Beauchamp, A. L. *Acta Crystallogr.* **1994**, *50C*, 42–44.
335. Marzilli, L. G.; Iwamoto, M.; Alessio, E.; Hansen, L.; Calligaris, M. *J. Am. Chem. Soc.* **1994**, *116*, 815–816.
336. Alessio, E.; Hansen, L.; Iwamoto, M.; Marzilli, L. G. *J. Am. Chem. Soc.* **1996**, *118*, 7593–7600.
337. Belanger, S.; Fortin, S.; Beauchamp, A. L. *Can. J. Chem.* **1997**, *75*, 37–45.
338. Admindzhanov, A. A.; Gagieva, S. Ch.; Kotegov, K. V. *Khim. Khim. Tekhnol.* **1991**, *34*, 21–25.
339. Amindzhanov, A. A.; Gagieva, S. Ch. *Khim. Khim. Tekhnol.* **1992**, *35*, 13–22.
340. Gagieva, S. Ch. *Zh. Neorg. Khim.* **2000**, *45*, 1156–1159.
341. Lebuis, A. M.; Beauchamp, A. L. *Can. J. Chem.* **1993**, *71*, 2060–2069.
342. Lebuis, A. M.; Beauchamp, A. L. *Acta Crystallogr.* **1994**, *50C*, 882–883.
343. Fontaine, X. L. R.; Fowles, E. H.; Layzell, T. P.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1991**, 1519–1524.
344. Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1993**, *204*, 63–71.
345. Suescun, L.; Mombrú, A. W.; Mariezcurrena, R. A.; Kremer, C.; Rivero, M.; Kremer, E.; Domínguez, S.; Mederos, A. *Acta Crystallogr.* **1999**, *55C*, 1785–1789.

346. Rybak, W. K.; Zagiczek, A. *J. Coord. Chem.* **1992**, *26*, 79–82.
347. Knoesen, O.; Gorls, H.; Lotz, S. *J. Organomet. Chem.* **2000**, *598*, 108–115.
348. Yam, W.-W.; Tam K.-K.; Cheng, M.-C.; Peng, S.-M.; Wang, Yu. *J. Chem. Soc., Dalton Trans.* **1992**, 1717–1723.
349. Chang, L. S.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1994**, *33*, 1614–1621.
350. Suescun, L.; Mombrú, A. W.; Mariezcurrena, R. A.; Pardo, H.; Russi, S.; Kremer, C.; Rivero, M.; Kremer, E. *Acta Crystallogr.* **2000**, *56C*, 930–931.
351. Kremer, C.; Rivero, M.; Kremer, E.; Suescun, L.; Mombrú, A. W.; Mariezcurrena, R.; Domínguez, S.; Mederos, A.; Midollini, S.; Castiñeiras, A. *Inorg. Chim. Acta* **1999**, *294*, 47–55.
352. Reddy, V. S.; Berning, D. E.; Katti, K. V.; Barnes, C. L.; Volkert, W. A.; Ketring, A. R. *Inorg. Chem.* **1996**, *35*, 1753–1757.
353. Yam, W.-W.; Pui, Y.-L.; Wong, M.-C.; Cheung, K.-K. *Inorg. Chim. Acta* **2000**, *300*, 721–732.
354. Bartley, S. L.; Dunbar, K. R.; Shih, K.-Yu; Fanwick, P. E.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1993**, 98–100.
355. Chiozzone, R.; González, R.; Kremer, C.; De Munno, G.; Faus, J. *Inorg. Chim. Acta* **2001**, *325*, 203–207.
356. Rende, D. E.; Kim, Y.; Beck, C. M.; Wojcicki, A. *Inorg. Chim. Acta* **1995**, *240*, 435–439.
357. Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Nicholson, T.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1339–1345.
358. Clegg, W.; Boyde, S.; Garner, C. D. *Acta Crystallogr.* **1988**, *44C*, 172–174.
359. Hübener, R.; Abram, U. *Acta Crystallogr.* **1993**, *49C*, 1068–1070.
360. Singh, J.; Powell, A. K.; Clarke, S. E. M.; Blower, P. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1115–1117.
361. Domercq, B.; Fourmigué, M. *Eur. J. Inorg. Chem.* **2001**, 1625–1629.
362. Pradhan, R.; Bhattacharyya, R. *Transition Met. Chem* **1999**, *24*, 64–66.
363. Dilworth, J. R.; Ibrahim, S. K. *Transition Met. Chem.* **1991**, *16*, 239–240.
364. Müller, U.; Noll, A. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2438–2440.
365. Jacob, J.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 1040–1041.
366. Jacob, J.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 3266–3267.
367. Jacob, J.; Lente, G.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **1999**, *38*, 3762–3763.
368. Lahti, D. W.; Espenson, J. H. *J. Am. Chem. Soc.* **2001**, *123*, 6014–6024.
369. Huang, R.; Espenson, J. H. *Inorg. Chem.* **2001**, *40*, 994–999.
370. Dilworth, J. R.; Griffiths, D. V.; Parrott, S. J.; Zheng, Y. *J. Chem. Soc., Dalton Trans.* **1997**, 2931–2936.
371. Pietzsch, H.-J.; Spies, H.; Leibnitz, P.; Reck, G. *Polyhedron* **1995**, *14*, 1849–1853.
372. Reisgys, M.; Spies, H.; Johannsen, B.; Leibnitz, P.; Pietzsch, H.-J. *Chem. Ber./Receuil* **1997**, *130*, 1343–1347.
373. Spies, H.; Fietz, T.; Pietzsch, H.-J.; Johannsen, B.; Leibnitz, P.; Reck, G.; Scheller, D.; Klostermann, K. *J. Chem. Soc., Dalton Trans.* **1995**, 2277–2280.
374. Spies, H.; Fietz, Th.; Zablotskaya, A.; Belyakov-Lukevics, E. *Chem. Heterocycl. Compd.* **1999**, *35*, 112–120.
375. Fietz, T.; Spies, H.; Pietzsch, H.-J.; Leibnitz, P. *Inorg. Chim. Acta* **1995**, *231*, 233–236.
376. Wüst, F.; Scheller, D.; Spies, H.; Johannsen, B. *Eur. J. Inorg. Chem.* **1998**, 789–793.
377. Spies, H.; Noll, B.; Noll, S.; Findeisen, M.; Leibnitz, P.; Schulze, P. E.; Johannsen, B. *Chem. Ber./Receuil* **1997**, *130*, 839–841.
378. Gupta, A.; Seifert, S.; Syhre, R.; Scheunemann, M.; Brust, P.; Johannsen, B. *Radiochimica Acta* **2001**, *89*, 43–49.
379. Rossi, R.; Marchi, A.; Magon, L.; Casellato, U.; Tamburini, S.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1991**, 263–268.
380. Kettler, P. B.; Chang, Y.-D.; Zubieta, J.; Abrams, M. J. *Inorg. Chim. Acta* **1994**, *218*, 157–165.
381. Edwards, C. F.; Griffith, W. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1992**, 957–962.
382. Bandoli, G.; Dolmella, A.; Gerber, T. I. A.; Perils, J.; du Preez, J. G. H. *Inorg. Chim. Acta* **1999**, *294*, 114–118.
383. Duatti, A.; Rossi, R.; Marchi, A.; Pasquetto, A.; Mazzi, U. *Inorg. Chim. Acta* **1984**, *81*, 21–24.
384. Sawusch, S.; Schilde, U.; Starke, I.; Lehmann, A.; Uhlemann, E. *Inorg. Chim. Acta* **1998**, *268*, 109–115.
385. Luo, H.; Rettig, S. J.; Orvig C. *Inorg. Chem.* **1993**, *32*, 4491–4497.
386. Hegetschweiler, K.; Egli, A.; Alberto, R.; Schmalle, H. W. *Inorg. Chem.* **1992**, *31*, 4027–4028.
387. Kremer, C.; Kremer, E.; Domingues, S.; Chinea, E.; Mederos, A. *Polyhedron* **1996**, *15*, 4341–4347.
388. Engelbrecht, H. P.; Otto, S.; Roodt, A. *Acta Crystallogr.* **1999**, *55C*, 1648–1650.
389. Gancheff, J.; Melian, C.; Kremer, C.; Dominguez, S.; Mederos, A.; Ventura, O. N.; Kremer, E. *J. Coord. Chem.* **2001**, *54*, 285–296.
390. Marzilli, L. G.; Hansen, L.; Taylor, A.; Lachicotte, R. *Met.-Based Drugs* **2000**, *7*, 141–145.
391. Grey, J. K.; Triest, M.; Butler, I. S.; Reber, C. *J. Phys. Chem. A* **2001**, *105*, 6269–6272.
392. Lawrance, G. A.; Sangster, D. F. *Polyhedron* **1986**, *5*, 1553–1558.
393. Kremer, C.; Dominguez, S.; Perez-Sanchez, M.; Mederos, A.; Kremer, E. *J. Radioanal. Nucl. Chem.* **1996**, *213*, 263–274.
394. Gambino, D.; Kremer, C.; Cartesio, S.; Leon, A.; Kremer, E. *J. Radioanal. Nucl. Chem.* **1989**, *136*, 341–351.
395. Kremer, C.; Leon, A.; Kremer, E. *J. Radioanal. Nucl. Chem.* **1993**, *176*, 143–152.
396. Melian, C.; Kremer, C.; Suescun, L.; Mombru, A.; Mariezcurrena, R.; Kremer, E. *Inorg. Chim. Acta,* **2000**, *306*, 70–77.
397. Ram, M. S.; Johnson, C. S.; Blackbourn, R. L.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 238–244.
398. Blackbourn, R. L.; Jones, L. M.; Ram, M. S.; Sabat, M.; Hupp, J. T. *Inorg. Chem.* **1990**, *29*, 1791–1792.
399. Ram, M. S.; Jones, L. M.; Ward, H. J.; Wong, Y. H.; Johnson, C. S.; Subramanian, P.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 2928–2938.
400. Bandoli, G.; Dolmella, A.; Gerber, T. I. A.; Luzipo, D.; du Preez, J. G. H. *Inorg. Chim. Acta* **2001**, *325*, 215–219.
401. Rao Neti, N.; Koelle, U. *Polyhedron* **1992**, *11*, 1615–1622.
402. Fortin, S.; Beauchamp, A. L. *Inorg. Chem.* **2000**, *39*, 4886–4893.
403. Bélanger, S.; Beauchamp, A. L. *Acta Crystallogr.* **1999**, *55C*, 517–521.
404. Chang, L.; Rall, J.; Tisato, F.; Deutsch, E.; Heeg, M. J. *Inorg. Chim. Acta* **1993**, *205*, 35–44.
405. Dirghangi, B. K.; Menon, M.; Pramanik, A.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 1095–1101.
406. Banerjee, S.; Bhattacharyya, S.; Dirghangi, B. K.; Menon, M.; Chakravorty, A. *Inorg. Chem.* **2000**, *39*, 6–13.

407. Chakraborty, I.; Bhattacharyya, S.; Banerjee, S.; Dirghangi, B. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1999**, 3747–3753.
408. Bhattacharyya, S.; Chakraborty, I.; Dirghangi, B. K.; Chakravorty, A. *Chem. Commun.* **2000**, 1813–1814.
409. Bhattacharyya, S.; Chakraborty, I.; Dirghangi, B. M.; Chakravorty, A. *Inorg. Chem.* **2001**, *40*, 286–293.
410. Banerjee, S.; Bhattacharyya, S.; Chakraborty, I.; Dirghangi, B. K.; Chakravorty, A. *Indian J. Chem. Sect. A.* **1999**, *38*, 857–858.
411. Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125–128.
412. Degnan, I. A.; Behm, J.; Cook, M. R.; Herrmann, W. A. *Inorg. Chem.* **1991**, *30*, 2165–2170.
413. Kettler, P. B.; Chang, Y. D.; Chen, Q.; Zubieta, J.; Abrams, M. J.; Larsen, S. K. *Inorg. Chim. Acta* **1995**, *231*, 13–20.
414. Tisato, F.; Bolzati, C.; Duatti, A.; Bandoli, G.; Refosco, F. *Inorg. Chem.* **1993**, *32*, 2042–2048.
415. Herberhold, M.; Jin, Guo-Xin; Milius, W. *J. Organomet. Chem.* **1996**, *512*, 111–116.
416. Gable, K. P.; AbuBaker, A.; Zientara, K.; Wainwright, A. M. *Organometallics* **1999**, *18*, 173–179.
417. DuMez, D. D.; Mayer, J. M. *Inorg. Chem.* **1995**, *34*, 6396–6401.
418. Brown, S. N.; Myers, A. W.; Fulton, J. R.; Mayer, J. M. *Organometallics* **1998**, *17*, 3364–3374.
419. Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119–12133.
420. Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1995**, *34*, 3560–3562.
421. Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091–4100.
422. DuMez, D. D.; Northcutt, T. O.; Matano, Y.; Mayer, J. M. *Inorg. Chem.* **1999**, *38*, 3309–3312.
423. Paulo, A.; Domingos, A.; Pires de Matos, A.; Santos, I.; Fernanda, M.; Carvalho, N. N.; Pombeiro, A. J. L. *Inorg. Chem.* **1994**, *33*, 4729–4737.
424. Nunes, D.; Domingos, A.; Paulo, A.; Patricio, L.; Santos, I.; Carvalho, N. N.; Pombeiro, A. J. L.; Fernanda, M. *Inorg. Chim. Acta* **1998**, *271*, 65–74.
425. Paulo, A.; Domingos, A.; Santos, I. *J. Chem. Soc., Dalton Trans.* **1999**, 3735–3740.
426. Paulo, A.; Domingos, A.; Santos, I. *Inorg. Chem.* **1996**, *35*, 1798–1807.
427. Paulo, A.; Reddy, K. R.; Domingos, A.; Santos, I. *Inorg. Chem.* **1998**, *37*, 6807–6813.
428. Paulo, A.; Domingos, A.; Garcia, R.; Santos, I. *Inorg. Chem.* **2000**, *39*, 5669–5674.
429. Carvalho, N. N.; Fernanda, M.; Nunes, D.; Paulo, A.; Pombeiro, A. J. L.; Santos, I. *Port. Electrochim. Acta* **1995**, *13*, 305–308.
430. Che, C. M.; Cheng, J. Y. K.; Cheung, K. K.; Wong, K. Y. *J. Chem. Soc., Dalton Trans.* **1997**, 2347–2350.
431. Sugimoto, H.; Sasaki, Y. *Chem. Lett.* **1998**, 197–198.
432. Reid, S. M.; Neuner, B.; Schrock, R. R.; Davis, W. M. *Organometallics* **1998**, *17*, 4077–4089.
433. Cochran, F. V.; Bonitatebus, P.J., Jr.; Schrock, R. R. *Organometallics* **2000**, *19*, 2414–2416.
434. Che, C. M.; Wang, Y. P.; Yeung, K. S.; Wong, K. Y.; Peng, S. M. *J. Chem. Soc., Dalton Trans.* **1992**, 2675–2677.
435. Xu, L.; Setyawati, I. A.; Pierreroy, J.; Pink, M.; Young, V. G., Jr.; Patrick, B. O.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **2000**, *39*, 5958–5963.
436. Banbery, H. J.; McQuillan, F. S.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *Polyhedron* **1990**, *9*, 615–618.
437. Parker, D.; Roy, P. S. *Inorg. Chem.* **1988**, *27*, 4127–4130.
438. Hansen, L.; Lampeka, Y. D.; Gavrish, S. P.; Xu, X.; Taylor, A. T.; Marzilli, L. G. *Inorg. Chem.* **2000**, *39*, 5859–5866.
439. Burrel, A. K.; Hall, S. B. *Inorg. Chim. Acta* **2000**, *298*, 112–115.
440. Blake, A. J.; Greig, J. A.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 2645–2647.
441. Luna, S. A.; Bolzati, B.; Duatti, A.; Zucchini, G. L.; Bandoli, G.; Refosco, F. *Inorg. Chem.* **1992**, *31*, 2595–2598.
442. Wang, Y. P.; Che, C. M.; Wong, K. Y.; Peng, S. M. *Inorg. Chem.* **1993**, *32*, 5827–5832.
443. Winckler Tsang, B.; Reibenspies, J.; Martell, A. E. *Inorg. Chem.* **1993**, *32*, 988–994.
444. Göldner, M.; Galich, L.; Cornelissen, U.; Homborg, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 985–995.
445. Ziener, U.; Dürr, K.; Hanack, M. *Synthetic Metals* **1995**, *71*, 2285–2286.
446. Tse, M. K.; Zhang, Z.; Chan, K. S. *Chem. Commun.* **1998**, 1199–1200.
447. Refosco, F.; Tisato, F.; Bandoli, G.; Bolzati, C.; Dolmella, A.; Moresco, A.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1993**, 605–618.
448. Bandoli, F.; Dolmella, A.; Tisato, F.; Refosco, F. *Acta Crystallogr.* **1994**, *50C*, 530–532.
449. Tisato, F.; Refosco, F.; Bolzati, C.; Cagnolini, A.; Gatto, S.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1997**, 1421–1427.
450. Michos, D.; Luo, X. L.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **1992**, 1735–1738.
451. Abram, U.; Alberto, R.; Dilworth, J. R.; Zheng, Y.; Ortner, K. *Polyhedron* **1999**, *18*, 2995–3003.
452. Bolzati, C.; Tisato, F.; Refosco, F.; Bandoli, G. *Inorg. Chim. Acta* **1996**, *247*, 125–127.
453. Bolzati, C.; Tisato, F.; Refosco, F.; Bandoli, G.; Dolmella, A. *Inorg. Chem.* **1996**, *35*, 6221–6229.
454. Loiseau, F.; Lucchese, Y.; Dartiguenave, M.; Belanger-Gariepy, F.; Beauchamp, A. L. *Acta Crystallogr.* **1996**, *52C*, 1968–1971.
455. Connac, F.; Lucchese, Y.; Gressier, M.; Dartiguenave, M.; Beauchamp, A. L. *Inorg. Chim. Acta* **2000**, *304*, 52–59.
456. Loiseau, F.; Lucchese, Y.; Dartiguenave, M.; Coulais, Y. *Polyhedron* **2000**, *19*, 1111–1116.
457. Luo, H.; Setyawati, I.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1995**, *34*, 2287–2299.
458. Kovacs, M. S.; Hein, P.; Sattarzadeh, S.; Patrick, B. O.; Emge, T. J.; Orvig, C. *J. Chem. Soc., Dalton Trans.* **2001**, 3015–3024.
459. Banbery, H. J.; Hussain, W.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 657–661.
460. Correia, J. D. G.; Domingos, A.; Santos, I.; Bolzati, C.; Refosco, F.; Tisato, F. *Inorg. Chim. Acta* **2001**, *315*, 213–219.
461. Katti, K. V.; Barnes, C. L. *Inorg. Chem.* **1992**, *31*, 4231–4235.
462. Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1993**, *212*, 23–29.
463. Rossi, R.; Marvelli, L.; Marchi, A.; Magon, L.; Bertolasi, V.; Ferretti, V. *J. Chem. Soc., Dalton Trans.* **1994**, 339–345.
464. Connac, F.; Lucchese, Y.; Dartiguenave, M.; Beauchamp, A. L. *Inorg. Chem.* **1997**, *36*, 256–259.
465. Oetliker, U.; Savoie, C.; Stanislas, S.; Reber, C.; Connac, F.; Beauchamp, A. L.; Loiseau, F.; Dartiguenave, M. *Chem. Commun.* **1998**, 657–658.
466. Blower, P. J.; Dilworth, J. R.; Leigh, G. J.; Neaves, B. D.; Normanton, F. B. *J. Chem. Soc., Dalton Trans.* **1985**, 2647–2653.

467. Rossi, R.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1992**, 435–437.
468. Luo, H.; Orvig, C. *Can. J. Chem.* **1996**, *74*, 722–729.
469. Smith, C. J.; Katti, K. V.; Volkert, W. A.; Barbour, L. J. *Inorg. Chem.* **1997**, *36*, 3928–3935.
470. Schibli, R.; Karra, S. R.; Gali, H.; Katti, K. V.; Higginbotham, C.; Volkert, W. A. *Radiochim. Acta* **1998**, *83*, 211–215.
471. Tisato, F.; Refosco, F.; Moresco, A.; Bandoli, G.; Dolmella, A.; Bolzati, C. *Inorg. Chem.* **1995**, *34*, 1779–1787.
472. Santimaria, M.; Maina, T.; Mazzi, U.; Nicolini, M. *Inorg. Chim. Acta* **1995**, *240*, 291–297.
473. Santimaria, M.; Mazzi, U.; Gatto, S.; Dolmella, A.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1997**, 1765–1771.
474. Correia, J. D. G.; Domingos, A.; Santos, I. *Eur. J. Inorg. Chem.* **2000**, 15123–1529.
475. Correia, J. D. G.; Domingos, A.; Paulo, A.; Santos, I. *J. Chem. Soc., Dalton Trans.* **2000**, 2477–2482.
476. Correia, J. D. G.; Domingos, A.; Santos, I.; Spies, H. *J. Chem. Soc., Dalton Trans.* **2001**, 2245–2250.
477. Sokolov, M.; Fyodorova, N.; Pervukhina, N.; Fedorov, V. *Inorg. Chem. Commun.* **2001**, *4*, 261–263.
478. Dilworth, J. R.; Lewis, J. S.; Miller, J. R.; Zheng, Y. *Polyhedron* **1993**, *12*, 221–225.
479. Pietzsch, H.-J.; Reisgys, M.; Spies, H.; Leibnitz, P.; Johannsen, B. *Chem. Ber./Recueil* **1997**, *130*, 357–361.
480. Fietz, T.; Spies, H.; Leibnitz, P.; Scheller, D. *J. Coord. Chem.* **1996**, *38*, 227–235.
481. Maresca, K. P.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chem. Commun.* **1998**, *1*, 209–212.
482. Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *300-302*, 462–470.
483. Al-Jeboori, M. J.; Dilworth, J. R.; Hiller, W. *Inorg. Chim. Acta* **1999**, *285*, 76–80.
484. Herrmann, W. A.; Fridgen, J.; Haider, J. J. *Peroxide Chem.* **2000**, 406–432.
485. Marchi, A.; Duatti, A.; Rossi, R.; Magon, L.; Mazzi, U.; Pasquetto, A. *Inorg. Chim. Acta* **1984**, *81*, 15–19.
486. Mazzi, U.; Refosco, F.; Tisato, F.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1623–1628.
487. Kühn, F. E.; Rauch, M. U.; Lobmaier, G. M.; Artus, G. R. J.; Herrmann, W. A. *Chem. Ber./Recueil* **1997**, *130*, 1427–1431.
488. Barz, M.; Rauch, M. U.; Thiel, W. R. *J. Chem. Soc., Dalton Trans.* **1997**, 2155–2161.
489. Sacerdoti, M.; Bertolasi, V.; Gilli, G.; Duatti, A. *Acta Crystallogr.* **1984**, *40C*, 968–970.
490. Shivakumar, M.; Banerjee, S.; Menon, M., Chakravorty, A. *Inorg. Chim. Acta* **1998**, *275-276*, 546–551.
491. Du Preez, J. G. H.; Gerber, T. I. A.; Kemp, H. J. *J. Coord. Chem.* **1992**, *26*, 177–186.
492. Duatti, A.; Marchi, A.; Rossi, R.; Magon, L.; Deutsch, E.; Bertolasi, V.; Bellucci, F. *Inorg. Chem.* **1988**, *27*, 4208–4213.
493. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *307*, 149–153.
494. Femia, F. J.; Chen, X.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *300-302*, 517–524.
495. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2001**, *316*, 33–40.
496. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *308*, 80–90.
497. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *306*, 112–115.
498. Bereau, V. M.; Khan, S. I.; Abu-Omar, M. M. *Inorg. Chem.* **2001**, *40*, 6767–6773.
499. Sawusch, S.; Jäger, N.; Schilde, U.; Uhlemann, E. *Struct. Chem.* **1999**, *10*, 105–119.
500. Tisato, F.; Refosco, F.; Moresco, A.; Bandoli, G.; Mazzi, U.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 2225–2232.
501. Abrahams, A.; Bandoli, G.; Gatto, S.; Gerber, T. I. A.; Du Preez, J. G. H. *J. Coord. Chem.* **1997**, *42*, 303–320.
502. Banbery, H. J.; McQuillan, F. S.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *Inorg. Chim. Acta* **1990**, *170*, 23–26.
503. Herrmann, W. A.; Rauch, M. U.; Artus, G. R. J. *Inorg. Chem.* **1996**, *35*, 1988–1991.
504. Van Bommel, K. J. C.; Verboom, W.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. *Inorg. Chem.* **1998**, *37*, 4197–4203.
505. Kooijman, H.; van Bommel, K. J. C.; Verboom, W.; Reinhoudt, D. N.; Kroon, J.; Spek, A. L. *Acta Crystallogr.* **2000**, *56C*, 749–757.
506. Huang, W.-T.; Lo, J.-M.; Yao, H.-H.; Liao, F.-L. *Acta Crystallogr.* **2000**, *56C*, e172–e173.
507. Seeber, R.; Mazzocchin, G. A.; Mazzi, U.; Refosco, F.; Tisato, F. *Polyhedron* **1986**, *5*, 1975–1982.
508. Seeber, R.; Mazzocchin, G. A.; Refosco, F.; Mazzi, U.; Tisato, F. *Polyhedron* **1987**, *6*, 1647–1652.
509. Bottomley, L. A.; Wojciechowski, P. E.; Holder, G. N. *Inorg. Chim. Acta* **1997**, *255*, 149–155.
510. Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1989**, *164*, 127–135.
511. Banbery, H. J.; McQuillan, F.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1989**, 1405–1407.
512. Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Nicolini, M. *Inorg. Chim. Acta* **1991**, *189*, 97–103.
513. Luo, H.; Liu, S.; Rettig, S. J.; Orvig, C. *Can. J. Chem.* **1995**, *73*, 2272–2281.
514. Lin, C.-H.; Huang, S.-T. *Synth. React. Inorg. Met.-Org. Chem.* **1995**, *25*, 1219–1237.
515. Van Bommel, K. J. C.; Verboom, W.; Hulst, R.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. *Inorg. Chem.* **2000**, *39*, 4099–4106.
516. Pillai, M. R. A.; Barnes, C. L.; Schlemper, E. O. *Polyhedron* **1994**, *13*, 701–708.
517. Abram, U.; Abram, S.; Maecke, H. R.; Koch, P. *Z. Anorg. Allg. Chem.* **1995**, *621*, 854–860.
518. Morgan, G. F.; Deblaton, M.; Hussein, W.; Thornback, J. R.; Evrard, G.; Durant, F.; Stach, J.; Abram, U.; Abram, S. *Inorg. Chim. Acta* **1991**, *190*, 257–264.
519. Abram, U.; Abram, S.; Stach, J.; Wollert, R.; Morgan, G. F.; Thornback, J. R.; Deblaton, M. *Z. Anorg. Allg. Chem.* **1991**, *600*, 15–19.
520. Gerber, T. I. A.; Bruwer, J.; Bandoli, G.; Perils, J.; DuPreez, J. G. H. *J. Chem. Soc., Dalton Trans.* **1995**, 2189–2192.
521. Mazzi, U.; Roncari, E.; Rossi, R.; Bertolasi, V.; Traverso, O.; Magon, L. *Transition Met. Chem.* **1980**, 5, 289–293.
522. Gerber, T. I. A.; Kemp, H. J.; DuPreez, J. G. H.; Bandoli, G. *J. Coord. Chem.* **1993**, *28*, 329–336.
523. Gerber, T. I. A.; Perils, J.; DuPreez, J. G. H.; Bandoli, G. *Acta Crystallogr.* **1997**, *53C*, 217–219.
524. Gatto, S.; Gerber, T. I. A.; Bandoli, G.; Perils, J.; DuPreez, J. G. H. *Inorg. Chim. Acta* **1998**, *269*, 235–240.
525. Quintal, S. M. O.; Nogueira, H. I. S.; Felix, V.; Drew, M. G. B. *New J. Chem.* **2000**, *24*, 511–517.
526. Botha, J. M.; Umakoshi, K.; Sasaki, Y.; Lamprecht, G. J. *Inorg. Chem.* **1998**, *37*, 1609–1615.
527. DuPreez, J. G. H.; Gerber, T. I. A.; Kemp, H. J.; VanBrecht, B. J. A. M. *J. Coord. Chem.* **1991**, *24*, 159–168.

528. DuPreez, J. G. H.; Gerber, T. I. A.; Kemp, H. J. *J. Coord. Chem.* **1992**, *25*, 139–148.
529. Panneerselvam, K.; Lu, T.-H.; Tung, S.-F.; Chattopadhyay, P.; Lo, J.-M.; Chung, C.-S. *Acta Crystallogr.* **1999**, *55C*, 1802–1804.
530. Shuter, E.; Hoveyda, H. R.; Karunaratne, V.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1996**, *35*, 368–372.
531. Arias, J.; Newlands, C. R.; Abu-Omar, M. M. *Inorg. Chem.* **2001**, *40*, 2185–2192.
532. Harben, S. M.; Smith, P. D.; Beddoes, R. L.; Collison, D.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1997**, 2777–2784.
533. Nock, B.; Maina, T.; Tisato, F.; Raptopoulou, C. P.; Terzis, A., Chiotellis, E. *Inorg. Chem.* **2000**, *39*, 5197–5202.
534. Femia, F. J.; Chen, X.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2001**, *316*, 145–148.
535. Bolzati, C.; Porchia, M.; Bandoli, G.; Boschi, A.; Malago, E.; Uccelli, L. *Inorg. Chim. Acta* **2001**, *315*, 205–212.
536. Bryson, N.; Dewan, J. C.; Lister-James, J.; Davison, A. *Inorg. Chem.* **1988**, *27*, 2154–2161.
537. Bryson, N.; Lister-James, J.; Jones, A. G.; Davis, W. M.; Davison, A. *Inorg. Chem.* **1990**, *29*, 2948–2951.
538. Kirsch, S.; Jankowsky, R.; Leibnitz, P.; Spies, H.; Johannsen, B. *J. Biol. Inorg. Chem.* **1999**, *4*, 48–55.
539. Chatterjee, M.; Achari, B.; Das, S.; Banerjee, R.; Chakrabarti, C.; Dattagupta, J. K.; Banerjee, S. *Inorg. Chem.* **1998**, *37*, 5424–5430.
540. Johnson, D. L.; Fritzberg, A. R.; Hawkins, B. L.; Kasina, S.; Eshima, D. *Inorg. Chem.* **1984**, *23*, 4204–4207.
541. Hansen, L.; Xu, X.; Yue, K. T.; Kuklenyik, Z.; Taylor, A., Jr.; Marzilli, L. G. *Inorg. Chem.* **1996**, *35*, 1958–1966.
542. Hansen, L.; Xu, X.; Yue, K. T.; Taylor, A., Jr.; Marzilli, L. G. *Inorg. Chem.* **1996**, *35*, 2785–2791.
543. Kirsch, S.; Noll, B.; Spies, H.; Leibnitz, P.; Scheller, D.; Krueger, T.; Johannsen, B. *J. Chem. Soc., Dalton Trans.* **1998**, 455–460.
544. Bouziotis, P.; Pirmettis, I.; Pelecanou, M.; Raptopoulou, C. P., Terzis, A.; Papadopoulos, M.; Chiotellis, E. *Chem. Eur. J.* **2001**, *7*, 3671–3680.
545. Spyriounis, D. M.; Pelecanou, M.; Stassinopoulou, C. I.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E. *Inorg. Chem.* **1995**, *34*, 1077–1082.
546. Glaser, M.; Spies, H.; Berger, R.; Hahn, F. E.; Lügger, T.; Johannsen, B. *Inorg. Chim. Acta* **1997**, *257*, 143–147.
547. Papadopoulos, M.; Pirmettis, I.; Raptopoulou, C.; Chiotellis, E.; Friebe, M.; Berger, R.; Spies, H.; Johannsen, B. *Appl. Radiat. Isot.* **1998**, *49*, 961–966.
548. Papadopoulos, M.; Pirmettis, I.; Tsoukalas, C.; Nock, B.; Maina, T.; Raptopoulou, C. P.; Pietzsch, H.-J.; Friebe, M.; Spies, H.; Johannsen, B.; Chiotellis, E. *Inorg. Chim. Acta* **1999**, *295*, 1–8.
549. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *307*, 88–96.
550. Femia, F. J.; Chen, X.; Maresca, K. P.; Shoup, T. M.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *306*, 30–37.
551. Rey, A.; Papadopoulos, M.; Mallo, L.; Pirmettis, I.; Leon, E.; Raptopoulou, C.; Manta, E.; Chiotellis, E.; Leon, A. *J. Labelled Compd. Radiopharm.* **2000**, *43*, 347–358.
552. Nock, B.; Pietzsch, H.-J.; Tisato, F.; Maina, T.; Leibnitz, P.; Spies, H.; Chiotellis, E. *Inorg. Chim. Acta* **2000**, *304*, 26–32.
553. Rey, A.; Pirmettis, I.; Pelecanou, M.; Papadopoulos, M.; Raptopoulou, C. P.; Mallo, L.; Stassinopoulou, C. I; Terzis, A.; Chiotellis, E.; León, A. *Inorg. Chem.* **2000**, *39*, 4211–4218.
554. Papadopoulos, M.; Tsoukalas, C.; Pirmettis, I.; Nock, B.; Maina, T.; Abedin, Z.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E. *Inorg. Chim. Acta* **1999**, *285*, 97–106.
555. Maina, T.; Tsoukalas, C.; Patsis, G.; Pirmettis, I.; Nock, B.; Papadopoulos, M.; Raptopoulou, C.; Terzis, A.; Chiotellis, E. *Polyhedron* **1999**, *18*, 3545–3552.
556. Fietz, T.; Leibnitz, P.; Spies, H.; Johannsen, B. *Polyhedron* **1999**, *18*, 1793–1797.
557. Zhang, C.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **2001**, *40*, 2437–2438.
558. Meegalla, S. K.; Plössl, K.; Kung, M.-P.; Stevenson, A.; Liable-Sands, L. M.; Rheingold, A. L.; Kung, H. F. *J. Am. Chem. Soc.* **1995**, *117*, 11037–11038.
559. Friebe, M.; Jankowsky, R.; Spies, H.; Seichter, W.; Papadopoulos, M.; Chiotellis, E.; Johannsen, B. *Polyhedron* **1998**, *17*, 3711–3720.
560. Bouziotis, P.; Papagiannopoulou, D.; Pirmettis, I.; Pelecanou, M.; Raptopoulou, C. P.; Stassinopoulou, C. I.; Terzis, A.; Friebe, M.; Spies, H.; Papadopoulos, M.; Chiotellis, E. *Inorg. Chim. Acta* **2001**, *320*, 174–177.
561. Pelecanou, M.; Pirmettis, I. C.; Nock, B. A.; Papadopoulos, M.; Chiotellis, E.; Stassinopoulou, C. I. *Inorg. Chim. Acta* **1998**, *281*, 148–152.
562. Nock, B.; Maina, T.; Tsortos, A.; Pelecanou, M.; Raptopoulou, P.; Papadopoulos, M.; Pietzsch, H.-J.; Stassinopoulou, C. I.; Terzis, A.; Spies, H.; Nounesis, G.; Chiotellis, E. *Inorg. Chem.* **2000**, *39*, 4433–4441.
563. Chi, D. Y.; Katzenellenbogen, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 7045–7046.
564. Chi, D. Y.; O'Neil, J. P.; Anderson, C. J.; Welch, M. J.; Katzenellenbogen, J. A. *J. Med. Chem.* **1994**, *37*, 928–937.
565. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *307*, 38–41.
566. Walovitch, R. C.; Makuch, J.; Knapik, G.; Watson, A. D.; Williams, S. J. *J. Nucl. Med.* **1988**, *29*, 747.
567. Jackson, T. W.; Kojima, M.; Lambrecht, R. M. *Aust. J. Chem.* **1993**, *46*, 1093–1097.
568. Francesconi, L. C.; Graczyk, G.; Wehrli, S.; Shaikh, S. N.; McClinton, D.; Liu, S.; Zubieta, J.; Kung, H. F. *Inorg. Chem.* **1993**, *32*, 3114–3124.
569. Anderson, J. E.; Murphy, C. M.; Sawtelle, S. M.; Edwards, D. S. *Inorg. Chim. Acta* **1994**, *225*, 323–326.
570. Jackson, T. W.; Kojima, M.; Lambrecht, R. M.; Craig, D. C.; Rae, A. D. *Aust. J. Chem.* **1996**, *49*, 239–242.
571. Chryssou, K.; Pelecanou, M.; Papadopoulos, M. S.; Raptopoulou, C. P.; Pirmettis, I. C.; Chiotellis, E.; Stassinopoulou, C. I. *Inorg. Chim. Acta* **1998**, *268*, 169–175.
572. Hambley, T. W.; Knott, R. K.; Jackson, T. W.; Kojima, M.; Lambrecht, R. M. *Acta Crystallogr.* **1995**, *51C*, 203–205.
573. Chi, D. Y.; Wilson, S. R.; Katzenellenbogen, J. A. *Inorg. Chem.* **1995**, *34*, 1624–1625.
574. Marzilli, L. G.; Banaszczyk, M. G.; Hansen, L.; Kuklenyik, Z.; Cini, R.; Taylor, A., Jr. *Inorg. Chem.* **1994**, *33*, 4850–4860.
575. Hansen, L.; Lipowska, M.; Taylor, A., Jr.; Marzilli, L. G. *Inorg. Chem.* **1995**, *34*, 3579–3580.
576. Rao, T. N.; Adhikesavalu, D.; Camerman, A.; Fritzberg, A. R. *J. Am. Chem. Soc.* **1990**, *112*, 5798–5804.
577. Chen, B.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1992**, *31*, 4683–4690.
578. Lin, C.-H.; Huang, S.-T. *Synth. React. Inorg. Met.-Org. Chem.* **1996**, *26*, 357–383.
579. Liao, F.-L.; Wang, S.-L.; Lin, C.-H.; Huang, S.-T. *J. Chin. Chem. Soc.* **1994**, *41*, 557–564.

580. Archer, C. M.; Dilworth, J. R.; Griffiths, D. V.; Al-Jeboori, M. J.; Kelly, J. D.; Lu, C.; Rosser, M. J.; Zheng, Y. *J. Chem. Soc., Dalton Trans.* **1997**, 1403–1410.
581. Al-Jeboori, M. J.; Dilworth, J. R.; Zheng, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 3215–3218.
582. van Bommel, K. J. C.; de Jong, M. R.; Metselaar, G. A.; Verboom, W.; Huskens, J.; Hulst, R.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. *Chem. Eur. J.* **2001**, *7*, 3603–3615.
583. Lin, C.-H.; Liao, F.-L.; Wang, S.-L. *Synth. React. Inorg. Met.-Org. Chem.* **1997**, *27*, 1167–1182.
584. Alarabi, H.; Bell, R. A.; Howard-Lock, H. E.; Kowanetz, J.; Lock, C. J. L. *Can. J. Chem.* **1996**, *74*, 574–582.
585. O'Neil, J. P.; Wilson, S. R.; Katzenellenbogen, J. A. *Inorg. Chem.* **1994**, *33*, 319–323.
586. Rajagopalan, R.; Grummon, G. D.; Bugaj, J.; Hallemann, L. S.; Webb, E. G.; Marmion, M. E.; Vanderheyden, J.-L.; Srinivasan, A. *Bioconjugate Chem.* **1997**, *8*, 407–415.
587. Sugano, Y.; Katzenellenbogen, J. A. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 361–366.
588. Hom, R. K.; Katzenellenbogen, J. A. *J. Org. Chem.* **1997**, *62*, 6290–6297.
589. Rao, T. N.; Adhikesavalu, D.; Camerman, A.; Fritzberg, A. R. *Inorg. Chim. Acta* **1991**, *180*, 63–67.
590. Hansen, L.; Taylor, A. Jr.; Marzilli, L. G. *Met.-Based Drugs* **1995**, *2*, 105–110.
591. Hansen, L.; Taylor, A., Jr.; Marzilli, L. G. *Met.-Based Drugs* **1994**, *1*, 31–39.
592. Johannsen, B.; Noll, B.; Leibnitz, P.; Reck, G.; Noll, S.; Spies, H. *Inorg. Chim. Acta* **1993**, *210*, 209–214.
593. Johannsen, B.; Noll, B.; Leibnitz, P.; Reck, G.; Noll, S.; Spiess, H. *Radiochim. Acta* **1993**, *63*, 133–137.
594. Hansen, L.; Cini, R.; Taylor, A., Jr.; Marzilli, L. G. *Inorg. Chem.* **1992**, *31*, 2801–2808.
595. Wong, E.; Fauconnier, T.; Bennett, S.; Valliant, J.; Nguyen, T.; Lau, F.; Lu, L. F. L.; Pollak, A.; Bell, R. A.; Thornback, J. R. *Inorg. Chem.* **1997**, *36*, 5799–5808.
596. Bell, R. A.; McCarry, B. E.; Vailliant, J. F. *Inorg. Chem.* **1998**, *37*, 3517–3520.
597. Glaser, M.; Howard, M. J.; Howland, K.; Powell, A. K.; Rae, M. T.; Wocadlo, S.; Williamson, R. A.; Blower, P. J. *J. Chem. Soc., Dalton Trans.* **1998**, 3087–3092.
598. Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Nicolini, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1693–1699.
599. Banbery, H. J.; McQuillan, F.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *Polyhedron* **1989**, *8*, 559–561.
600. Tisato, F.; Mazzi, U.; Bandoli, G.; Cros, G.; Darbieu, M.-H.; Coulais, Y.; Guiraud, R. *J. Chem. Soc., Dalton Trans.* **1991**, 1301–1307.
601. Cros, G.; Belhadj Tahar, H.; de Montauzon, D.; Gleizes, A.; Coulais, Y.; Guiraud, R.; Bellande, E.; Pasqualini, R. *Inorg. Chim. Acta* **1994**, *227*, 25–31.
602. Gerber, T.; Kemp, H.; du Preez, J.; Bandoli, G. *Radiochim. Acta* **1993**, *63*, 129–132.
603. Mévellec, F.; Roucoux, A.; Noiret, N.; Patin, H.; Toupet, L. *Polyhedron* **1999**, *18*, 2537–2541.
604. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *307*, 154–159.
605. Cattabriga, M.; Marchi, A.; Marvelli, L.; Rossi, R.; Vertuani, G.; Pecoraro, R.; Scatturin, A.; Bertolasi, V.; Ferretti, V. *J. Chem. Soc., Dalton Trans.* **1998**, 1453–1460.
606. Mevellec, F.; Roucoux, A.; Noiret, N.; Patin, H. *J. Chem. Soc., Dalton Trans.* **2001**, 3603–3610.
607. Gerber, T. I. A.; DuPreez, J. G. H.; Kemp, H. J. *J. Coord. Chem.* **1994**, *33*, 245–255.
608. DuPreetz, J. G. H.; Gerber, T. I. A.; Kemp, H. J. *J. Coord. Chem.* **1993**, *28*, 121–124.
609. Lipowska, M.; Hayes, B. L.; Hansen, L.; Taylor, A., Jr.; Marzilli, L. G. *Inorg. Chem.* **1996**, *35*, 4227–4231.
610. Lipowska, M.; Hansen, L.; Taylor, A., Jr.; Marzilli, L. G. *Inorg. Chem.* **1996**, *35*, 4484–4489.
611. Abram, U.; Hübener, R. *Inorg. Chim. Acta* **1993**, *206*, 231–235.
612. Battistuzzi, G.; Bonamartini Corradi, A.; Dallari, D.; Saladini, M.; Battistuzzi, R. *Polyhedron* **1999**, *18*, 57–63.
613. Battistuzzi, R.; Manfredini, T.; Battaglia, L. P.; Bonamartini Corradi, A.; Marzotto, A. *J. Crystallogr. Spectrosc. Res.* **1989**, *19*, 513–534.
614. Battistuzzi, G.; Borsari, M.; Battistuzzi, R. *Polyhedron* **1997**, *16*, 2093–2104.
615. Battistuzzi, G.; Cannio, M.; Battistuzzi, R. *Polyhedron* **2000**, *19*, 2163–2170.
616. Mattes, R.; Scholand, H. *Inorg. Chim. Acta* **1986**, *116*, L39.
617. Möhlenkamp, A.; Mattes, R. *Z. Naturforsch.* **1992**, *47B*, 969–977.
618. Marchi, A.; Uccelli, L.; Marvelli, L.; Rossi, R.; Giganti, M.; Bertolasi, V.; Ferretti, V. *J. Chem. Soc., Dalton Trans.* **1996**, 3105–3109.
619. Demaimay, F.; Roucoux, A.; Noiret, N.; Patin, H. *J. Organometallic Chem.* **1999**, *575*, 145–148.
620. Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1988**, 1857–1859.
621. Cotton, F. A.; Kibala, P. A.; Matusz, M. *Polyhedron* **1988**, *7*, 83–86.
622. Müller, A.; Lemke, M.; Krickemeyer, E.; Bögge, H.; Penk, M. *Monatshefte für Chemie* **1993**, *124*, 857–866.
623. Duatti, A.; Tisato, F.; Refosco, F.; Mazzi, U.; Nicolini, M. *Inorg. Chem.* **1989**, *28*, 4564–4565.
624. Goodman, J. T.; Rauchfuss, T. B. *Angew. Chem. Int. Ed.* **1997**, *36*, 2083–2085.
625. Dehnicke, K.; Liese, W.; Köhler, P. *Z. Naturforsch.* **1977**, *32B*, 1487.
626. Dehnicke, K.; Prinz, H.; Kafitz, W.; Kujanek, R. *Liebigs Ann. Chem.* **1981**, 20–27.
627. Pasqualini, R.; Comazzi, V.; Bellande, E. *Fr. Demande* **1992**, 34pp.
628. Duatti, A.; Bolzati, C.; Uccelli, L.; Refosco, F.; Tisato, F. *PCT Int. Appl.* **1998**, 48pp.
629. Abram, U. Personal communication.
630. Abram, U.; Hagenbach, A. *Z. Anorg. Allg. Chem.* **2002**, 628, 1719–1720.
631. Voigt, A. *Thesis*, University of Leipzig, EPR spectroscopy on $[Re^{II}(NY)]$- and $[Re^{VI}(NE)]$ complexes (Y = S,O,E = Lewis acid), 2000.
632. Bonfada, É.; Abram, U.; Strähle, J. *Z. Anorg. Allg. Chem.* **1998**, *624*, 757–762.
633. Purcell, W.; Potgieter, I. M.; Damoense, L. J.; Leipoldt, J. G. *Transition Met. Chem* **1992**, *17*, 387–389.
634. Britten, J. F.; Lock, C. J. L.; Wei, Y. *Acta Crystallogr.* **1993**, *49C*, 1277–1280.
635. Damoense, L. J.; Purcell, W.; Leipoldt, J. G. *Transition Met. Chem* **1994**, *19*, 619–622.
636. Purcell, W.; Damoense, L. J.; Leipoldt, J. G. *Inorg. Chim. Acta* **1992**, *195*, 217–220.
637. Schmidt-Brücken, B.; Abram, U. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1714–1716.
638. Schmidt-Brücken, B.; Abram, U. *Z. Anorg. Allg. Chem.* **2001**, *627*, 7–8.
639. Hübener, R.; Abram, U.; Strähle, J. *Inorg. Chim. Acta* **1994**, *224*, 193–197.
640. Hübener, R.; Abram, U.; Strähle, J. *Inorg. Chim. Acta* **1994**, *216*, 223–228.

641. Chivers, T.; Edelman, F. *Polyhedron* **1986**, *5*, 1661–1699.
642. Abram, U.; Walker, I., *Acta Crystallogr*. **1995**, *51C*, 1250–1251.
643. Bailey, S. E.; Eikey, R. A.; Abu-Omar, M. M.; Zink, J. I. *Inorg. Chem*. **2002**, *41*, 1755–1760.
644. Rossi, R.; Marchi, A.; Marvelli, L.; Magon, L.; Peruzzini, M.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans*. **1993**, 723–729.
645. Neyhart, G. A.; Seward, K. J.; Boaz, J.; Sullivan, B. P. *Inorg. Chem*. **1991**, *30*, 4486–4488.
646. Vining, W. J.; Neyhart, G. A.; Nielsen, S.; Sullivan, B. P. *Inorg. Chem*. **1993**, *32*, 4214–4217.
647. Yam, V. W.-W.; Tam, K.-K. *J. Chem. Soc., Dalton Trans*. **1994**, 391–392.
648. Bertolasi, V.; Marchi, A.; Marvelli, L.; Rossi, R.; Bianchini, C.; de los Rios, I.; Peruzzini, M. *Inorg. Chim. Acta* **2002**, *327*, 140–146.
649. Marchi, A.; Marvelli, L.; Rossi, R.; Magon, L.; Uccelli, L.; Bertolasi, V.; Ferretti, V.; Zanobini, F. *J. Chem. Soc., Dalton Trans*. **1993**, 1281–1286.
650. Marotta, E.; Gioacchini, A. M.; Tisato, F.; Cagnolini, A.; Uccelli, L.; Traldi, P. *Rapid Comm. Mass Spectr*. **2001**, *15*, 2046–2049.
651. Mrwa, A.; Rummel, S.; Starke, M. *Z. Chem*. **1985**, *25*, 186–187.
652. Sievertsen, S.; Homborg, H. *Z. Anorg. Allg. Chem*. **1994**, *620*, 1439–1442.
653. Ziener, U.; Hanack, M. *Chem. Ber*. **1994**, *127*, 1681–1685.
654. Frick, K.; Ziener, U.; Hanack, M. *Eur. J. Inorg. Chem*. **1999**, 1309–1313.
655. Buchler, J. W.; De Cian, A.; Fischer, J.; Kruppa, S. B.; Weiss, R. *Chem. Ber*. **1990**, *123*, 2247–2253.
656. Bernardi, R.; Zanotti, M.; Bernardi, G.; Duatti, A. *J. Chem. Soc., Chem. Commun*. **1992**, 1015–1016.
657. Abram, U.; Ritter, S. *Inorg. Chim. Acta* **1993**, *210*, 99–105.
658. Abram, U.; Ritter, S. *Inorg. Chim. Acta* **1994**, *215*, 159–163.
659. Abram, U.; Ritter, S. *Inorg. Chim. Acta* **1994**, *216*, 31–36.
660. Fletcher, S. R.; Skapski, A. C. *J. Chem. Soc., Dalton Trans*. **1972**, 1079–1082.
661. Rowbottom, J. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans*. **1972**, 826–830.
662. Pasqualini, R.; Bellande, E.; Comazzi, V.; Laine, J. *PCT Int. Appl*. **1993**, 66pp.
663. Uhlemann, E.; Spies, H.; Pietzsch, H.-J.; Herzschuh, R. *Z. Naturforsch*. **1992**, *47B*, 1441–1443.
664. Bolzati, C.; Uccelli, L.; Duatti, A.; Venturini, M.; Morin, C.; Chéradame, S.; Refosco, F.; Ossola, F.; Tisato, F. *Inorg. Chem*. **1997**, *36*, 3582–3585.
665. Ritter, S.; Abram, U. *Z. Anorg. Allg. Chem*. **1994**, *620*, 1443–1448.
666. Abram, U.; Schulz Lang, E.; Abram, S.; Wegmann, J.; Dilworth, J. R.; Kirmse, R.; Woollins, J. D. *J. Chem. Soc., Dalton Trans*. **1997**, 623–630.
667. Abram, U.; Schulz Lang, E.; Dilworth, J. R. *Acta Crystallogr*. **1997**, *53C*, 289–292.
668. Leung, W.-H.; Chim, J. L. C.; Williams, I. D., Wog, W.-T. *Inorg. Chem*. **1999**, *38*, 3000–3005.
669. Chatt, J.; Heaton, B. T. *Chem. Commun*. **1968**, 274.
670. Chatt, J.; Heaton, B. T. *J. Chem. Soc. A* **1971**, 705–707.
671. Kafitz, W.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem*. **1982**, *490*, 175–181.
672. Dantona, R.; Schweda, E.; Strähle, J. *Z. Naturforsch*. **1984**, *39B*, 733–735.
673. Ritter, S.; Hübener, R.; Abram, U. *J. Chem. Soc., Chem. Commun*. **1995**, 2047–2048.
674. Ritter, S.; Abram, U. *Z. Anorg. Allg. Chem*. **1996**, *622*, 965–973.
675. Ritter, S.; Abram, U. *Inorg. Chim. Acta* **1995**, *231*, 245–248.
676. Abram, U.; Schmidt-Brücken, B.; Ritter, S. *Polyhedron* **1999**, *18*, 831–838.
677. Abram, U.; Hagenbach, A.; Voigt, A.; Kirmse, R. *Z. Anorg. Allg. Chem*. **2001**, *627*, 955–964.
678. Ritter, S. *Thesis*, Synthesis, Characterisation, Structures and Reactivity of Complexes with Rhenium-Nitrogen Multiple Bonds. University of Tübingen, 1995.
679. Abram, U.; Schmidt-Brücken, B.; Hagenbach, A.; Hecht, M.; Kirmse, R.; Voigt, A. *Z. Anorg. Allg. Chem*. **2003**, *629*, 838.
680. Lyne, P. D.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans*. **1995**, 1635–1643.
681. Vyboishchikov, S. F.; Frenking, G. *Theor. Chem. Acc* **1999**, *102*, 300–308.
682. Abram, U. *Z. Anorg. Allg. Chem*. **1999**, *625*, 839–841.
683. Abram, U. *Inorg. Chem. Commun*. **1999**, *2*, 227–229.
684. Gauch, E.; Strähle, J. *Z. Anorg. Allg. Chem*. **2000**, *626*, 1153–1158.
685. Hagenbach, A.; Strähle, J. *Z. Anorg. Allg. Chem*. **2001**, *627*, 726–730.
686. Griffith, D. V.; Parrott, S. J.; Togrou, M.; Dilworth, J. R.; Zheng, Y.; Ritter, S.; Abram, U. *Z. Anorg. Allg. Chem*. **1998**, *624*, 1409–1414.
687. Abram, U. *Z. Anorg. Allg. Chem*. **2000**, *626*, 318–320.
688. Stelzer, J. B.; Hagenbach, A.; Abram, U. *Z. Anorg. Allg. Chem*. **2002**, *628*, 703–706.
689. Haug, A.; Strähle, J. *Z. Anorg. Allg. Chem*. **1998**, *624*, 931–933.
690. Hagenbach, A.; Strähle, J. *Z. Anorg. Allg. Chem*. **2000**, *626*, 1613–1619.
691. Dietrich, A.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem*. **2000**, *626*, 1268–1270.
692. Beuter, G.; Englert, U.; Strähle, J. *Z. Naturforsch*. **1988**, *43B*, 145–148.
693. Hagenbach, A.; Strähle, J. *Z. Anorg. Allg. Chem*. **1999**, *625*, 1181–1186.
694. Gauch, E.; Hoppe, H.; Strähle, J. *J. Organomet. Chem*. **2000**, 593–594175-179.
695. Gauch, E.; Strähle, J. *Z. Anorg. Allg. Chem*. **2000**, *626*, 1313–1316.
696. Schmid, B.; Schweda, E.; Strähle, J. *Z. Anorg. Allg. Chem*. **1998**, *624*, 1111–1115.
697. Leung, W.-H.; Chim, J. L. C.; Lai, W.; Lam, L.; Wong, W.-T.; Chan, W. H.; Yeung, C.-H. *Inorg. Chim. Acta* **1999**, *290*, 28–35.
698. Zheng, H.; Leung, W.-H.; Chim, J. L. C.; Lai, W.; Lam, C.-H.; Williams, I. D.; Wong, W.-T. *Inorg. Chim. Acta* **2000**, *306*, 184–192.
699. Haug, A.; Strähle, J. *Z. Anorg. Allg. Chem*. **1998**, *624*, 1746–1750.
700. Schmid, B.; Strähle, J. *Z. Anorg. Allg. Chem*. **1998**, *624*, 1429–1433.
701. Schwarz, S.; Strähle, J. *Z. Anorg. Allg. Chem*. **2002**, *628*, 1556–1560.
702. Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev*. **1980**, *31*, 123–175.

703. Forsellini, E.; Casellato, U.; Graziani, R.; Carletti, M. C.; Magon, L. *Acta Crystallogr.* **1984**, *40C*, 1795–1797.
704. Wittern, U.; Strähle, J.; Abram, U. *Z. Naturforsch.* **1995**, *50B*, 997–1003.
705. Wittern, U.; Strähle, J.; Abram, U. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1338–1343.
706. Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Di Bernardo, P. *Transition Met. Chem.* **1985**, *10*, 151–153.
707. Bandoli, G.; Gerber, T. I. A.; Perils, J.; DuPreez, J. G. H. *Inorg. Chim. Acta* **1998**, *278*, 96–100.
708. Imrie, C.; Dilworth, J. R.; Zheng, Y.; Abrahams, A.; Gerber, T. I. A.; Nyamori, V. O. *J. Chem. Soc., Dalton Trans.* **2001**, 2624–2633.
709. Arterburn, J. B.; Fogarty, I. M.; Hall, K. A.; Ott, K. C.; Bryan, J. C. *Angew. Chem.* **1996**, *108*, 3039–3040.
710. Arterburn, J. B.; Rao, K. V.; Perry, M. C. *Angew. Chem.* **2000**, *112*, 787–788.
711. Arterburn, J. B.; Rao, K. V.; Goreham, D. M.; Valenzuela, M. V.; Holguin, M. S.; Hall, K. A.; Ott, K. C.; Bryan, J. C. *Organometallics* **2000**, *19*, 1789–1795.
712. Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1988**, *142*, 23–25.
713. Maatta, E. A.; Kim, C. *Inorg. Chem.* **1989**, *28*, 623–624.
714. Kim, Y. W.; Jung, J. H.; Park, H. S.; Lee, S. W. *Bull. Korean Chem. Soc.* **1994**, *15*, 891–896.
715. Kim, Y. W.; Jung, J. H.; Lee, S. W. *Bull. Korean Chem. Soc.* **1994**, *15*, 150–153.
716. Yam, V. W. W.; Tam, K. K.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1995**, 2779–2783.
717. Ritter, S.; Abram, U. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1786–1792.
718. Weinstock, I. A.; Schrock, R. R.; Williams, D. S.; Crowe, W. E. *Organometallics* **1991**, *10*, 1–2.
719. Williams, D. S.; Schofield, M. H.; Schrock, R. R. *Organometallics* **1993**, *12*, 4560–4571.
720. Williams, D. S.; Anhaus, J. T.; Schofield, M. H.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1991**, *113*, 5480–5481.
721. Bakir, M.; Paulson, S.; Goodson, P.; Sullivan, B. P. *Inorg. Chem.* **1992**, *31*, 1127–1129.
722. Suing, A. L.; Dewan, C. R.; White, P. S.; Thorp, H. H. *Inorg. Chem.* **2000**, *39*, 6080–6085.
723. Lee, S. W.; Choi, N. S. *Acta Crystallogr.* **1999**, *55C*, 2018–2020.
724. Ahmet, M. T.; Coutinho, B.; Dilworth, J. R.; Miller, J. R.; Parrott, S. J.; Zheng, Y.; Harman, M.; Hursthouse, M. B.; Malik, A. *J. Chem. Soc., Dalton Trans.* **1995**, 3041–3048.
725. Refosco, F.; Tisato, F.; Moresco, A.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1995**, 3475–3482.
726. Myashita, Y.; Mahboob, N.; Tsuboi, S.; Yamada, Y.; Fujisawa, K.; Okamoto, K. I. *Acta Crystallogr.* **2001**, *57C*, 558–559.
727. Sloan, O. D.; Thornton, P. *Polyhedron* **1988**, *7*, 329–330.
728. Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *Inorg. Chem. Commun.* **2001**, *4*, 95–99.
729. Refosco, F.; Bolzati, C.; Tisato, F.; Bandoli, G. *J. Chem. Soc., Dalton Trans.* **1998**, 923–930.
730. Bakir, M.; Sullivan, B. P. *J. Chem. Soc., Dalton Trans.* **1995**, 1733–1738.
731. Masood, M. A.; Sullivan, B. P.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 5360–5362.
732. Masood, M. A.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 2488–2490.
733. Fung, W. H.; Cheng, W. C.; Peng, S. M.; Che, C. M. *Polyhedron* **1995**, *14*, 1791–1794.
734. Masui, C. S.; Mayer, J. M. *Inorg. Chim. Acta* **1996**, *251*, 325–333.
735. Banerjee, S.; Bhattacharyya, S.; Chakraborty, I.; Dirghangi, B. K. *Acta Crystallogr.* **1999**, *55C*, 2000–2002.
736. Marchi, A.; Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R. *Transition Met. Chem.* **1984**, *9*, 299–302.
737. Archer, C. M.; Dilworth, J. R.; Jobanputra, P.; Harman, M. E.; Hursthouse, M. B.; Karaulov, A. *Polyhedron* **1991**, *10*, 1539–1543.
738. Soe, K. N.; Ichimura, A.; Kitagawa, T. *Inorg. Chim. Acta* **1993**, *207*, 21–25.
739. Dilworth, J. R.; Neaves, B. D.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L223–L224.
740. Seifert, S.; Leibnitz, P.; Spies, H.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L223–L224.
741. Seifert, S.; Leibnitz, P.; Spies, H. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1037–1040.
742. Bishop, M. W.; Chatt, J.; Dilworth, J. R.; Neaves, B. D.; Dahlstrom, P.; Hyde, J.; Zubieta, *J. Organomet. Chem.* **1981**, *213*, 109–124.
743. Kennedy, B. J.; Heath, G. A. *Inorg. Chim. Acta* **1991**, *187*, 149–153.
744. Yeh, S. M.; Bartlett, N. *Rev. Chim. Miner.* **1986**, *23*, 676–689.
745. Dilworth, J. R.; Hutson, A. J.; Morton, S.; Harman, M.; Hursthouse, M.; Zubieta, J.; Archer, C. M.; Kelly, J. D. *Polyhedron* **1992**, *11*, 2151–2155.
746. Elder, R. C.; Yuan, J.; Helmer, B.; Pipes, D.; Deutsch, K.; Deutsch, E. *Inorg. Chem.* **1997**, *36*, 3055–3063.
747. Bandoli, G.; Dolmella, A.; Gerber, T. I. A.; Perils, J.; du Preez, J. G. H. *Inorg. Chim. Acta* **2000**, *303*, 24–29.
748. Rajca, G.; Schwarz, W.; Weidlein, J.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *522*, 83–91.
749. Cambridge Crystallographic Data Base, Cambridge, 2002.
750. Inorganic Crystal Structure Data Base, FIZ Karlsruhe, 2002..
751. Gromilov, S. A.; Shubin, Yu.V.; Korenev, S. V.; Gubanov, A. I.; Yusenko, K. V. *Russ. Chem. Bull.* **2000**, *49*, 1310–1312.
752. Wolff von Gudenberg, D.; Frenzen, G.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1995**, *621*, 525–530.
753. Englert, U.; Koelle, U.; Nageswara, R. N. *Z. Kristallogr.* **1994**, *209*, 780.
754. Sawusch, S.; Schilde, U. *Z. Kristallogr.* **1999**, *214*, 79–80.
755. Kurbanov, T. K.; Dovlyatshina, R. A.; Nadzhafova, S. B.; Usubaliev, B. T. *Zh. Neorg. Khim.* **1985**, *30*, 664–667.
756. Barbour, L. J.; MacGillivray, L. R.; Atwood, J. L. *J. Chem. Crystallogr.* **1996**, *26*, 59–61.
757. Maverick, A. W.; Lord, M. D.; Yao, Qin; Henderson, L. J. Jr. *Inorg. Chem.* **1991**, *30*, 553–558.
758. Kennedy, B. J.; Heath, G. A. *Inorg. Chim. Acta* **1992**, *195*, 101–108.
759. Strubinger, S. K. D.; Sun, I.-W.; Cleland, W. E. Jr.; Hussey, C. L. *Inorg. Chem.* **1990**, *29*, 4246–4252.
760. Flint, C. D.; Lang, P. F. *J. Chem. Soc., Dalton Trans.* **1987**, 1929–1932.
761. Prillwitz, P.; Preetz, W. *Z. Naturforsch.* **1994**, *49B*, 753–758.
762. Linke, H.; Preetz, W. *Z. Anorg. Allg. Chem.* **1998**, *624*, 595–601.
763. Preetz, W.; Kelm, W. *Z. Anorg. Allg. Chem.* **1985**, *531*, 7–16.
764. Kelm, W.; Preetz, W. *Z. Anorg. Allg. Chem.* **1988**, *565*, 7–22.
765. Chakravorti, M. C.; Gangopadhyay, T. *Transition Met. Chem.* **1989**, *14*, 312–314.
766. Ramappa, P. G.; Ramachandra, K. S. *J. Inst. Chem. (India)* **1987**, *59*, 115.

767. Strueß, S.; Preetz, W. *Z. Naturforsch.* **1999**, *54B*, 357–362.
768. Kraudelt, H.; Schilde, U.; Uhlemann, E. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1797–1799.
769. Dziegielewski, J. O.; Machura, B.; Bartczak, T. J. *Polyhedron* **1996**, *15*, 2813–2817.
770. Hahn, F. E.; Imhof, L.; Lügger, T. *Inorg. Chim. Acta* **1997**, *261*, 109–112.
771. Engelhardt, L. M.; Figgis, B. N.; Sobolev, A. N.; Reynolds, P. A. *Aust. J. Chem.* **1996**, *49*, 489–496.
772. Pearson, C.; Beauchamp, A. L. *Inorg. Chim. Acta* **1995**, *237*, 13–18.
773. Luo, Hongyan; Orvig, C.; Rettig, S. J. *Acta Crystallogr.* **1996**, *52C*, 1377–1380.
774. Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Inorg. Chem.* **1999**, *38*, 3384–3389.
775. Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Inorg. Chem.* **2001**, *40*, 6825–6831.
776. Bucknor, S.; Cotton, F. A.; Falvello, L. R.; Reid, A. H. Jr.; Schmulbach, C. D. *Inorg. Chem.* **1986**, *25*, 1021–1027.
777. Abram, U.; Carballo, R.; Cabaleiro, S.; Garcia-Fontan, S.; Vazquez-Lopez, E. M. *Polyhedron* **1999**, *18*, 1495–1499.
778. Harben, S. M.; Smith, P. D.; Beddoes, R. L.; Helliwell, M.; Collison, D.; Garner, C. D. *Acta Crystallogr.* **1998**, *54C*, 941–943.
779. Rhodes, L. F.; Caulton, K. G.; Rybak, W. K.; Ziolkowski, J. J. *Polyhedron* **1986**, *5*, 1891–1893.
780. Hübener, R.; Abram, U. *Inorg. Chim. Acta* **1993**, *211*, 121–123.
781. Hübener, R.; Abram, U.; Strähle, J. *Acta Crystallogr.* **1995**, *51C*, 976–978.
782. Lis, T.; Starynowicz, P. *Acta Crystallogr.* **1985**, *41C*, 1299–1302.
783. Gardiner, I. M.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3688–3695.
784. Pearson, C.; Beauchamp, A. L. *Inorg. Chem.* **1998**, *37*, 1242–1248.
785. Figgis, B. N.; Sobolev, A. N.; Schultz, A. J.; Reynolds, P. A. *Acta Crystallogr.* **2001**, *57C*, 1151–1153.
786. Reynolds, P. A.; Moubaraki, B.; Murray, K. S.; Cable, J. W.; Engelhardt, L. M.; Figgis, B. N. *J. Chem. Soc., Dalton Trans.* **1997**, 263–267.
787. Gardiner, I. M.; Bruck, M. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 1769–1771.
788. Wolff von Gudenberg, D.; Sens, I.; Müller, U.; Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1992**, *613*, 49–54.
789. Bertolasi, V.; Ferretti, V.; Gilli, G.; Duatti, A.; Marchi, A.; Magon, L. *J. Chem. Soc., Dalton Trans.* **1987**, 613–617.
790. Hunter, G.; Kilcullen, N. *J. Chem. Soc., Dalton Trans.* **1989**, 2115–2119.
791. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *310*, 237–241.
792. Takahira, T.; Umakoshi, K.; Sasaki, Y. *Acta Crystallogr.* **1994**, *50C*, 1870–1872.
793. Ikari, S.; Ito, T.; McFarlane, W.; Nasreldin, M.; Ooi, B.-L.; Sasaki, Y.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1993**, 2621–2628.
794. Lis, T. *Acta Crystallogr.* **1975**, *31B*, 1594–1597.
795. Atkinson, J. W.; Hong, M.-C.; House, D. A.; Kyritsis, P.; Li, Y.-J.; Nasreldin, M.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1995**, 3317–3322.
796. Chiozzone, R.; Gonzáles, R.; Kremer, C.; De Munno, G.; Cano, J.; Lloret, F.; Julve, M.; Faus, J. *Inorg. Chem.* **1999**, *38*, 4745–4752.
797. Tomkiewicz, A.; Bartczak, T. J.; Kruszynski, R.; Mrozinski, J. *J. Molecular Struct.* **2001**, *595*, 225–231.
798. Chiozzone, R.; Gonzáles, R.; Kremer, C.; De Munno, G.; Armentano, D.; Cano, J.; Lloret, F.; Julve, M.; Faus, J. *Inorg. Chem.* **2001**, *40*, 4242–4249.
799. Ichimura, A.; Yamamoto, Y.; Kajino, T.; Kitagawa, T.; Kuma, H.; Kushi, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1130–1131.
800. Griffith, W. P.; Kiernan, P. M.; Bregeault, J. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1411–1417.
801. Marty, W.; Renaud, P.; Gampp, H. *Helv. Chim. Acta* **1987**, *70*, 375–380.
802. Taura, T. *Inorg. Chim. Acta* **1989**, *163*, 131–132.
803. Drew, M. G. B.; Tisley, D. G.; Walton, R. A. *J. Chem. Soc. D* **1970**, 600–601.
804. Davis, M.; Belanger-Gariepy, F.; Zargarian, D. *Acta Crystallogr.* **1997**, *53C*, 428–430.
805. Holder, G. N.; Bottomley, L. A. *Transition Met. Chem* **1991**, *16*, 579–582.
806. Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *Chem. Commun.* **1970**, 30–31.
807. Cotton, F. A.; Luck, R. *Inorg. Chem.* **1989**, *28*, 2181–2186.
808. Mitsopoulou, C. A.; Mahieu, N.; Motevalli, M.; Randall, E. W. *J. Chem. Soc. Dalton* **1996**, 4563–4566.
809. Luo, X.-L.; Michos, D.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 4286–4288.
810. Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 12541–12549.
811. Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1975**, *14*, 1987–1992.
812. Root, D. R.; Blevins, C. H.; Lichtenberger, D. L.; Sattelberger, A. P.; Walton, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 953–959.
813. Tisato, F.; Refosco, F.; Dolmella, A.; Bandoli, G. *Polyhedron* **1998**, *17*, 3947–3953.
814. Rakowski DuBois, M.; Vasquez, L. D.; Peslherbe, L.; Noll, B. C. *Organometallics* **1999**, *18*, 2230–2240.
815. Orth, S. D.; Barrera, J.; Sabat, M.; Barman, W. D. *Inorg. Chem.* **1993**, *32*, 594–601.
816. Arp, O.; Preetz, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 219–224.
817. Holzbock, J.; Sawodny, W.; Thewalt, U. *Z. Anorg. Allg. Chem.* **2000**, *626*, 321–322.
818. Vrtis, R. N.; Rao, C. P.; Warner, S.; Lippard, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 2669–2670.
819. Warner, S.; Lippard, S. J. *Inorg. Chem.* **1989**, *28*, 3008–3013.
820. Warner, S.; Cheatham, L. K.; Tulip, T. H.; Williams, I. D.; Lipppard, S. J. *Inorg. Chem.* **1991**, *30*, 1221–1226.
821. Masciocchi, N.; Moret, M.; Ardizzoia, G. A.; La Monica, G. *Acta Crystallogr.* **1995**, *51C*, 201–203.
822. Spies, H.; Glaser, M.; Hahn, F. E.; Lügger, T.; Scheller, D. *Inorg. Chim. Acta* **1995**, *232*, 235–239.
823. Hahn, F. E.; Imhof, L. *Organometallics* **1997**, *16*, 763–769.
824. Bouquillon, S.; Du Moulinet D'Hardemare, A.; Chemin, N.; Vidal, M.; Mathieu, J. P. *Polyhedron* **1996**, *15*, 3821–3828.
825. Abrams, M. J.; Davison, A.; Faggiani, R.; Jones, A. G.; Lock, C. J. L. *Inorg. Chem.* **1984**, *23*, 3284–3288.
826. Gambino, D.; Otero, L.; Kremer, E.; Piro, O. E.; Castellano, E. E. *Polyhedron* **1997**, *16*, 2263–2270.
827. Gambino, D.; Benítez, J.; Otero, L.; Kremer, E.; Baran, E. J.; Piro, O. E. *Polyhedron* **1999**, 2099–2107.
828. Otero, L.; Benítez, J.; Gambino, D.; Kremer, E.; Baran, E. J.; Mombrú, A.; Suescun, L.; Mariezcurrena, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1866–1872.
829. Dilworth, J. R.; Hu, J.; Thompson, R. M.; Hughes, D. L. *J. Chem. Soc., Chem. Commun.* **1992**, 551–553.

830. Dilworth, J. R.; Hu, J.; Miller, J. R.; Hughes, D. L.; Zubieta, J. A.; Chen, Q. *J. Chem. Soc., Dalton Trans.* **1995**, 3153–3164.
831. Papadopoulos, M. S.; Bouziotis, P.; Pirmettis, I. C.; Raptopoulou, C. P.; Terzis, A.; Chiotellis, E. *Inorg. Chim. Acta* **1999**, *290*, 247–250.
832. Schrier, P. W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 3929–3933.
833. Vanderheyden, J.-L.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1985**, *24*, 1666–1673.
834. Bakir, M.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1987**, *6*, 907–913.
835. Cotton, F. A.; Daniels, L. M. *Inorg. Chim. Acta* **1988**, *142*, 255–262.
836. Guedes da Silva, M. F. C.; Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1991**, *403*, C1–C3.
837. Kirchhoff, J. R.; Heinemann, W. R.; Deutsch, E. *Inorg. Chem.* **1987**, *26*, 3108–3113.
838. Kirchhoff, J. R.; Heinemann, W. R.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 3608–3614.
839. Roodt, A.; Sullivan, J. C.; Meisel, D.; Deutsch, E. *Inorg. Chem.* **1991**, *30*, 4545–4549.
840. Salih, T. A.; Duarte, M. T.; Frausto de Silva, J. J. R.; Galvão, A. M.; Guedes da Silva, M. F. C.; Hitchcock, P. B.; Hughes, D. L.; Pickett, C. J.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1993**, 3015–3023.
841. Chang, Lihsueh; Aizawa, S.; Heeg, M. J.; Deutsch, E. *Inorg. Chem.* **1991**, *30*, 4920–4927.
842. Chang, Lihsueh; Deutsch, E.; Heeg, M. J. *Transition Met. Chem* **1993**, *18*, 335–341.
843. Ramos, B. L.; Jarbawi, T. B.; Heinemann, W. R. *Electroanalysis* **1999**, *11*, 320–326.
844. Caspar, J. V.; Sullivan, P. B.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2104–2109.
845. Rall, J.; Weingart, F.; Ho, D. M.; Heeg, M. J.; Tisato, F.; Deutsch, E. *Inorg. Chem.* **1994**, *33*, 3442–3451.
846. Helberg, L. E.; Orth, S. D.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1996**, *35*, 5584–5594.
847. Fortin, S.; Beauchamp, A. L. *Inorg. Chem.* **2001**, *40*, 105–112.
848. Fortin, S.; Fabre, P. L.; Dartiguenave, M.; Beauchamp, A. L. *J. Chem. Soc., Dalton Trans.* **2001**, 3520–3527.
849. Gunnoe, T. B.; Meiere, S. H.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **2000**, *39*, 6127–6130.
850. Neuner, B.; Schrock, R. R. *Organometallics*. **1996**, *15*, 5–6.
851. Göldner, M.; Hückstädt, H.; Homborg, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 897–901.
852. Ghosh, P.; Pramanik, A.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1883–1886.
853. Menon, M.; Pramanik, A.; Bag, N.; Chakravorty, A. *Inorg. Chem.* **1994**, *33*, 403–404.
854. Bhattacharyya, S.; Banerjee, S.; Dirhangi, B. K.; Menon, M.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1999**, 155–160.
855. Jurisson, S.; Francesconi, L. C.; Linder, K. E. *Eur. Pat. Appl.* **1991**, 5pp.
856. Jurisson, S.; Francesconi, L.; Linder, K. E.; Treher, E.; Malley, M. F.; Gougoutas, J. Z.; Nunn, A. D. *Inorg. Chem.* **1991**, *30*, 1820–1827.
857. Jurisson, S.; Halihan, M. M.; Lydon, J. D.; Barnes, C. L.; Nowotnik, D. P.; Nunn, A. D. *Inorg. Chem.* **1998**, *37*, 1922–1928.
858. Abram, U.; Lorenz, B. *Z. Naturforsch.* **1993**, *48B*, 771–777.
859. McConnachie, C. A.; Stiefel, E. I. *Inorg. Chem.* **1997**, *36*, 6144–6145.
860. Mullen, G. E. D.; Went, M. J.; Wocadlo, S.; Powell, A.; Blower, P. J. *Angew. Chem.* **1997**, *109*, 1254–1256.
861. Mullen, G. E. D.; Blower, P. J.; Price, D. J.; Powell, A. K.; Howard, M. J.; Went, M. J. *Inorg. Chem.* **2000**, *39*, 4093–4098.
862. Sawusch, S.; Schilde, U. *Z. Kristallogr.* **1999**, *214*, 81–82.
863. Leeaphon, M.; Rohl, K.; Thomas, R. J.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1993**, *32*, 5562–5568.
864. Cowley, A. R.; Dilworth, J. R.; Donnelly, P. S.; Woollard-Shore, J. *J. Chem. Soc., Dalton Trans.* **2003**, 748–754.
865. Blower, P. J.; Dilworth, J. R.; Maurer, R. I.; Mullen, G. D.; Reynolds, C. A.; Zheng, Y. *J. Inorg. Biochem.* **2001**, *85*, 15–22.
866. Al-Shihri, A. S. M.; Dilworth, J. R.; Howe, S. D.; Silver, J.; Thompson, R. M. *Polyhedron* **1993**, *12*, 2297–2305.
867. Spies, H.; Glaser, M.; Pietzsch, H.-J.; Hahn, F. E.; Kintzel, O.; Lügger, T. *Angew. Chem.* **1994**, *106*, 1416–1419.
868. Spies, H.; Glaser, M.; Pietzsch, H.-J.; Hahn, F. E.; Lügger, T. *Inorg. Chim. Acta* **1995**, *240*, 465–478.
869. Glaser, M.; Spies, H.; Lügger, T.; Hahn, F. E. *J. Organomet. Chem.* **1995**, *503*, C32–C35.
870. Maina, T.; Pecorale, A.; Dolmella, A.; Bandoli, G.; Mazzi, U. *J. Chem. Soc., Dalton Trans.* **1994**, 2437–2443.
871. Loiseau, F.; Connac, F.; Lucchese, Y.; Dartiguenave, M.; Fortin, S.; Beauchamp, A. L.; Coulais, Y. *Inorg. Chim. Acta* **2000**, *306*, 94–100.
872. Bandoli, G.; Mazzi, U.; Spies, H.; Münze, R.; Ludwig, E.; Uhlemann, E.; Scheller, D. *Inorg. Chim. Acta* **1987**, *132*, 177–185.
873. Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Organomet. Chem.* **1982**, *224*, 285–294.
874. Lewis, D. J.; Luck, R. L.; Silverton, J. V. *Acta Crystallogr.* **1993**, *49C*, 1424–1426.
875. Bakir, M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2016–2017.
876. Carvalho, M. F. N. N.; Duarte, M. T.; Galvao, A. M.; Pombeiro, A. J. L.; Henderson, R.; Fuess, H.; Svoboda, I. *J. Organomet. Chem.* **1999**, *583*, 56–62.
877. Carvalho, M. F. N. N.; Galvao, A. M.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **2000**, 3393–3400.
878. Pombeiro, A. J. L.; Richards, R. L. *Transition Met. Chem* **1985**, *10*, 463–466.
879. Guedes da Silva, M. F. C.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L. *Inorg. Chem.* **2002**, *41*, 219–228.
880. Libson, K.; Woods, M.; Sullivan, J. C.; Watkins II, J. W.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1988**, *27*, 999–1003.
881. Kirchhoff, J. R.; Allen, M. R.; Cheesman, B. V.; Okamoto, K. I.; Heineman, W. R.; Deutsch, E. *Inorg. Chim. Acta* **1997**, *262*, 195–202.
882. Marcus, R. A. *Annu. Phys. Chem.* **1964**, *15*, 155–196.
883. Lee, Y. F.; Kirchhoff, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 3599–3600.
884. Costello, M. T.; Schrier, P. W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **1993**, *212*, 157–163.
885. Qi, Ju-Sheng; Schrier, P. W.; Fanwick, P. E.; Walton, R. A. *J. Chem. Soc., Chem. Commun.* **1991**, 1737–1739.
886. Allison, J. D.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1984**, *3*, 1515–1520.
887. 900 Bond, A. M.; Colton, R.; Humphrey, D. G.; Mahon, P. J.; Snook, G. A.; Tedesco, V.; Walter, J. N. *Organometallics* **1998**, *17*, 2977–2985.

888. Lazzaro, A.; Vertuani, G.; Bergamini, P.; Mantovani, N.; Marchi, A.; Marvelli, L.; Rossi, R.; Bertolasi, V.; Ferretti, V. *J. Chem. Soc., Dalton Trans.* **2002**, 2843–2851.
889. Stebler, M.; Gutiérrez, A.; Ludi, A.; Bürgi, H.-B. *Inorg. Chem.* **1987**, *26*, 1449–1451.
890. Chin, R. M.; Dubois, R. H.; Helberg, L. E.; Sabat, M.; Bartucz, T. Y.; Lough, A. J.; Morris, R. H.; Harman, W. D. *Inorg. Chem.* **1997**, *36*, 3553–3558.
891. Helberg, L. E.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1995**, *34*, 2033–2041.
892. Collman, J. P.; Garner, J. M.; Kim, K.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 4513–4516.
893. Collman, J. P.; Garner, J. M.; Woo, L. K. *J. Am. Chem. Soc.* **1989**, *111*, 8141–8148.
894. Göldner, M.; Kienast, A.; Homborg, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 141–146.
895. Göldner, M.; Hückstadt, H.; Murray, K. S.; Moubaraki, B.; Homborg, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 288–294.
896. Matondo, S. O. C.; Mountford, P.; Watkin, D. J.; Jones, W. B.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1995**, 161–162.
897. Leigh, G. J.; Morris, R. H.; Pickett, C. J.; Stanley, D. R.; Chatt, J. *J. Chem. Soc., Dalton Trans.* **1981**, 800–804.
898. Carvalho, M. F. N. N.; Pombeiro, A. J. L. *Polyhedron* **1989**, *13/14*, 1778–1779.
899. Carvalho, M. F. N. N.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1990**, *384*, 121–131.
900. Carvalho, M. F. N. N.; Pombeiro, A. J.; Schubert, U.; Orama, O.; Pickett, C. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1985**, 2079–2084.
901. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Miani, F.; Pelizzi, G. *Inorg. Chem.* **2000**, *39*, 3283–3293.
902. Albertin, G.; Antoniutti, S.; Bordignon, E.; Visentin, E. *Inorg. Chem.* **2001**, *40*, 5465–5467.
903. Neyhart, G. A.; Seward, K.; Sullivan, B. P. *Inorg. Synth.* **1997**, *31*, 262–267.
904. Zhang, Q. F.; Chim, J. L. C.; Lai, W.; Wong, W. T.; Leung, W. H. *Inorg. Chem.* **2001**, *40*, 2470–2471.
905. Donovan-Mtunzi, S.; Richards, R. L.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1984**, 2429–2433.
906. Donovan-Mtunzi, S.; MacDonald, C. J.; Richards, R. L.; Hawkes, G. E.; Mason, J. *J. Chem. Soc., Dalton Trans.* **1985**, 2473–2477.
907. Chatt, J.; Dilworth, J. R.; Gunz, H. P.; Leigh, G. J. *J. Organomet. Chem.* **1974**, *64*, 245–254.
908. Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1991**, *30*, 767–774.
909. Heinekey, D. M.; Voges, M. H.; Barnhart, D. M. *J. Am. Chem. Soc.* **1996**, *118*, 10792–10802.
910. Fröhlich, N.; Frenking, G. *Phys. Organomet. Chem.* **1999**, *2*, 173–226.
911. Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577–588.
912. Heinekey, D. M.; Oldham, W. J. Jr. *Chem. Rev.* **1993**, *93*, 913–926.
913. Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155–284.
914. Allen, D. L.; Green, L. H.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 541–549.
915. Abrams, M. J.; Davison, A.; Jones, A. G.; Costello, C. E.; Pang, H. *Inorg. Chem.* **1983**, *22*, 2798–2800.
916. Stacy, N. E.; Conner, K. A.; McMillin, D. R.; Walton, R. A. *Inorg. Chem.* **1986**, *25*, 3649–3652.
917. Edwards, D. A.; Tetrick, S. M.; Walton, R. A. *J. Organomet. Chem.* **1988**, *349*, 383–391.
918. Farr, J. L.; Abrams, M. J.; Costello, C. E.; Davison, A.; Lippard, S. J.; Jones, A. G. *Organometallics* **1985**, *4*, 139–142.
919. Cameron, C. J.; Derringer, D. R.; Walton, R. A. *Inorg. Chim. Acta* **1989**, *165*, 141–143.
920. Chatt, J.; Hussain, W.; Leigh, G. J.; Ali, H. M.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1131–1136.
921. Hughes, D. L.; Pombeiro, A. J. L.; Pickett, C. J.; Richards, R. L. *J. Organomet. Chem.* **1983**, *248*, C26–C28.
922. Pombeiro, A. J. L. *Rev. Port. Quim.* **1985**, *27*, 483–491.
923. Wang, Y.; Frausto Da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1993**, *454*, 211–216.
924. Pombeiro, A. J. L.; Almeida, S. S. P. R.; Silva, M. F. C. G.; Jeffrey, J. C.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1989**, 2381–2387.
925. Pombeiro, A. J. L. *Polyhedron* **1989**, *8*, 1595–1600.
926. Pombeiro, A. J. L.; Hughes, D. L.; Pickett, C. J.; Richards, R. L. *Chem. Comm.* **1986**, 246–247.
927. Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L. *Chem. Commun.* **1988**, 1052–1053.
928. Frausto da Silva, J. J. R.; Guedes da Silva, M. F. C.; Henderson, R. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Organomet. Chem.* **1993**, *461*, 141–145.
929. Amatore, C.; Frausto da Silva, J. J. R.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L.; Verpeaux, J. N. *Chem. Commun.* **1992**, 1289–1291.
930. Guedes da Silva, M. F. C.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L.; Amatore, C.; Verpeaux, J. N. *NATO ASI Ser. C* **1993**, *385*, 483–487.
931. Ferreira, C. M. P.; Guedes da Silva, M. F. C.; Kukushkin, V. Y.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1998**, 325–326.
932. Guedes da Silva, M. F. C.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1996**, *526*, 237–250.
933. Guedes da Silva, M. F. C.; Duarte, M. T.; Galvao, A. M.; Frausto da Silva, J. R. R.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1992**, *433*, C14–C18.
934. Guedes da Silva, M. F. C.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L. *Port. Electrochim. Acta* **1993**, *11*, 93–97.
935. Guedes da Silva, M. F. C.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L.; Amatore, C.; Verpeaux, J. N. *Organometallics* **1994**, *13*, 3943–3951.
936. Pombeiro, A. J. L.; Richards, R. L. *J. Organomet. Chem.* **1986**, *306*, C33–C35.
937. De C. T. Carrondo, M. A. A. F.; Domingos, A. M. T. S.; Jeffrey, G. A. *J. Organomet. Chem.* **1985**, *289*, 377–383.
938. Carvalho, M. F. N. N.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1209–1216.
939. Pombeiro, A. J. L. *Inorg. Chim. Acta* **1992**, *198-200*, 179–186.
940. Carvalho, M. F. N. N.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1991**, *410*, 347–355.
941. Carvalho, M. F. N. N.; Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1993**, *469*, 179–187.
942. Carvalho, M. F. N. N.; Duarte, M. T.; Galvao, A. M.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1994**, *469*, 79–87.
943. Lemos, M. A. N. D. A.; Guedes da Silva, M. F. C.; Pombeiro, A. J. L. *Inorg. Chim. Acta* **1994**, *226*, 9–16.

944. Guedes da Silva, M. F. C.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1996**, 2763–2772.
945. Carvalho, M. F. N. N.; Duarte, M. T.; Galvao, A. M.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1996**, *511*, 163–169.
946. Guedes da Silva, M. F. C.; Lemos, M. A. N. D. A.; Frausto da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **2000**, 373–380.
947. Chang, L.; Deutsch, E. *Inorg. Synth.* **1997**, *31*, 253–256.
948. Rivero, M.; Kremer, C.; Gancheff, J.; Kremer, E.; Suescun, L.; Mombru, A.; Mariezcurrena, R.; Dominguez, S.; Mederos, A.; Midollini, S. *Polyhedron* **2000**, *19*, 2249–2254.
949. Chatt, J.; Dilworth, J. R.; Leigh, G. J.; Gupta, V. D. *J. Chem. Soc. A* **1971**, 2631–2639.
950. Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 612–618.
951. Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1994**, *33*, 3026–3027.
952. Cooper, J. B.; Drew, M. G. B.; Beer, P. D. *J. Chem. Soc., Dalton Trans.* **2000**, 2721–2728.
953. Cooper, J. B.; Drew, M. G. B.; Beer, P. D. *J. Chem. Soc., Dalton Trans.* **2001**, 392–401.
954. Deschenaux, R.; Greppi, A.; Ruch, T.; Kriemler, H. P.; Raschdorf, F.; Ziessel, R. *Tetrahedron Lett.* **1994**, *35*, 2165–2168.
955. Cary, D. R.; Zaitseva, N. P.; Gray, K.; O'Day, K. E.; Darrow, C. B.; Lane, S. M.; Peyser, T. A.; Satcher, J. H. Jr.; Van Antwerp, W. P.; Nelson, A. J.; Reynolds, J. G. *Inorg. Chem.* **2002**, *41*, 1662–1669.
956. Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 1038–1040.
957. Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661–3671.
958. Meiere, S. H.; Harman, W. D. *Organometallics* **2001**, *20*, 3876–3883.
959. Friedman, L. A.; Harman, W. D. *J. Am. Chem. Soc.* **2001**, *123*, 8967–8973.
960. Pombeiro, A. J. L.; Hitchcock, P. B.; Richards, R. L. *J. Chem. Dalton Trans.* **1987**, 319–325.
961. Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1987**, 2299–2303.
962. Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Hussein, A. *J. Chem. Soc., Dalton Trans.* **1988**, 1853–1856.
963. Zanello, P.; Cinquantini, A.; Laschi, F.; Rossi, R.; Duatti, A.; Marchi, A.; Magon, L. *Polyhedron* **1988**, *7*, 195–201.
964. Alberto, R.; Schibli, R.; Waibel, R.; Abram, U.; Schubiger, P. A. *Coord. Chem. Rev.* **1999**, *190-192*, 901–919.
965. Schibli, R.; Schubiger, P. A. *Eur. J. Nucl. Med.* **2002**, *29*, 1529–1542.
966. Alberto, R.; Egli, A.; Abram, U.; Hegetschweiler, K.; Gramlich, V.; Schubiger, P. A. *J. Chem. Soc. Dalton Trans.* **1994**, 2815–2820.
967. Egli, A.; Hegetschweiler, K.; Alberto, R.; Abram, U.; Schibli, R.; Hedinger, R.; Gramlich, V.; Kissner, R.; Schubiger, P. A. *Organometallics.* **1997**, *9*, 1833–1840.
968. Abram, U.; Hübener, R.; Alberto, R.; Schibli, R. *Z. Anorg. Allg. Chem.* **1996**, *622*, 813–818.
969. Kramer, D. J.; Davison, A.; Davis, W. M.; Jones, A. G. *Inorg. Chem.* **2002**, *41*, 6181–6183.
970. Kramer, D. J.; Davison, A.; Jones, A. G. *Inorg. Chim Acta* **2001**, *312*, 215–220.
971. Bakir, M.; McKenzie, J. A. M. *J. Chem. Soc., Dalton Trans.* **1997**, 3571–3578.
972. Grewe, J.; Hagenbach, A.; Stromburg, B.; Alberto, R.; Vazquez-Lopez, E.; Abram, U. *Z. Anorg. Allg. Chem.* **2003**, *629*, 303–311.
973. Schibli, R.; Alberto, R.; Abram, U.; Abram, S.; Egli, A.; Schubiger, P. A.; Kaden, T. A. *Inorg. Chem.* **1998**, *37*, 3509–3516.
974. Abram, U.; Abram, S.; Alberto, R.; Schibli, R. *Inorg. Chim. Acta* **1996**, *248*, 193–202.
975. Chen, X. Y.; Femia, F. J.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2001**, *315*, 147–152.
976. Carballo, R.; Casas, J. S.; Garcia-Martinez, E.; Pereiras-Gabian, G.; Sanchez, A.; Sordo, J.; Vazquez-Lopez, E.; Garcia-Monteagudo, J. C.; Abram, U. *J. Organomet. Chem.* **2002**, *656*, 1–10.
977. Fawcett, J. P.; Poe, A. J.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *61*, 315–321.
978. Cowie, M.; Bennett, M. J. *Inorg. Chem.* **1972**, *16*, 1556–1661.
979. Adams, R. D.; Chodosh, D. F. *J. Organomet. Chem.* **1975**, *87*, C48–C51.
980. Albers, O.; Coville, N. J. *S. Afr. J. Chem.* **1982**, *35*, 139–143.
981. Robinson, D. J.; Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1307–1308.
982. Albers, M. O.; Boeyens, J. C. A.; Coville, N. J.; Harris, G. W. *J. Organomet. Chem.* **1984**, *260*, 99–104.
983. Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1985**, *4*, 914–922.
984. Harris, G. W.; Coville, N. J. *Organometallic* **1985**, *4*, 908–914.
985. Harvey, P. D.; Butler, I. S.; Harris, G. W.; Coville, N. J. *Inorg. Chem.* **1986**, *25*, 3608–3613.
986. Kreiter, C. G.; Franzreb, K. H.; Michels, W.; Schubert, U.; Ackermann, K. *Z. Naturforsch.* **1985**, *40B*, 1188–1198.
987. Meckstroth, W. K.; Walters, R. T.; Waltz, W. I.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 1842–1846.
988. Ho, T.-I.; Chang, C.-M.; Wang, S. R.; Cheng, C. P. *J. Chem. Soc., Dalton Trans.* **1988**, 123–127.
989. Crocker, L. S.; Mattson, B. M.; Heinekey, D. M. *Organometallics* **1990**, *9*, 1011–1016.
990. Crocker, L. S.; Mattson, B. M.; Schulte, G. K.; Heinekey, D. M. *Inorg. Chem.* **1988**, *27*, 3722–3725.
991. Crocker, L. S.; Heinekey, D. M.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 405–406.
992. Giusto, D.; Cova, G. *Gazz. Chim. Ital.* **1972**, *102*, 265–272.
993. Casey, J. A.; Murmann, R. K. *J. Am. Chem. Soc.* **1970**, *92*, 78–84.
994. Gusev, D.; Llamazares, A.; Artus, G.; Jacobsen, H.; Berke, H. *Organometallics* **1999**, *18*, 75–89.
995. Bhattacharyya, R.; Roy, P. S.; Dasmahapatra, A. K. *J. Chem. Soc., Dalton Trans.* **1988**, 793–802.
996. Smith, J.; Purcell, W.; Lamprecht, G. J.; Leipoldt, J. G. *Polyhedron* **1995**, *14*, 1795–1797.
997. Bhattacharyya, R.; Roy, P. S. *Inorg. Chim. Acta* **1984**, *87*, 99–104.
998. Kersting, M.; Hoffmann, R. *Inorg. Chem.* **1990**, *29*, 279–284.
999. Abram, U.; Voigt, A.; Kirmse, R.; Ortner, K.; Hübener, R.; Carballo, R.; Vazquez-Lopez, E. *Z. Anorg. Allg. Chem.* **1998**, *624*, 1662–1668.
1000. Dziegielewski, J. O.; Machura, B.; Kupka, T.; Bartczak, T. J.; Czurak, W. *Pol. J. Chem.* **1998**, *72*, 1009–1016.
1001. Dziegielewski, J. O.; Machura, B.; Bartczak, T. J.; Czurak, W.; Kusz, J.; Warczewski, J. *J. Coord. Chem.* **1999**, *48*, 125–135.

1002. Voigt, A.; Abram, U.; Böttcher, R.; Strauch, P.; Kirmse, R. *Inorg. Chem. Commun.* **1998**, *1*, 389–391.
1003. Bartczak, T. J.; Czurak, W.; Dziegielewski, J. O.; Machura, B.; Jankowska, A.; Kusz, J.; Warczewski, J. *J. Coord. Chem.* **2001**, *52*, 361–373.
1004. Dziegielewski, J. O.; Filipek, K.; Machura, B. *Polyhedron* **1995**, *14*, 555–561.
1005. Dziegielewski, J. O.; Machura, B.; Marek, J. *Polyhedron* **1996**, *15*, 3713–3716.
1006. Bartczak, T. J.; Czurak, W.; Dziegielewski, J. O.; Machura, B.; Jankowska, A.; Kusz, J.; Warczewski, J. *Polyhedron* **1999**, *18*, 2313–2320.
1007. Hund, H.-U.; Ruppli, U.; Berke, H. *Helv. Chim. Acta* **1993**, *76*, 963–975.
1008. Nietliespach, D.; Bosch, H. W.; Berke, H. *Chem. Ber.* **1994**, *127*, 2403–2415.
1009. Van der Zeijden, A. A. H.; Veghini, D.; Berke, H. *Inorg. Chem.* **1992**, *31*, 5106–5116.
1010. Eremenko, I. L.; Bakhmutov, V. I.; Otl, F.; Berke, H. *Zh. Neorg. Khim.* **1993**, *38*, 1653–1660.
1011. Veghini, D.; Berke, H. *Inorg. Chem.* **1996**, *35*, 4770–4778.
1012. Jacobsen, H.; Schmalle, H. W.; Messmer, A.; Berke, H. *Inorg. Chim. Acta* **2000**, *306*, 153–159.
1013. Jacobsen, H.; Heinze, K.; Llamazares, A.; Schmalle, H. W.; Artus, G.; Berke, H. *J. Chem. Soc., Dalton Trans.* **1999**, 1717–1728.
1014. Llamazares, A.; Schmalle, H. W.; Berke, H. *Organometallics* **2001**, *20*, 5277–5288.
1015. Dziegielewski, J. O.; Machura, B.; Malecki, J.; Bartczak, T. J.; Czurak, W. *Pol. J. Chem.* **2000**, *74*, 191–198.
1016. Wang, Y.; Fraústo da Silva, J. J. R.; Pombeiro, A. J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1992**, *430*, C56–C59.
1017. Wang, Y.; Fraústo da Silva, J. J. R.; Pombeiro, J. L.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1994**, *476*, C9–C11.
1018. Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1533–1541.
1019. Blower, P. J.; Bishop, P. T.; Dilworth, J. R.; Hsieh, T. C.; Hutchinson, J.; Nicholson, T.; Zubieta, J. *Inorg. Chim. Acta* **1985**, *101*, 63–65.
1020. Smith, J.; Purcell, W.; Lamprecht, G. J.; Roodt, A. *Polyhedron* **1996**, *15*, 1389–1395.
1021. Pomp, C.; Wieghardt, K.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1988**, *27*, 3789–3796.
1022. Göldner, M.; Geniffke, B.; Franken, A.; Murray, K. S.; Homborg, H. *Z. Anorg. Allg. Chem.* **2001**, *627*, 935–947.
1023. Mitra, T.; Sen, S.; Sen, B. K.; Bandyopadhyay, P. *Z. Anorg. Allg. Chem.* **1987**, *548*, 217–224.
1024. Hartmann, G.; Mews, R. *Angew. Chem.* **1985**, *97*, 218–219.
1025. Hiller, W.; Mohyla, J.; Strähle, J.; Hauck, H. G.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*, 72–78.
1026. Conradi, E.; Hauck, H. G.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1986**, *539*, 39–49.
1027. Müller, U.; Vogler, S.; Dehnicke, K.; Fenske, D. *Acta Crystallogr.* **1990**, *46C*, 1989–1992.
1028. Vogler, S.; Dehnicke, K.; Hiller, W. *Z. Naturforsch.* **1989**, *44B*, 1509–1512.
1029. Hauck, H. G.; Patt-Siebel, U.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1987**, *546*, 177–182.
1030. Hauck, H.-G.; Willing, W.; Müller, U.; Dehnicke, K. *Z. Naturforsch.* **1986**, *41B*, 825–830.
1031. Anhaus, J.; Siddiqi, Z. A.; Roesky, H. W.; Batts, J. W.; Elerman, Y. *Z. Naturforsch.* **1985**, *40B*, 740–744.
1032. Hauck, H.-G.; Willing, W.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1986**, *534*, 77–84.
1033. Voigt, A.; Abram, U.; Kirmse, R. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1658–1663.
1034. Abram, U.; Ritter, S. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1223–1228.
1035. Hirsch-Kuchma, M.; Nicholson, T.; Davison, A.; Jones, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 3189–3192.
1036. Nicholson, T.; Zubieta, J. *Polyhedron* **1988**, *7*, 171–185.
1037. Nicholson, T.; Shaikh, N.; Zubieta, J. *Inorg. Chim. Acta* **1985**, *99*, L45–L46.
1038. Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1987**, *26*, 2094–2104.
1039. Nicholson, T.; Zubieta, J. *Inorg. Chim. Acta* **1987**, *134*, 191–193.
1040. Nicholson, T.; Zubieta, J. *Inorg. Chim. Acta* **1985**, *100*, L35–L36.
1041. Hsieh, T.-C.; Nicholson, T.; Zubieta, J. *Inorg. Chem.* **1988**, *27*, 241–250.
1042. Ali, H. M.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1986**, 213–215.
1043. Coutinho, B.; Dilworth, J. R.; Jobanputra, P.; Thompson, R. M.; Schmid, S.; Strähle, J.; Archer, C. *J. Chem. Soc., Dalton Trans.* **1995**, 1663–1669.
1044. Carr, S. W.; Fontaine, X. L. R.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 769–774.
1045. Bouquillon, S.; Dartiguenave, M. *J. Coord. Chem.* **1994**, *31*, 257–263.
1046. Ribeiro, M. T. A.; Pombeiro, A. J. L.; Dilworth, J. R.; Zheng, Yifan; Miller, J. R. *Inorg. Chim. Acta* **1993**, *211*, 131–132.
1047. Dilworth, J. R.; Lewis, J. S.; Miller, J. R.; Zheng, Yifan. *J. Chem. Soc., Dalton Trans.* **1995**, 1357–1361.
1048. Albertin, G.; Antoniutti, S.; Bacchi, A.; Ballico, G. B.; Bordignon, E.; Pelizzi, G.; Ranieri, G.; Ugo, P. *Inorg. Chem.* **2000**, *39*, 3265–3279.
1049. Hirsch-Kuchma, M.; Nicholson, T.; Davison, A.; Davis, W. M.; Jones, A. G. *Inorg. Chem.* **1997**, *36*, 3237–3241.
1050. Hirsch-Kuchma, M.; Nicholson, T.; Davison, A.; Davis, W. M.; Jones, A. G. *J. Chem. Soc., Dalton Trans.* **1997**, 3185–3188.
1051. Cowley, A. R.; Dilworth, J. R.; Donnelly, P. S. *Inorg. Chem.* **2003**, *42*, 929–931.
1052. Dilworth, J. R.; Harrison, S. A.; Walton, D. R. M.; Schweda, E. *Inorg. Chem.* **1985**, *24*, 2594–2595.
1053. Nicholson, T.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1985**, 367–368.
1054. Dilworth, J. R.; Henderson, R. A.; Dahlstrom, P.; Nicholson, T.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1987**, 529–540.
1055. Gernert, M. B.; Kooijman, H.; Hiller, W. P.; Dilworth, J. R.; Parrott, S. J. *Acta Crystallogr.* **1996**, *52C*, 545–548.
1056. Danopoulos, A. A.; Wilkinson, G.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1994**, 907–915.
1057. Da Costa, M. T. A. R. S.; Dilworth, J. R.; Duarte, M. T.; Frausto da Silva, J. J. R.; Galvao, A. M.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1998**, 2405–2410.
1058. Nicholson, T.; Mahmood, A.; Morgan, G.; Jones, A. G. *Inorg. Chim. Acta* **1991**, *179*, 53–57.
1059. Nicholson, T.; Cook, J.; Davison, A.; Rose, D. J.; Maresca, K. P.; Zubieta, J. A.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *252*, 421–426.
1060. Nicholson, T.; Cook, J.; Davison, A.; Rose, D. J.; Maresca, K. P.; Zubieta, J. A.; Jones, A. G. *Inorg. Chim. Acta* **1996**, *252*, 427–430.

1061. Femia, F.; Chen, Xiaoyuan; Maresca, K. P.; Babich, J. W.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *307*, 160–163.
1062. Rose, D. J.; Maresca, K. P.; Nicholson, T.; Davison, A.; Jones, A. G.; Babich, J.; Fischman, A.; Graham, W.; DeBord, J. R. D.; Zubieta, J. *Inorg. Chem.* **1998**, *37*, 2701–2716.
1063. Knox, K.; Ginsberg, A. P. *Inorg. Chem.* **1964**, *3*, 555–558.
1064. Abrahams, C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558–567.
1065. Bronger, W.; Brassard, L.; Müller, P.; Lebech, B.; Schultz, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1143–1146.
1066. Bronger, W.; Auffermann, G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1147–1150.
1067. Huang, B.; Yvon, K.; Fischer, P. *J. Alloys Compd.* **1993**, *197*, 97–99.
1068. Bronger, W.; Auffermann, G.; Schilder, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 497–500.
1069. Howard, J. A. K.; Mead, K. A.; Spencer, J. L. *Acta Crystallogr.* **1983**, *39C*, 555–559.
1070. Emge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012–4017.
1071. Teller, R. G.; Carroll, W. E.; Bau, R. *Inorg. Chim. Acta* **1984**, *87*, 121–127.
1072. Brammer, L.; Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L.; Stringer, A. M. *J. Chem. Soc., Chem. Commun.* **1991**, 241–243.
1073. Lyons, D.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1985**, 587–590.
1074. Zeiher, E. H. K.; DeWit, D. G.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 7006–7011.
1075. Smith, K. J.; Ondracek, A. L.; Gruhn, N. E.; Lichtenberger, D. L.; Fanwick, P. E.; Walter, R. A. *Inorg. Chim. Acta* **2000**, *300-302*, 23–31.
1076. Wessel, J.; Lee, J. C. Jr.; Peris, E.; Yap, G. P. A.; Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Koetzle, T. F.; Eisenstein, O.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem.* **1995**, *107*, 2711–2713.
1077. Cotton, F. A.; Luck, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5757–5761.
1078. Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 6–8.
1079. Costello, M. T.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2563–2564.
1080. Luo, X. L.; Howard, J. A. K.; Crabtree, R. H. *Magn. Reson. Chem.* **1991**, *29*, S89–S93.
1081. Haynes, G. R.; Martin, R. L.; Hay, P. J. *J. Am. Chem. Soc.* **1992**, *114*, 28–36.
1082. Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1987**, 715–720.
1083. Bruno, J. W.; Caulton, K. G. *J. Organomet. Chem.* **1986**, *315*, C31–C16.
1084. Alvarez, D. Jr.; Lundquist, E. G.; Ziller, J. W.; Evans, W. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1989**, *111*, 8392–8398.
1085. Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Can. J. Chem.* **2001**, *79*, 964–976.
1086. Lunder, D. M.; Green, M. A.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1989**, *28*, 4527–4531.
1087. Kristjánsdóttir, S. S.; Loendorf, A. J.; Norton, J. R. *Inorg. Chem.* **1991**, *30*, 4470–4471.
1088. Chiu, K. W.; Howard, C. G.; Rzepa, H. S.; Sheppard, R. N.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 441–451.
1089. Gibson, V. C.; Graimann, C. E.; Hare, P. M.; Green, M. L. H.; Bandy, J. A.; Grebenik, P. D.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1985**, 2025–2035.
1090. Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 6912–6918.
1091. Lin, Zhenyang; Hall, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 4446–4448.
1092. Luck, R. L.; O'Neill, R. S. *Polyhedron* **2001**, *20*, 773–782.
1093. Cameron, C. J.; Moehring, G. A.; Walton, R. A. *Inorg. Synth.* **1990**, *27*, 14–18.
1094. Loza, M. L.; Crabtree, R. H. *Inorg. Chim. Acta* **1995**, *236*, 63–66.
1095. Bayse, C. A.; Luck, R. L.; Schelter, E. J. *Inorg. Chem.* **2001**, *40*, 3463–3467.
1096. Carr, S. W.; Fowles, E. H.; Fontaine, X. L. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1990**, 573–579.
1097. Costello, M. T.; Fanwick, P. E.; Green, M. A.; Walton, R. A. *Inorg. Chem.* **1991**, *30*, 861–864.
1098. Howard, J. A. K.; Mason, S. A.; Johnson, O.; Diamond, I. C.; Crennell, S.; Keller, P. A.; Spencer, J. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1502–1503.
1099. Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813–4821.
1100. Costello, M. T.; Harris, T. A.; Walton, R. A. *Inorg. Chim. Acta* **1996**, *249*, 101–103.
1101. Fontaine, X. L. R.; Layzell, T. P.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1994**, 917–924.
1102. Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027–3039.
1103. Kohli, M.; Lewis, D. J.; Luck, R. L.; Silverton, J. V.; Sylla, K. *Inorg. Chem.* **1994**, *33*, 879–883.
1104. Gusev, D. G.; Nietlispach, D.; Vymenits, A. B.; Bakhmutov, V. I.; Berke, H. *Inorg. Chem.* **1993**, *32*, 3270–3276.
1105. Luo, X. L.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **1991**, 587–590.
1106. Bianchini, C.; Peruzzini, M.; Zanobini, F.; Magon, L.; Marvelli, L.; Rossi, R. *J. Organomet. Chem.* **1993**, *451*, 97–106.
1107. Costello, M. T.; Fanwick, P. E.; Green, M. A.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 2359–2365.
1108. Michos, D.; Luo, X.-L.; Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **1992**, 1735–1738.
1109. Kim, Y.; Deng, H.; Gallucci, J. C.; Wojcicki, A. *Inorg. Chem.* **1996**, *35*, 7166–7173.
1110. Kim, Y.; Deng, H.; Gallucci, J. C.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798–2800.
1111. Jia, G.; Lough, A. J.; Morris, R. H. *J. Organomet. Chem.* **1993**, *461*, 147–156.
1112. Skupinski, W. A.; Huffman, J. C.; Bruno, J. W.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8128–8136.
1113. Albinati, A.; Bakhmutov, V. I.; Belkova, N. V.; Bianchini, C.; De los Rios, I.; Epstein, L.; Gutsul, E. J.; Marvelli, L.; Peruzzini, M.; Rossi, R.; Shubina, E.; Vorontsov, E. V.; Zanobini, F. *Eur. J. Inorg. Chem.* **2002**, 1530–1539.
1114. Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1985**, *24*, 3898–3903.
1115. Dziegielewski, J. O.; Mrzigod, J.; Machura, B. *Spectrosc. Biol. Mol.: New Dir. Eur. Conf.* **1999**, 659–660.
1116. Belkova, N. V.; Shubina, E. S.; Ionidis, A. V.; Epstein, L. M.; Jacobsen, H.; Messmer, A.; Berke, H. *Inorg. Chem.* **1997**, *36*, 1522–1525.
1117. Southern, J. S.; Green, M. T.; Hillhouse, G. L.; Guzei, I. A.; Rheingold, A. L. *Inorg. Chem.* **2001**, *40*, 6039–6046.
1118. Albertin, G.; Antonuitti, S.; Garcia-Fontan, S.; Carballo, R.; Padoan, F. *J. Chem. Soc., Dalton Trans.* **1998**, 2071–2082.
1119. Bolano, S.; Bravo, J.; Carballo, R.; Garcia-Fontan, S.; Abram, U.; Vazquez-Lopez, E. M. *Polyhedron* **1999**, *18*, 1431–1436.
1120. Bolana, S.; Bravo, J.; García-Fontán, S. *Inorg. Chim. Acta* **2001**, *315*, 81–87.

1121. Chatt, J.; Coffey, R. *J. Chem. Soc. A* **1969**, 1963–1966.
1122. Lee, J. C. Jr.; Yao, W.; Crabtree, R. H. *Inorg. Chem.* **1996**, *35*, 695–699.
1123. Patel, B. P.; Yao, W.; Yap, G. P. A.; Rheingold, A. L.; Crabtree, R. H. *Chem. Commun.* **1996**, 991–992.
1124. Bosque, R.; Maseras, F.; Eisenstein, O.; Patel, B. P.; Yao, W.; Crabtree, R. H. *Inorg. Chem.* **1997**, *36*, 5505–5511.
1125. Patel, B. P.; Kavallieratos, K.; Crabtree, R. H. *J. Organomet. Chem.* **1997**, *528*, 205–207.
1126. Yap, G. P. A.; Rheingold, A. L.; Das, P.; Crabtree, R. H. *Inorg. Chem.* **1995**, *34*, 3474–3476.
1127. Richardson, T. B.; de Gala, S.; Crabtree, R. H.; Siegbahn, P. E. M. *J. Am. Chem. Soc.* **1995**, *117*, 12875–12876.
1128. Patel, B. P.; Tan, P.; Pistorio, B. J.; Yao, W.; Crabtree, R. H. *New J. Chem.* **1997**, *21*, 131–132.
1129. Rabie, U. M.; Patel, B. P.; Crabtree, R. H.; Mahmoud, M. R. *Inorg. Chem.* **1997**, *36*, 2236–2238.
1130. Moehring, G. A.; Williams, C. C.; Buford, J.; Kaviani, M.; Sulko, J.; Fanwick, P. E. *Inorg. Chem.* **1998**, *37*, 3848–3852.
1131. Allison, J. D.; Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1986**, 67–72.
1132. Moehring, G. A.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 2910–2912.
1133. Hamilton, D. G.; Luo, X.-L.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3198–3203.
1134. Matano, Y.; Brown, S. N.; Northcutt, T. O.; Mayer, J. M. *Organometallics* **1998**, *17*, 2939–2941.
1135. Paulo, A.; Ascenso, J.; Domingos, A.; Galvão, A.; Santos, I. *J. Chem. Soc., Dalton Trans.* **1999**, 1293–1300.
1136. Kim, Y.; Galluci, J.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 8600–8602.
1137. Baize, M. W.; Gallucci, J. C.; Wojcicki, A. *Inorg. Chim. Acta* **1997**, *259*, 339–344.
1138. Schwarz, D. E.; Dopke, J. A.; Rauchfuss, T. B.; Wilson, S. R. *Angew. Chem.* **2001**, *113*, 2413–2415*Angew. Chem. Int. Ed. Engl* **2001**, *40*, 2351–2352.
1139. Leeaphon, M.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1991**, *113*, 1424–1426.
1140. Leeaphon, M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1991**, *30*, 4986–4995.
1141. Leeaphon, M.; Ondracek, A. L.; Thomas, R. J.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1995**, *117*, 9715–9724.
1142. Ondracek, A. L.; Wu, W.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1996**, *35*, 5249–5253.
1143. Dilworth, J. R.; Hu, J.; Miller, J. R.; Lu, S.; Wu, Q. *Polyhedron* **1996**, *15*, 953–959.
1144. Harris, T. A.; McKinney, T. M.; Wu, W.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1996**, *15*, 3289–3298.
1145. Luo, X.-L.; Schulte, G. K.; Demou, P.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 4268–4273.
1146. Lin, Z.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 2569–2572.
1147. Howard, J. A.; Keller, P. A.; Vogt, T.; Taylor, A. L.; Dix, N. D.; Spencer, J. L. *Acta Crystallogr.* **1992**, *48B*, 438–444.
1148. Barea, G.; Maseras, F.; Jean, Y.; Lledós, A. *Inorg. Chem.* **1996**, *35*, 6401–6405.
1149. Luo, X.-L.; Baudry, D.; Boydell, P.; Charpin, P.; Nierlich, M.; Ephritikhine, M.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 1511–1517.
1150. Loza, M. L.; de Gala, S. R.; Crabtree, R. H. *Inorg. Chem.* **1994**, *33*, 5073–5078.
1151. Kaur, P.; Perera, S. D.; Jelínek, T.; Stíbr, B.; Kennedy, J. D.; Clegg, W.; Thornton-Pett, M. *Chem. Commun.* **1997**, 217–218.
1152. Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 4522–4527.
1153. Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 3203–3209.
1154. Bucknor, S.; Cotton, F. A.; Falvello, L. R.; Reid, A. H. Jr.; Schmulbach, C. D. *Inorg. Chem.* **1987**, *26*, 2954–2959.
1155. Allison, J. D.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 163–168.
1156. Allison, J. D.; Cotton, F. A.; Powell, G. L.; Walton, R. A. *Inorg. Chem.* **1984**, *23*, 159–164.
1157. Abrahams, S. C.; Ginsberg, A. P.; Koetzle, T. F.; Marsh, P.; Sprinkle, C. R. *Inorg. Chem.* **1986**, *25*, 2500–2510.
1158. Ginsberg, A. P.; Abrahams, S. C.; Marsh, P.; Ataka, K.; Sprinkle, C. R. *J. Chem. Soc., Chem. Commun.* **1984**, 1321–1323.
1159. Costello, M. T.; Moehring, G. A.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 1578–1581.
1160. Costello, M. T.; Fanwick, P. E.; Meyer, K. E.; Walton, R. A. *Inorg. Chem.* **1990**, *29*, 4437–4441.
1161. Green, M. A.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 695–696.
1162. Hinman, J. G.; Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Inorg. Chem.* **2001**, *40*, 2480–2481.
1163. Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 395–397.
1164. Meyer, K. E.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1990**, *112*, 8586–8587.
1165. Meyer, K. E.; Root, D. R.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 3067–3076.
1166. Meyer, K. E.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 4486–4491.
1167. Haupt, H. J.; Flörke, U.; Balsaa, P. *Acta Crystallogr.* **1988**, *44C*, 61–63.
1168. Klouras, N.; Flörke, U.; Haupt, H. J.; Woyciechowski, M. *Acta Crystallogr.* **1990**, *46C*, 2096–2100.
1169. Flörke, U.; Haupt, H. J. *Z. Kristallogr.* **1990**, *193*, 309–312.
1170. Chen, S. J.; Dunbar, K. R. *Inorg. Chem.* **1990**, *29*, 529–534.
1171. Haupt, H. J.; Woyciechowski, M.; Flörke, U. *Z. Anorg. Allg. Chem.* **1991**, *592*, 153–170.
1172. Haupt, H. J.; Wittbecker, R.; Flörke, U. *J. Organomet. Chem.* **1996**, *518*, 213–219.
1173. Flörke, U.; Haupt, H. J. *Z. Kristallogr.* **1990**, *191*, 291–294.
1174. Flörke, U.; Haupt, H. J. *Z. Kristallogr.* **1990**, *192*, 278–281.
1175. Flörke, U.; Haupt, H. J. *Z. Kristallogr.* **1990**, *191*, 298–299.
1176. Flörke, U.; Haupt, H. J. *Z. Kristallogr.* **1990**, *191*, 296–297.
1177. Flörke, U.; Haupt, H. J. *Z. Kristallogr.* **1990**, *191*, 300–302.
1178. Flörke, U.; Haupt, H. J. *Z. Kristallogr.* **1990**, *191*, 303–305.
1179. Flörke, U.; Haupt, H. J.; Schnieder, H. *Acta Crystallogr.* **1991**, *47C*, 2531–2535.
1180. Shih, K. Y.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1991**, *39*, 3971–3973.
1181. Chernega, A. N.; Green, M. L. H.; Haggitt, J.; Stephens, A. H. H. *J. Chem. Soc., Dalton Trans.* **1998**, 755–767.
1182. Barron, A. R.; Lyons, D.; Wilkinson, G.; Motevalli, M.; Howes, A. J.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 279–285.
1183. Westerberg, D. E.; Sutherland, B. R.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1988**, *110*, 1642–1643.
1184. Moehring, G. A.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 1861–1866.
1185. Moehring, G. A.; Walton, R. A. *J. Chem. Soc., Dalton Trans.* **1988**, 1701–1703.

1186. Sutherland, B. R.; Ho, D. M.; Huffman, J. C.; Caulton, F. G. *Angew. Chem.* **1987**, *99*, 147–149.
1187. Connelly, N. G.; Howard, J. A. K.; Spencer, J. L.; Woodley, P. K. *J. Chem. Soc., Dalton Trans.* **1984**, 2003–2009.
1188. Bruno, J. W.; Huffman, J. C.; Green, M. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 8310–8312.
1189. He, Zhongli; Neibecker, D.; Lugan, N.; Mathieu, R. *Organometallics* **1992**, *11*, 817–821.
1190. Fontaine, X. L. R.; Layzell, T. P.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1994**, 379–383.
1191. Baker, R. T.; Glassman, T. E.; Ovenall, D. W.; Calabrese, J. C. *Isr. J. Chem.* **1991**, *31*, 33–53.
1192. Moldes, I.; Mathieu, R. *J. Organomet. Chem.* **1994**, *480*, 185–189.
1193. Moldes, I.; Nefedov, S.; Lugan, N.; Mathieu, R. *J. Organomet. Chem.* **1995**, *490*, 11–19.
1194. He, Z.; Nefedov, S.; Lugan, N.; Neibecker, D.; Mathieu, R. *Organometallics* **1993**, *12*, 3837–3845.
1195. Cazanoue, M.; He, Z.; Neibecker, D.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1991**, 307–309.
1196. He, Z.; Neibecker, D.; Mathieu, *J. Organomet. Chem.* **1993**, *460*, 213–217.
1197. Michos, D.; Luo, X. L.; Crabtree, R. H. *Inorg. Chem.* **1993**, *32*, 2118–2122.
1198. Moldes, I.; Delavaux-Nicot, B.; Lugan, N.; Mathieu, R. *Inorg. Chem.* **1994**, *33*, 3510–3514.
1199. Carr, S. W.; Fowles, E. H.; Fontaine, X. L. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1990**, 573–579.
1200. Batsanov, A. D.; Howard, J. A. K.; Love, J. B.; Spencer, J. L. *Organometallics* **1995**, *14*, 5657–5664.
1201. Freeman, J. W.; Arif, A. M.; Ernst, R. D. *Inorg. Chim. Acta* **1995**, *240*, 33–40.
1202. Alvarez, D. Jr.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 5500–5508.
1203. Alvarez, D. Jr.; Caulton, K. G.; Evans, W. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5674–5676.
1204. Cendrowski-Guillaume, S. M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1996**, 1487–1491.
1205. Haefeli, U.; Tiefenauer, L. X.; Schubiger, P. A.; Weder, H. G. *Nucl. Med. Biol.* **1991**, *18*, 449–454.
1206. Deutsch, E.; Libson, K.; Vanderheyden, J. L.; Ketring, A. R.; Maxon, H. R. *Nucl. Med. Biol.* **1986**, *13*, 465–477.
1207. Singh, J.; Reghebi, K.; Lazarus, C. R.; Clarke, S. E. M.; Callahan, A. P.; Knapp, F. F. Jr.; Blower, P. J. *Nucl. Med. Commun.* **1993**, *14*, 197–203.
1208. Garcia-Salinas, L.; Ferro-Flores, G.; Arteaga-Murphy, C.; Pedraza-Lopez, M.; Hernandez-Gutierrez, S.; Azorin-Nieto, J. *Appl. Rad. Isot.* **2001**, *54*, 413–418.
1209. Mahmood, A.; Friebe, M.; Bolzati, C.; Jones, A. G.; Davison, A. *PCT Int. Appl.* **2001**, .
1210. Mathieu, L.; Chevalier, P.; Galy, G.; Berger, M. *Int. J. Appl. Radiat. Isot.* **1979**, *30*, 725–727.
1211. Panek-Finda, H. *PCT Int. Appl.* **1992**, WO9200758.
1212. Pinkerton, T. C.; Heineman, W. R.; Deutsch, E. *Anal. Chem.* **1980**, *52*, 1106–1110.
1213. 1230 Arano, Y.; Ono, M.; Wakisaka, K.; Uenzono, T.; Akisawa, H.; Motonari, Y.; Makata, Y.; Konishi, J.; Yokoyama, A. *Radioisotopes* **1995**, *44*, 514–522.
1214. Hashimoto, K.; Bagiawati, S.; Izumo, M.; Kobayashi, K. *Appl. Radiat. Isot.* **1996**, *47*, 195–199.
1215. Skaddan, M. B.; Katzenellenbogen, J. A. *Bioconjugate Chem.* **1999**, *10*, 119–129.
1216. DiZio, J. P.; Fiaschi, R.; Davison, A.; Jones, A. G.; Katzenellenbogen, J. A. *Bioconjugate Chem.* **1991**, *2*, 353–366.
1217. DiZio, J. P.; Anderson, C. J.; Davison, A.; Ehrhardt, G. J.; Carllson, K. E.; Welch, M. J.; Katzenellenbogen, J. A. *J. Nucl. Med.* **1992**, *33*, 558–569.
1218. Tessier, C.; Beauchamp, A. L.; Rochon, F. D. *J. Inorg. Biochem.* **2001**, *85*, 77–78.
1219. Pearson, D. A.; Lister-James, J.; McBride, W. J.; Wilson, D. M.; Martel, L. J.; Civitello, E. R.; Taylor, J. E.; Moyer, B. R.; Brian, R.; Dean, R. T. *J. Med. Chem.* **1996**, *39*, 1361–1371.
1220. Arteaga de Murphy, C.; Pedraza-Lopez, M.; Ferro-Flores, G.; Murphy-Stack, E.; Chavez-Mercado, L.; Asencio, J. A.; Garcia-Salinas, L.; Hernandez-Gutierrez, S. *Nucl. Med. Biol.* **2001**, *28*, 319–326.
1221. Giblin, M. F.; Jurisson, S. S.; Quinn, T. P. *Bioconjugate Chem.* **1997**, *8*, 347–353.
1222. Kniess, T.; Noll, S.; Noll, B.; Spies, H.; Johannsen, B. *J. Radioanal. Nucl. Chem.* **1999**, *240*, 657–660.
1223. Mach, R. H.; Wheeler, K. T.; Blair, S.; Yang, B.; Day, C. S.; Blair, J. B.; Choi, S.-R.; Kung, H. F. *J. Labelled Compd Radiopharm.* **2001**, *44*, 899–908.
1224. Wüst, F.; Skaddan, M. B.; Leibnitz, P.; Spies, H.; Katzenellenbogen, J. A.; Johannsen, B. *Bioorg. Med. Chem.* **1999**, *7*, 1827–1835.
1225. Wüst, F.; Spies, H.; Johannsen, B. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2729–2734.
1226. Hoepping, A.; Spiess, H.; Johannsen, B. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2871–2874.
1227. Amartey, J. K.; Parhar, R. S.; Al-Jammaz, I. *Nucl. Med. Biol.* **2001**, *28*, 225–233.
1228. Johannsen, B.; Scheunemann, M.; Spies, H.; Brust, P.; Wober, J.; Syhre, R.; Pietzsch, H.-J. *Nucl. Med. Biol.* **1996**, *23*, 429–438.
1229. Gali, H.; Hoffman, T. J.; Sieckman, G. L.; Owen, N. K.; Katti, K. V.; Volkert, W. A. *Bioconjugate Chem.* **2001**, *12*, 354–363.
1230. Schibli, R.; Schwarzbach, R.; Alberto, R.; Ortner, K.; Schmalle, H.; Dumas, C.; Egli, A.; Schubiger, P. A. *Bioconjugate Chem.* **2002**, *13*, 750–756.
1231. Spradau, T. W.; Katzenellenbogen, J. A. *Organometallics* **1998**, *17*, 2009–2017.
1232. Pietzsch, H.-J.; Gupta, A.; Reisgys, M.; Drews, A.; Seifert, S.; Syhre, R.; Spies, H.; Alberto, R.; Abram, U.; Schubiger, A.; Johannsen, B. *Bioconjugate Chem.* **2000**, *11*, 414–424.

Comprehensive Coordination Chemistry II
ISBN (set): 0-08-0437486
Volume 5, (ISBN 0-08-0443273); pp 271–402

5.4
Iron

M. V. TWIGG
Johnson Matthey, Royston, UK
and
J. BURGESS
University of Leicester, UK

5.4.1 GENERAL SURVEY

5.4.1.1 Introduction

The aim of this chapter is to document progress in the coordination chemistry of iron since the preparation of the two chapters on this element in *Comprehensive Coordination Chemistry* (*CCC*, 1987).[1,2] This area has flourished greatly in the nearly two decades since this first edition was published in 1987, and it is impossible to provide comprehensive coverage in the space available. Indeed we include probably considerably less than 20% of relevant publications. We have covered as wide a range of complexes as possible, documenting the intervening period (from early 1985 for iron(II), from the start of 1984 for iron(III)) fairly evenly, though with some emphasis on papers published in 2000, 2001, and early 2002, to provide points of entry to as many aspects as possible while at the same time providing generously referenced, if extremely concise, treatment of the most important and active areas. We have also included some aspects which were not mentioned in the first edition but are now of topical interest.

Section 5.4.1 has been kept brief, containing only the most important general matters and certain topics that cover a wide range of ligand types. Thereafter the bulk of this chapter (Sections 5.4.2 – 5.4.7) is arranged according to ligand type, in turn arranged according to Periodic Table arrangement of ligand donor atoms. For the many cases where complexes contain more than one type of ligand we have either documented the complex(es) under the heading appropriate to the more important ligand, or mentioned the complex under both (occasionally three) headings. Contrary to the general practice elsewhere in these volumes the principle division in Sections 5.4.2 onward is according to ligand type, with division by oxidation state secondary to this. This reversal of practice has been dictated by the great importance of mixed valence species in such areas as bioinorganic redox systems, magnetic materials, pigments, and fundamental studies of intramolecular electron transfer, and indeed of redox processes in general. Abbreviations for ligands that make only one appearance are generally defined at the point they appear in the text, whereas ligand abbreviations that appear in more than one place are listed and defined at the end of this chapter.

There have been two books devoted to the chemistry of iron,[3,4] and many reviews devoted to various aspects of its coordination chemistry, including structures[5] and photochemistry (iron(III)).[6] Iron complexes appear in a multi-author volume on the history of coordination chemistry,[7] but there is disappointingly little about iron—just a brief mention of hexacyanoferrates in connection with pigments—in an otherwise excellent overview of the history of chemistry.[8]

5.4.1.2 The Element

Pure iron is a fairly soft silver/white ductile and malleable moderately dense (7.87 g cm^{-3}) metal melting at 1,535 °C. It exists in three allotropic forms: body-centered cubic (alpha), face-centered cubic (gamma), and a high temperature body-centered cubic (delta). The average value for the lattice constant at 20 °C is 2.86638(19)Å. The physical properties of iron markedly depend on the presence of low levels of carbon or silicon. The magnetic properties are sensitive to the presence of low levels of these elements, and at room temperature pure iron is ferromagnetic, but above the Curie point (768 °C), it is paramagnetic.

There are four naturally occurring isotopes of iron (^{54}Fe 5.82%, ^{56}Fe 91.66%, ^{57}Fe 2.19%, ^{58}Fe 0.33%), and nine others are known. The most abundant isotope (^{56}Fe) is the most stable nuclear configuration of all the elements in terms of nuclear binding energy per nucleon. This stability, in terms of nuclear equilibrium established in the last moments of supernova events, explains the widespread occurrence of iron in the cosmos. The isotope ^{57}Fe has practical applications, most notably in Mössbauer spectroscopy, which has been widely exploited to characterize iron coordination complexes.

Iron dissolves in dilute mineral acids with evolution of hydrogen and formation of iron(II) salts. However, concentrated nitric acid and other powerful oxidants passivate the metal. Iron

filings or turnings are still used commercially to reduce aromatic nitro compounds, for example nitroarenes to the corresponding amines. In one variation of this process a morphological variant of Fe_3O_4 is produced which is used as a pigment.

Iron has a rich surface coordination chemistry that forms the basis of its important catalytic properties. There are many catalytic applications in which metallic iron or its oxides play a vital part, and the best known are associated with the synthesis of ammonia from hydrogen and nitrogen at high pressure (Haber–Bosch Process), and in hydrocarbon synthesis from CO/CO_2/hydrogen mixtures (Fischer–Tropsch synthesis). The surface species present in the former includes hydrides and nitrides as well as NH, NH_2, and coordinated NH_3 itself. Many intermediates have been proposed for hydrogenation of carbon oxides during Fischer–Tropsch synthesis that include growing hydrocarbon chains.

Iron oxides also have catalytic activity in mild hydrogenation reactions; for instance magnetite has long been used to bring water–gas (a mixture of hydrogen and carbon monoxide) to equilibrium with excess steam. The surface species present are less well defined than for the above reactions and those forming methanol on copper. These iron oxide species, like the iron–carbon, –nitride, and –hydride species mentioned above, may be considered at the very extreme of, or indeed beyond, coordination chemistry, but there is no hard and fast dividing line along the path linking these units to classical coordination complexes.

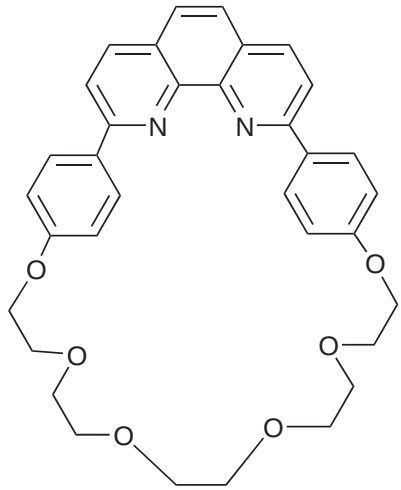
5.4.1.3 Oxidation States

Although the vast majority of coordination complexes of iron contain the metal in oxidation state two or three the lower oxidation states of one and zero are not uncommon, especially in areas bordering on organometallic chemistry. Oxidation state four is of relevance to bioinorganic electron transfer systems, while oxidation state six is represented by the ferrate(VI) anion, well known but rather little studied. Other oxidation states, from -1 to $+8$, have been at least mentioned in the past two decades. The more unusual oxidation states are briefly reviewed here, in ascending order.

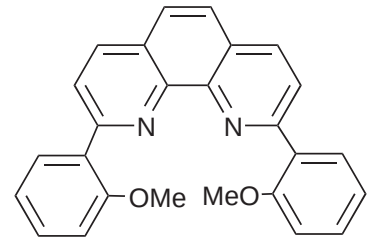
The stabilities of iron($-$I) in water and in liquid ammonia have been assessed based on an electrostatic model. The respective $\Delta G_f^\circ(Fe^-)$ values are $+505\,kJ\,mol^{-1}$ and $+439\,kJ\,mol^{-1}$, which are very similar to the values calculated for nitrogen, $\Delta G_f^\circ(N^-) = +506\,kJ\,mol^{-1}$ and $+451\,kJ\,mol^{-1}$.[9] The iron(0) complex $[Fe(CN)_4]^{4-}$ has been isolated in a reasonably pure state, from the reduction of $FeBr_2$, $FeBr_3$, or $Fe(NCS)_2$ by caesium metal in liquid ammonia in the presence of an excess of CsCN.[10] Iron(0) complexes may also be represented by the diazabutadiene complex $[Fe(dab)_2]$,[11] iron(I) complexes by the dibenzotetramethyltetraaza[14]annulene complex mentioned in Section 5.4.3.7.1.[12] $(Et_4N)_3[S_2Mo(\mu\text{-}S)_2Fe(\mu\text{-}S)_2MoS_2]$ may be regarded as a bis-$[MoS_4^{2-}]$ complex of iron(I).[13] The polyether–diimine macrocycle (**1**) forms a catenate $[Fe(cat)]^{2+}$ which is also readily reducible to $[Fe(cat)]^+$ and to $[Fe(cat)]^0$; the formally Fe^I species is remarkably stable.[14] Further examples of complexes in the actual or formal oxidation states 0 or $+1$ may be found under the diimine heading (Section 5.4.3.5.6).

There is often ambiguity in assigning oxidation states for complexes of ligands with strong π-interactions. Thus the substitution-inertness of the 1-, 2-, and 3-electron reduction products of $[Fe(diimine)_3]^{2+}$, diimine = bipy, phen, or bipym, and their spectroscopic properties, argue for their representation as iron(II) complexes containing one, two, or three anion radical ligands rather than as complexes of iron(I), iron(0), and iron($-$I).[15] Similar comments apply to the $[Fe(bmpphen)_2]^+$ and $[Fe(bmpphen)_2]^0$ species from electroreduction of $[Fe(bmpphen)_2]^{2+}$, bmpphen = 2,9-bis(2-methoxyphenyl)-1,10-phenanthroline, (**2**).[16] In similar vein, it is now apparent that for the iron complex produced in the long-established "Brown Ring Test" the formulation Fe^{III}—NO^- is to be preferred to Fe^I—NO^+ (see Section 5.4.3.8). Conversely chloroiron corrolates, and their imidazole derivatives, are formally iron(IV), but in fact are better regarded, in the light of NMR and ESR evidence, as iron(III) derivatives of corrolate π-cation radicals.[17]

There have been claims for soluble hydroxo-Fe^{IV} species, from ferrate decomposition, in strongly alkaline solution,[18] and for a transient $Fe^{IV}O^{2+}$ intermediate in the oxidation of Fe^{2+}aq by O_3.[19] Iron(IV) is stabilized by an amido-tetraazamacrocycle in the complex (**3**) (cf. amide ligands stabilizing Cu^{III}, Ni^{III}),[20] by the triamidoamine ligand and cyanide in $[Fe\{(Bu^tMe_2SiNCH_2CH_2)_3N\}(CN)]$, in which the iron(IV) is tetrahedrally coordinated,[21] and by (**4**) in [Fe(**4**)Cl], in which the iron(IV) is trigonal bipyramidally coordinated (PS_3Cl-donor set).[22] There have been many bioinorganic redox systems where ferryl, $Fe^{IV}{=}O^{2+}$, intermediates are believed to be involved, as, for just one example, in metmyoglobin catalysis of the decomposition

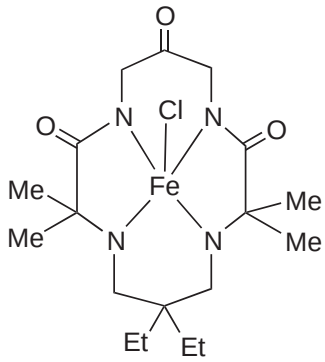


(**1**)

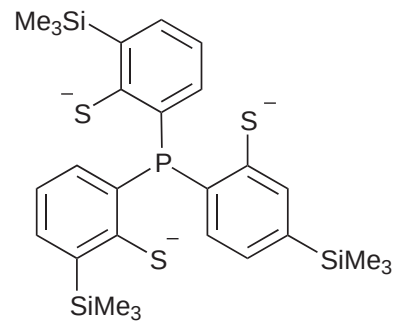


(**2**)

of hydrogen peroxide.[23,24] Electrochemical oxidation of $[Fe(tpp)F_2]^-$ generates an iron(IV) species,[25] while evidence for an iron(V)–porphyrin species was obtained in the course of an investigation of electrocatalytic hydroxylation. This iron(V) species contains an octafluoroporphyrin ligand and is believed to have either two F^- or an F^- and an O^{2-} coordinated to the metal.[26] Electronic spectra and reactivity of iron(IV) porphyrins have been reviewed,[27] as have resonance Raman spectra of iron(IV) and iron(V) porphyrin derivatives.[28] A tetra-negative *S*,*N*,*N*,*S*-donor ligand stabilizes iron(IV)[29] and iron(V) (see Sections 5.4.4.2 and 5.4.6.4).[30] Intermediates containing $Fe^{V}{=}O$ units are believed to be involved in Gif-type oxidations (O_2 or H_2O_2 oxidation of hydrocarbons in the presence of iron complexes, e.g., picolinates).[31] Iron(VI) may be represented here by the kinetics of ferrate(VI) oxidation of seleno-DL-methionine, which complement an earlier study of ferrate(VI) oxidation of methionine.[32] Determination of the structure of Na_4FeO_4[33] has permitted completion of the series of Fe—O bond distances in FeO_4^{n-} anions. These are 1.889Å, 1.807Å, 1.720Å, and 1.647Å for $Fe^{III}O_4^{5-}$, $Fe^{IV}O_4^{4-}$, $Fe^{V}O_4^{3-}$, and $Fe^{VI}O_4^{2-}$. At the oxidation state extreme it has been claimed that Fe^{VIII} is produced on disproportionation of ferrate, $Fe^{VI}O_4^{2-}$, if various possible reductants and catalysts are excluded.[34]



(**3**)



(**4**)

Whereas in many metalloprotein redox systems the oxidation states +2, +3, and +4 are involved, horseradish peroxidase catalysis appears to involve five oxidation states. The interest to coordination chemists of this study goes well beyond bioinorganic systems, for here, as in several cases reported earlier, the X-rays used to obtain the high-resolution structures induced chemical changes during structure determination. The X-rays liberate electrons, which may change the oxidation state of the metal.[35]

There are many important mixed valence and fractional formal oxidation state compounds (e.g., Fe_3O_4) and complexes of iron. Mixed valence trinuclear μ-oxo-carboxylato-complexes are dealt with in Section 5.4.5.4.2, polynuclear complexes held together by sulfide bridges in Section 5.4.5.9.2.

5.4.1.4 Spin States; Spin Cross-over

This section provides a general introduction, with a few complexes cited in illustration. Many further examples will be mentioned at appropriate points in Sections 5.4.2 onward. For iron(II) the two spin states are high-spin ($^5T_2$; $S = 2$) and low-spin ($^1A_1$; $S = 0$). For iron(III) the common spin states are high-spin ($^6A_1$; $S = 5/2$) and low-spin ($^2T_2$; $S = 1/2$). However, the intermediate spin state of 3/2 is now known for a number of iron(III) complexes, while in a few cases the mixed spin state $S = 3/2$, 5/2 has been observed (see porphyrin complexes, Section 5.4.3.7.2). Section 5.4.5.4.3 details S values for several polynuclear complexes.

Spin cross-over complexes exist both for iron(II) and for iron(III). The spin cross-over phenomenon is of considerable intrinsic interest and also potentially of great practical importance. The marked magnetic and optical[36,37] changes attendant on the low-spin/high-spin changeover make spin cross-over compounds strong candidates for controlling molecular switching;[38] and thermal hysteresis confers memory possibilities. Applications in temperature sensors, optical switching, information storage and retrieval, and memory devices[39] will be optimized by the use of polymeric species, where interactions and cooperativity magnify the desired effects.[40] Density functional calculations have been carried out for the high-spin and the low-spin forms of nine iron(II) complexes, including the familiar $[Fe(phen)_2(NCS)_2]$ and several bis-ligand complexes of terdentate ligands such as tris(2-pyridylmethyl)amine and tris(1-pyrazolyl)methane.[41]

There has been a detailed overview of the properties—crystal structures, magnetic properties, Mössbauer and vibrational spectroscopy—of iron(II) spin cross-over complexes,[42] a shorter general review of these complexes,[43] and a review covering the design and synthesis of such complexes.[44] Spin cross-over between the various states is determined by temperature and pressure and by ligand field strengths, which can be tuned by ligand variation, using either electronic or steric substituent effects. A review of structural changes accompanying spin-state transitions summarizes information on a range of Fe^{2+} and Fe^{3+} complexes, after detailing the specific and important case of $[Fe(2\text{-pic})_3]Cl_2 \cdot MeOH$ (2-pic = 2-picolylamine = 2-(aminomethyl)pyridine).[45] Spin cross-over kinetics for Fe^{II} complexes have been reviewed,[46] and enthalpies, entropies, and rate constants for a range of Fe^{II} and Fe^{III} spin cross-over complexes documented.[47] Thermodynamic and kinetic parameters, iron–ligand bond distance and volume changes, and calorimetric (including DSC) data relating to the low-spin/high-spin transition in solution and in the solid state obtained prior to 1991 have been fully documented and discussed.[48] A selection of thermodynamic and kinetic parameters relating to selected spin cross-over complexes, of 2-(2-pyridyl)imidazole (pyim) and *n*-(2-pyridylmethyl)picolinamidine (ppa),[49] tetrakis(2-pyridylmethyl)-*trans*-1,2-cyclohexanediamine (tpchxn),[50] 3-(1,10-phenanthrol-2-yl)-5-methyl-1,2,4-oxadiazole (phenmethoxa),[51] and 1,4,7-triazacyclononane (tacn),[52] in various solvents, is given in Table 1 (a little further information on dynamics may be found in Section 5.4.4.1.2). Activation

Table 1 Thermodynamic and kinetic parameters for low-spin ↔ high-spin ($^1A_1 \leftrightarrow {}^5T_2$) cross-over in solution.

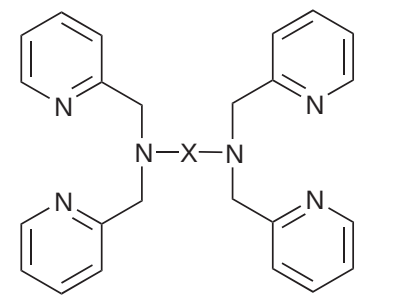
		ΔV°	$\Delta V^\ddagger_{15}$	$\Delta V^\ddagger_{51}$	ΔH°	$\Delta H^\ddagger_{15}$	$\Delta H^\ddagger_{51}$	ΔS°	$\Delta S^\ddagger_{15}$	$\Delta S^\ddagger_{51}$
$Fe(pyimH)_3^{2+}$	MeOH / 20% MeCN	+5.3	0.0	−5.3	15.5	26.7	11.2	+53	−23	−75
	MeCN	+14.3	+8.9	−5.4	32.3	46.6	14.3	+102	+41	−61
	Me_2CO	+10.3	+4.9	−5.4	15.9	32.0	16.1	+49	−7	−56
$Fe(ppa)_2^{2+}$	Me_2CO	+8.7	+2.6	−6.1	20.3	33.7	13.4	+52	−18	−70
$Fe(tpchxn)^{2+}$	MeCN	+11.5	+5.4	−6.1	24.2	26.0	1.8	+75	−27	−102
$Fe(phenmethoxa)^{2+}$	Me_2CO	+12.3	+3.9	−8.4	23.8	32.6	8.8	+94		
$Fe(tacn)_2^{2+}$	D_2O				23			+67		
	CDC_3N				21			+66		
	$(CD_3)_2CO$				24			+73		
	$(CD_3)_2SO$				22			+68		

Volumes are in $cm^3\,mol^{-1}$, enthalpies in $kJ\,mol^{-1}$, entropies in $J\,K^{-1}\,mol^{-1}$; sources and ligand abbreviations are given in the text.

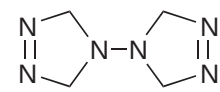
parameters may be primarily determined by the ease with which the coordinated ligands can twist—the hexadentate ligands (**5**) cause considerable impediment to the movement required for spin change, reflected in the determined activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$). The ease of twisting may be determined by solvation effects as much as by intrinsic rigidity of the complex itself.[53] The effect of solvent of crystallization on the ease of spin-state transitions has been explored, by high-resolution deuterium NMR spectroscopy, for polymeric $[Fe(1,2,4\text{-triazole})_3](ClO_4)_2 \cdot nD_2O$ and its 4-amino derivative.[54] An unusual application of isokinetic relationships has been to spin cross-over systems, especially of Fe^{II} complexes.[55]

Activation volumes for spin cross-over are, apart from one designedly exceptional system, between 0 and $+10\,cm^3\,mol^{-1}$ for low spin → high spin and close to $+6\,cm^3\,mol^{-1}$ for the reverse, for a range of tris-diimine (e.g., 2-pyridylimidazole), bis-terimine, and hexadentate linked-bis-terimine complexes. The derived volume profiles indicate that transition states are approximately midway between initial and final states.[50] X-Ray absorption spectroscopy (XANES) gives useful information on structural changes associated with pressure-induced spin cross-over, as was demonstrated for a selection of well-established "traditional cross-over" systems, such as $[Fe(phen)_2(NCS)_2]$, and several novel spin cross-over complexes. "Transition pressures" are reported for all these systems, and discussed in terms of pressure effects both on structural phase transitions and iron–ligand bond distances, and also on hydrogen-bonding networks. Increasing the pressure on a high-spin sample of the hydrate or ethanol solvate of $[Fe(pic)_3]Cl_2$ involves both of these factors. Pressure effects sometimes show that a change in spin state is not a single simple process. Thus increasing the pressure applied to high-spin $[Fe(btrz)_2(NCS)_2]$, where btrz = 4,4′-bis-1,2,4-triazole (**6**), produces a second high-spin modification before the change to the low-spin state.[56] Further information on this and a number of other iron–triazole and iron–tetrazole complexes exhibiting spin cross-over behavior is given in Section 5.4.3.6 below. The *cis*-1,2-bis(diphenylphosphino)ethene complexes $[Fe(Ph_2PCH{=}CHPPh_2)_2X_2]$, X = Cl or Br, undergo pressure-induced spin-state transitions at about 8 kbar and about 60 kbar, respectively.[57] Several iron complexes are mentioned in a review of pressure effects on spin cross-over and associated effects on electronic spectra.[58]

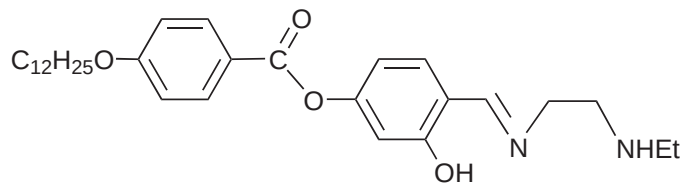
The synthesis of the NO_3^- and PF_6^- salts of the iron(III) complex of the terdentate phenolate anion of the liquid crystal Schiff base (**7**) provides the first example of the coexistence of spin transition and liquid crystal properties in a single compound. The ligand now needs to be tuned to increase the spin cross-over transition temperature and decrease the transition temperature to the liquid crystal state.[59]



(**5**)



(**6**)



(**7**)

A different, indeed unique, type of spin cross-over behavior is claimed for the mixed valence dithiooxalate salt $Pr^n{}_4N[Fe^{II}Fe^{III}(dto)_3]$.[60] Here the spin change is associated with electron transfer, with the bridging dithiooxalate favoring Fe^{III}—S bonding at higher temperatures, Fe^{III}—O bonding at lower temperatures:[61]

$$(dto)_2Fe^{II}(S_2C_2O_2)Fe^{III}(dto)_2 \underset{110K}{\overset{120K}{\rightleftharpoons}} (dto)_2Fe^{III}(S_2C_2O_2)Fe^{II}(dto)_2 \quad (3)$$

It may be recalled that mononuclear $[Fe^{III}(dto)_3]$ contains an FeS_6 core, but dto is *O*,*O*′-bonded to Fe^{III} in $[Fe^{III}\{(dto)Ag\}_3]$.[62,63]

5.4.1.5 Spectroscopy

Electronic and vibrational spectroscopy continues to be important in the characterization of iron complexes of all descriptions. Charge-transfer spectra, particularly of solvatochromic ternary diimine–cyanide complexes, can be useful indicators of solvation, while IR and Raman spectra of certain mixed valence complexes have contributed to the investigation of intramolecular electron transfer. Assignments of metal–ligand vibrations in the far IR for the complexes $[Fe(\mathbf{8})_3]^{2+}$ were established by means of $^{54}Fe/^{56}Fe$ isotopic substitution.[64] A review of pressure effects on electronic spectra of coordination complexes includes much information about apparatus and methods and about theoretical aspects, though rather little about specific iron complexes.[58]

Proton NMR spectroscopy is valuable in characterization, particularly in the case of low-spin iron(II) complexes, but can be informative for a range of paramagnetic species, including metalloproteins.[65] Proton NMR has also proved valuable in determining kinetic parameters for a variety of moderately fast reactions. There are extremely few data on ^{57}Fe NMR of iron complexes, which reflects the particularly unsuitable properties of this nucleus – $S = 1/2$, but it has low sensitivity, low abundance, and long relaxation times.[66,67] However data are available for, e.g., cyanide, bipy, and protoporphyrin IX ($ppixH_2$) derivatives,[68] with ^{57}Fe NMR spectroscopy used in probing iron–ligand interactions and estimating stability constants for adduct formation for [Fe(ppix)(CO)].[69]

Iron complexes are particularly good candidates for examination by Mössbauer spectroscopy,[70] including complexes of biological relevance.[71] Mössbauer spectroscopy gives much valuable information, though sometimes data are difficult to understand and interpret. However iron is one of rather few elements for which there is (or even can be) a wealth of data. Mössbauer spectra arise from re-absorption by ^{57}Fe of gamma-rays derived from an excited state of ^{57}Fe in a source formed in the radioactive decay of ^{57}Co, which has a half-life of 270 days. ^{57}Fe is sufficiently abundant for excellent spectra to be obtained routinely with natural iron containing compounds, whilst materials enriched in ^{57}Fe give very good spectra in less time. However, in some cases (e.g., where samples have low overall iron content) it may prove essential to use enriched iron. A reference material, usually stainless steel or sodium nitroprusside, $Na_2[Fe(CN)_5NO]\cdot 2H_2O$, is assigned a value of zero and the shift of the sample measured relative to it. This chemical shift (δ) is affected by the electronic environment of the iron and is temperature dependant. It arises from interaction of *s*-electrons at the nucleus and is a linear function of their density there. With high-spin complexes δ depends on oxidation state: from $+1.0\,mm\,s^{-1}$ to $+1.6\,mm\,s^{-1}$ for iron(II), and from $+0.45\,mm\,s^{-1}$ to $+0.75\,mm\,s^{-1}$ for iron(III) complexes. Ligand type also influences the value of δ. Large chemical shifts are not observed with low-spin complexes; both iron(II) and iron(III) low-spin complexes have δ in the range $0.0\,mm\,s^{-1}$ to $+0.3\,mm\,s^{-1}$. The iron $I = 1/2$ to $I = 3/2$ nuclear transition is split by an electric quadrupole to give a two line Mössbauer spectrum (the quadrupole splitting energy ΔE_q), and if the sample is also in a magnetic field a six line spectrum results when the nuclear spin degeneracy is removed. An electric field gradient at the iron nucleus can arise from asymmetric occupancy of *d* orbitals, or from asymmetry of the ligand field. Accordingly high-spin iron(III) complexes with identical ligands have small ΔE_q values, but similar iron(II) complexes have a two line Mössbauer spectrum. The symmetrical electronic configuration and ligand environment of low-spin iron(II) complexes with identical ligands, for example $[Fe(CN)_6]^{4-}$, has a single line Mössbauer absorbance, while the asymmetric electronic configuration of low-spin iron(III) complexes results in them having a spectrum similar to those of low-spin iron(II). Many low-spin $[FeX_4Y_2]$ and $[FeX_5Y]$ complexes with asymmetric ligand environments

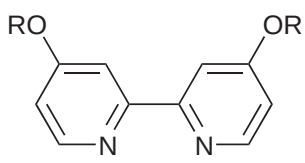
have had their two peak Mössbauer spectra recorded. Mössbauer spectroscopy using synchrotron radiation operates in the time domain instead of the usual energy domain; this new approach has been applied to the study of iron porphyrin complexes.[72]

Mössbauer spectroscopy, together with IR and Raman, NMR, and ESR, has proved especially useful in probing kinetics of fast reactions, sometimes giving rate constants directly, sometimes, in appropriate combinations of techniques, giving an indication of possible ranges or limits. Examples of this type of application include very fast intramolecular electron transfer, as in mixed valence Fe_3O complexes (see Section 5.4.5.4.2), and spin state interconversion. Thus, for example, spin state interconversion is fast on the Mössbauer timescale ($k > \sim 10^7\ s^{-1}$) for iron(III) complexes of dithiocarbamate, monothiocarbamate, and N_4O_2-donor Schiff bases, slow for most other spin cross-over iron complexes. However interconversion of one N_4O_2 Schiff base complex has been shown to be rapid on the Mössbauer timescale but slow on the ESR timescale ($k \sim 10^{10}\ s^{-1}$) (see *N*,*O*-Donors, Section 5.4.4.1.2).

5.4.1.6 Kinetics and Mechanisms

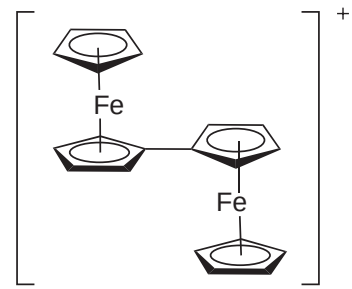
Kinetics and mechanisms of substitution and redox reactions of Fe^{II} and Fe^{III} complexes have been discussed in their overall inorganic context[73,74] and were fully documented periodically up until 1994.[75–79] Reactions of aqua- and solvento-species have been reviewed in the general context of solvent exchange and complex formation.[80] It is now clear that the mechanisms of solvent exchange and complex formation are, in the absence of unusual complications, I_d at Fe^{2+}aq, I_a at Fe^{3+}, and I_d at $FeOH^{2+}$aq. Kinetic investigations, with the occasional mechanistic exception, are outlined in Section 5.4.5.1. The importance of activation volumes in mechanistic diagnosis of reaction mechanisms for inorganic complexes in recent years has been discussed.[81–89] Kinetic and structural *trans*-effects in octahedral complexes, including some iron(II) dioximate and porphyrin complexes, have been documented descriptively in an extensive review.[90]

Low-spin t_{2g}^6 iron(II) complexes, such as $[Fe(CN)_6]^{4-}$ and $[Fe(diimine)_3]^{2+}$, are useful substrates in the study of electron transfer, in that substitution-inertness generally ensures that the reductant does not dissociate for the duration of the electron transfer process. Similarly $Fe^{II}(CN)_5$ is a useful component for intramolecular electron transfer studies (see Section 5.4.2.2.5), indeed comparisons of the oppositely charged $Fe^{II}(CN)_5^{3-}$ and $Ru^{II}(NH_3)_5^{3+}$ systems can help in sorting out electrostrictive solvation effects, in reactivities and activation volumes. The study of very fast intramolecular electron transfer in mixed valence complexes has already been mentioned in connection with probing by appropriate spectroscopic techniques. Such studies are complemented by, and should be considered alongside, analogous studies on a variety of mixed valence bi-ferrocenium cations, such as (**9**).[74] The extent of valence localization in the mixed valence bis-fulvalenedi-iron(II) cation is significantly pressure-dependent.[91] These and other electron transfer reactions—inner-sphere, outer-sphere, and intramolecular—are dealt with at appropriate points below.



R = dodecyl; octadecyl

(**8**)



(**9**)

5.4.1.7 Size and Solvation

A compilation of metal to donor atom distances in complexes, as determined by X-ray and neutron diffraction techniques up to early 1988, provides a comprehensive summary of such data

for iron complexes.[92] The volumes of the iron(III) complex anions $[FeCl_4]^-$, $[FeF_6]^{3-}$, and $[Fe(CN)_6]^{3-}$ have been estimated as 0.155 nm^3, 0.155 nm^3, and 0.265 nm^3 from calculations based on relations between lattice energies, thermochemical radii, and molecular volumes (and an appropriate single ion assumption) carried out for appropriate salts of these complex anions.[93] Thermochemical radii of these anions, and of $[FeWSe_2(CO)]^{2+}$, are included in a tabulation of more than 400 self-consistent values for an enormous range of polyatomic ions.[94]

Partial molar volumes have been derived, by calculation and from experiment, for the $[Fe(phen)_3]^{2+}$, $[Fe(bipy)_3]^{2+}$, $[Fe(gmi)_3]^{2+}$, $[Fe(cmi)_3]^{2+}$, $[Fe(Me_2bsb)_3]^{2+}$, $[Fe(CN)_6]^{3-}$, and $[Fe(edta)]^-$ complex ions in aqueous solution.[95] Preferential solvation of a variety of iron(II) and iron(III) complexes in methanol–water mixtures has been assessed through transfer chemical potentials derived from solubility measurements. A selection of trends, from strongly hydrophilic tris-oxalatoferrate(III) to a complex of a very lipophilic Schiff base, is shown in Figure 1.[96]

Solvation is important in several areas of the coordination chemistry of iron. Its role in affecting reactivity in various aspects of substitution and electron transfer reactions has been much investigated in recent years, while ligand and complex solvation are of central importance to pharmacological aspects of iron complexes. In the latter area it is necessary to achieve appropriate solvation properties for, e.g., oral administration, absorption in the gastrointestinal tract, and trans-membrane passage of chelator and of complex. In this area solvation is generally assessed through partition (distribution) coefficients and hydrophobic/lipophilic balances (HLB).[97–100] Solvation of complexes may also be assessed through hydration enthalpies or, less infrequently, partial molar volumes (cf. above); preferential (selective) solvation may be probed through solubilities and thence transfer chemical potentials. These last feature in this review in

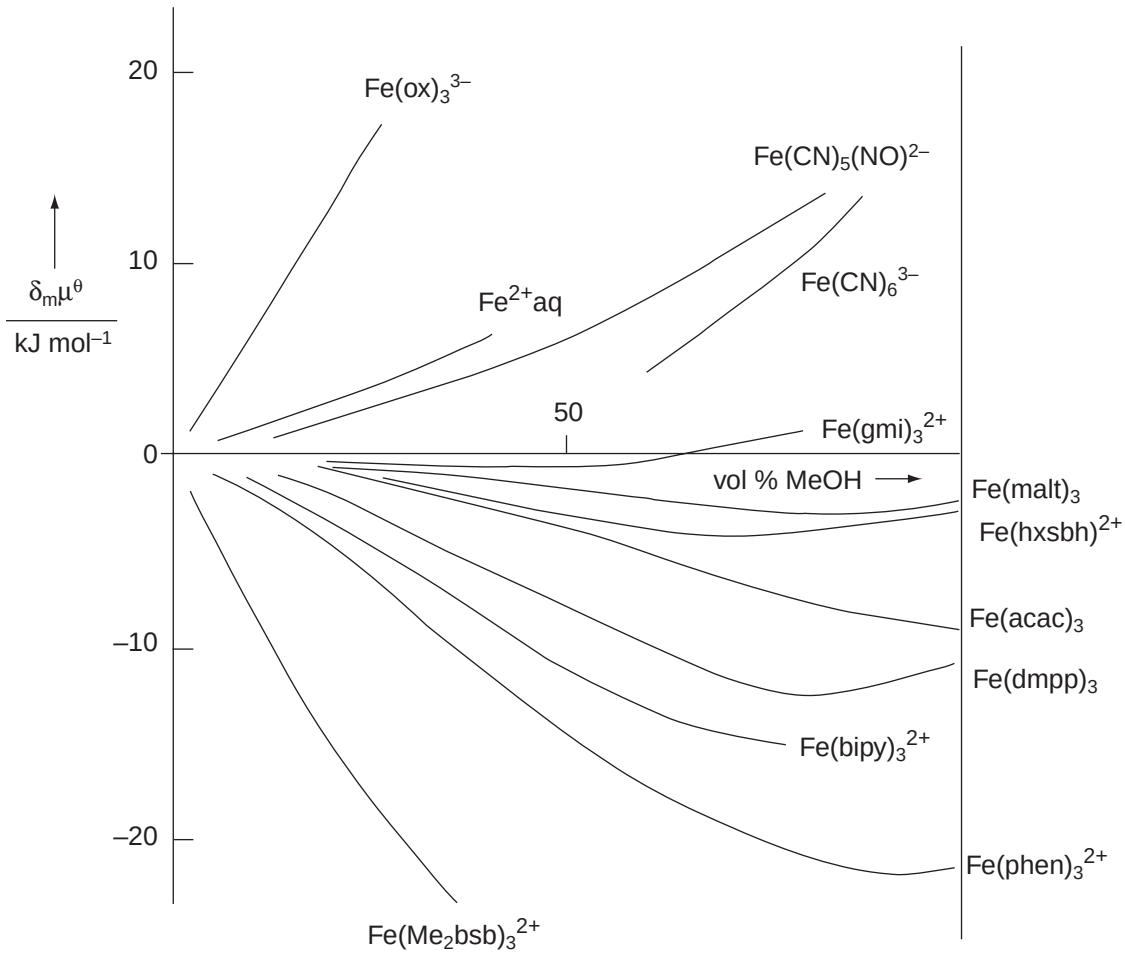


Figure 1 Transfer chemical potentials for selected iron complexes from water into aqueous methanol (on the molar scale, at 298 K). Ligand abbreviations not appearing in the list at the end of this chapter are: acac = acetylacetonate (2,4-pentanedionate); dmpp = 1,2-dimethyl-3-hydroxy-4-pyridinonate, the anion from (**24**); malt = maltolate (2-methyl-3-hydroxy-4-pyranonate, the anion from (**233**)).

Table 2 Solvational (electrostrictive) volume changes ($cm^3\ mol^{-1}$) for the half-reactions shown.[105,107] [a]

Diimine	*bipy*	*phen*
$[Fe(H_2O)_6]^{3+/2+}$	+4	
$[Fe(diimine)_3]^{3+/2+}$	+19.9	+18.6
$[Fe(diimine)_2(CN)_2]^{+/0}$	+5.3	[b]
$[Fe(diimine)(CN)_4]^{-/2-}$	−13.8	−13.6
$[Fe(CN)_6]^{3-/4-}$	−26.8	

[a] The value for $Fe^{3+/2+}aq$ is $+4\,cm^3\ mol^{-1}$. [b] No value reported – presumably $[Fe(phen)_2(CN)_2]$ is too sparingly soluble.

relation to the analysis of reactivity trends in binary aqueous solvent mixtures into their initial state and transition state contributions.[101–104] Detailed discussion of reaction and activation volumes for electron transfer reactions requires that such volumes be dissected into their intrinsic and solvation components. Iron–cyanide and iron–diimine complexes provide useful vehicles for this, since the crystallographic radii of the iron(II) and iron(III) forms of hexacyanoferrate and of tris-diimine cations such as $[Fe(bipy)_3]^{n+}$ and $[Fe(phen)_3]^{n+}$ are in each case essentially equal. There is thus a negligible contribution from such couples to intrinsic volume changes for redox reactions. If the determined volume change for a redox reaction can be split with the aid of an appropriate single ion assumption into its components for the two couples, then the contributions from iron–cyanide or –diimine complexes can be ascribed to solvation changes. In this way the values shown in Table 2 were derived; the great range of values for the series shown reflects the great difference between the solvational requirements of strongly hydrophilic cyanide and those of ligated bipy or phen, whose solvent-accessible peripheries are strongly hydrophobic.[105,106] The situation with regard to $Fe^{3+}aq/Fe^{2+}aq$ is more complicated, due to the significant intrinsic volume change in this case.[107]

Other aspects of solvation have included the use of surfactants (SDS, CTAB, Triton X-100), sometimes in pyridine-containing solution, to solubilize and de-aggregate hemes, i.e., to "dissolve" them in water (see porphyrin complexes, Section 5.4.3.7.2). An example is provided by the solubilization of an iron–copper diporphyrin to permit a study of its reactions with dioxygen and with carbon monoxide in an aqueous environment.[108] Iron complexes have provided the lipophilic and hydrophilic components in the bifunctional phase transfer catalysts $[Fe(diimine)_2Cl_2]Cl$[109] and $[Et_3BzN][FeCl_4]$,[110] respectively.

5.4.1.8 Stability Constants and Speciation

Table 3 lists stability constants for complex formation from Fe^{2+} and a range of common ligands, all values being from one investigation.[111] Further information on stabilities of iron complexes may be found in several later sections, especially Sections 5.4.5.5 and 5.4.5.6 on hydroxypyridinones and siderophores.

Table 3 Stability constants for formation of Fe^{2+} complexes, in aqueous solution at 298 K.[111] [a]

	$log\ \beta_1$	$log\ \beta_2$	$log\ \beta_3$
Malonate	2.24		
Oxalate	3.05	5.01	
Glycinate	3.73	6.65	8.87
1,2-Ethanediamine	4.26	7.73	10.17
Iminodiacetate	5.45	9.82	
Diethylenetriamine	5.66	9.61	
Triethylenetetramine	7.12		
Nitrilotriacetate	8.05	11.53	
Ethane-1,2-diamine-*N*,*N*′-diacetate	8.63	10.67	

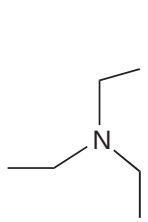
[a] Experimental uncertainties in log β claimed to be ±0.03 or smaller.

Information about speciation, composition and precipitation for 20 iron(III)–ligand, 19 iron-(II)–ligand, and 17 ternary iron(II)-carbonate–ligand aqueous systems, for ligands such as cyanide, oxalate, glycine, hydroxycarboxylates, and polyaminocarboxylates, has been computed and is graphically presented alongside similar data for 44 other elements.[112]

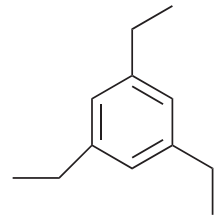
In a review on the design of ligands for selective complexation of metal ions in aqueous media[113] and a book on the principles underlying stability constants and on the design of metal complexes for various medical applications[114] iron complexes and their solution chemistry take their appropriate place.

5.4.1.9 Tripodal and Encapsulating Ligands

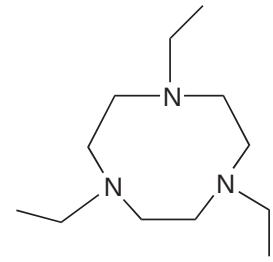
The requirements for stable, strongly coordinating and substitution-inert complexes of the Fe^{2+} and Fe^{3+} cations have led to the design of a large number of complexes containing tripodal or encapsulating polydentate ligands. Despite the variety of chelating moieties involved—especially diimines (Section 5.4.3.5), catechols and hydroxamates (Section 5.4.5.6), and porphyrins[115]—there are just a few commonly used approaches to designing and generating such ligands.[116] Most tripodal ligands are based on a vertex of the type shown as (**10**), (**11**), or (**12**), or are tris-*n*-substituted triazacycloalkanes or cyclic triazines. Many encapsulating ligands have two such groups as caps, or two caps of type (**13**) or (**14**). There are also many examples scattered through this chapter of tetradentate and pentadentate ligands, which may be regarded as dipodal, generated by analogous synthetic approaches.



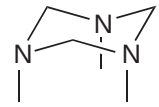
(**10**)



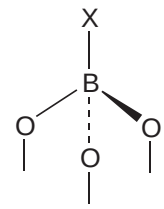
(**11**)



(**12**)



(**13**)



(**14**)

5.4.1.10 Template and Supramolecular Chemistry

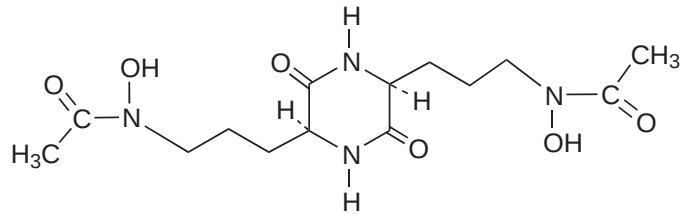
This section follows naturally from the preceding section in that the encapsulating ligands and complexes mentioned there are often generated by template reactions. The use of octahedral templates rather than the ubiquitous tetrahedral copper(I) for catenand assembly has very rarely been exploited,[117,118] but interest in moving from tetrahedral Cu^{+} to octahedral metal centers such as Fe^{2+} as templates is increasing.[119] Recently the reaction sequence for the construction of benzylic imine catenates using octahedral metal centers, including Fe^{2+}, as templates has been established.[120] The polyether–diimine macrocycle (**1**) forms catenates $[Fe(cat)]^{2+}$, $[Fe(cat)]^{+}$, and $[Fe(cat)]^{0}$.[14]

There are two levels of self-assembly in the formation of tetra-, penta- and hexanuclear products from polybipyridyls and iron(II) salts $FeCl_2$, $FeBr_2$ or $FeSO_4$ – the products are anion-dependent. The coordination of three bipy units, from different ligand molecules, to the

Fe^{2+} centers produces a helical structure; interaction of these helical strands with anions results in further molecular organization to form the final toroidal product. Parallels can be drawn between these helical and toroidal structures and secondary and tertiary structure in biological systems.[121] Thermodynamic and kinetic intermediates have been characterized in the self-assembly of a di-iron triple stranded helicate with bis(2,2′-bipyridyl) ligands.[122]

The formation of circular or linear forms seems to depend on balances between kinetic and thermodynamic control; iron(II)–poly-2,2′-diimine systems with their substitutionally inert metal centers provide useful systems for disentangling thermodynamic and kinetic contributions. The mechanism of formation of circular helicates is believed to entail a kinetically favored triple helicate intermediate.[123] Self-assembly of chiral dinuclear binaphthol-linked iron(III)–porphyrin complexes into extended polynuclear species takes place through the intermediacy of μ-oxo dimers.[124] "Predetermined" μ-oxo-di-iron-dimers may be used in this type of synthesis.[125]

The first example of a helical complex with pre-determined chirality was the dinuclear complex $[Fe_2(rdt)_3]$, where $rdtH_2$ is the fungal iron chelator rhodotorulic acid, (**15**), a dihydroxamate siderophore.[126] Several more helical and chiral Fe^{2+} and Fe^{3+} complexes are documented in the diimine and in the hydroxamate and catechol sections. A doubly looped ("bow tie") complex has been constructed with the aid of a tris-terimine ligand (Section 5.4.3.5.7).



(**15**)

Bis-pyridine compounds containing the conjugated spacers —CH=CH—, —N=N—, —CH=N—N=CH—, or —CMe=N—N=CMe— linking the four-positions of the two pyridine rings and having one pentacyanoferrate(II) group attached can be threaded through a cyclodextrin; coordination of a second pentacyanoferrate(II) moiety to the other pyridine then produces a rotaxane. Kinetic and mechanistic features of these systems have been described.[127] A 1:1 intermediate has been characterized and monitored in the first example of rotaxane formation using ferrocenyl-β-cyclodextrin stoppers.[128] Substituent variation may control the production of iron(II) vs. iron(III) in calixarene preparations.[129]

Iron figures prominently in a review[116] and a book[130] devoted to supramolecular chemistry, especially in the sections dedicated to siderophores, and also appears in various guises in a book on cyclodextrin chemistry.[131]

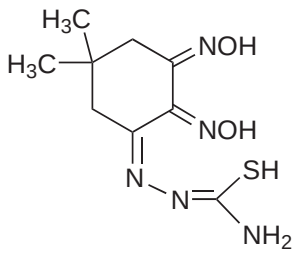
5.4.1.11 Applications and Relevance

5.4.1.11.1 Analysis

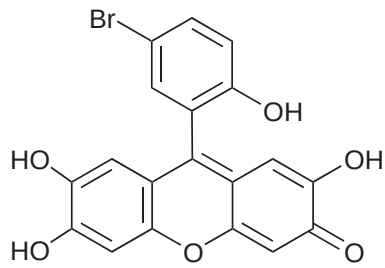
Iron complexes play two complementary roles in analysis. They feature prominently in the detection and estimation of iron in various forms and guises, and they also feature as reagents in the detection and estimation of a number of other elements. Both aspects are well illustrated in Schilt's classic text.[132]

In recent years there has been very much less activity in the development of ligands as reagents for iron analysis, or for the preparation of complexes for the determination of other metals. However, several pyridyl azines have been synthesized for analytical procedures[133]—e.g., the bis-3-hydroxy derivative of 2-pyridinaldazine has been proposed as an analytical reagent for several first-row transition metal 2+ cations, including Fe^{2+}.[134] 5,5′-Dimethyl-1,2,3-cyclohexanetrione-1,2-dioxime-3-thiosemicarbazone, dcdt (**16**), gives an intensely colored tris-ligand complex $[Fe^{II}(N,N'\text{-dcdt})_3]$ (violet, $\varepsilon_{550} = 8{,}900$; $\log \beta_3 = 14.2$) suitable for spectrophotometric determination of iron in foods, wines, and minerals.[135] Nonetheless the main activity has been in the development and refinement of various instrumental techniques employing well-established reactions and reagents. Thus, for example, there has been much activity in the development of flow

injection analysis[136] for iron, e.g., in blood,[137] in serum,[138] in saliva,[139] and in cerebrospinal fluid.[140] A flow injection spectrophotometric method using 5-bromosalicylfluorone, (**17**), and cetyltrimethylammonium bromide has been developed for the simultaneous determination of iron and aluminum.[141] A greatly improved method for the analysis of iron in serum uses polyoxyethylene sorbitan monolaurate (Tween-20) to mobilize the iron, which is determined spectrophotometrically with 4,7-diphenyl-1,10-phenanthroline.[142] Two standard addition kinetic methods for the simultaneous determination of Fe^{II} and Fe^{III} are based on $[Fe(phen)_3]^{2+}$ formation before and after Fe^{III} reduction[143] and on the vastly different rates of complex formation of Fe^{II} and Fe^{III} with gallic acid.[144] Iron(III)–hexamine gel has been suggested as a new chelating ion exchange material for analytical separations.[145]



(**16**)



(**17**)

Despite the continuing development and refinement of instrumental techniques for the analysis of total iron the estimation of iron(II) in geological and environmental samples still appears to be best carried out by redox titration methods,[146] which are of course dependent for their success on the proper application of coordination chemistry.

5.4.1.11.2 Pigments and colorants

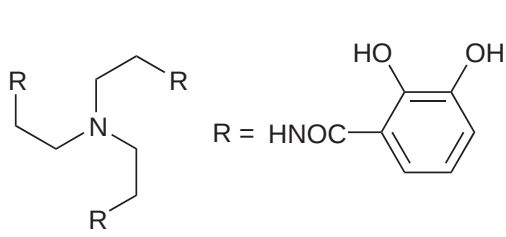
Several iron compounds and complexes have been, and are, in use as pigments and colorants. Various oxides and hydroxides are used in paints and wood stains, and as food coloring additives; several hexacyanoferrate derivatives have long been used as pigments or pigment components. The chemistry of these groups is documented in Sections 5.4.2.1 and 5.4.5.1 below, but here we can usefully mention a number of books which deal with colors of iron-containing species, one in the context of iron chemistry,[147] the others mainly in the overall context of inorganic and organic pigments, colorants, and dyes. One has detailed information on iron complexes, including the relation between color and spectroscopy,[148] others, including a historical perspective,[149] make brief mention of iron-containing species.[150–152] Iron oxide pigments make a brief appearance in a useful short review on testing and evaluating the optical and color properties of pigments;[153] several complexes and compounds of iron are mentioned in a detailed overview of inorganic pigments.[154]

5.4.1.11.3 Nutrition, metabolism, and pharmacology

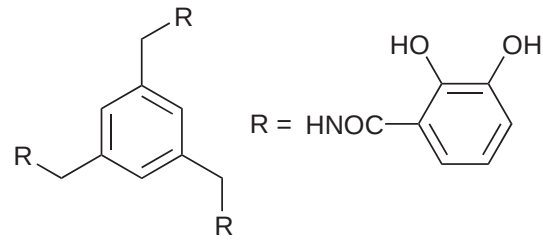
Iron is an essential element, for humans and for many forms of life, but even a modest excess can be toxic as the human body does not have an effective iron excretion mechanism. It is therefore necessary to maintain an appropriate level of iron in the body, to supply iron in absorbable form if it is deficient (anemia) and to remove iron if present in excess. Inorganic coordination chemistry plays an important role in dealing with these complementary conditions of deficiency and of excess. The latter condition is much more common than often supposed, for there are a number of conditions, such as hemochromatosis and thallasemia, where the build-up of iron in essential organs is eventually lethal. Mild iron poisoning is not infrequent in children, while even iron fortification of foodstuffs can have adverse effects.[155] Mild iron poisoning can be treated with bicarbonate or phosphate, which presumably complex and precipitate the iron.[156]

In relation to nutrition, the classic text by McCance and Widdowson has had one of its periodic updates and expansions, into a main volume and a series of supplements—mineral

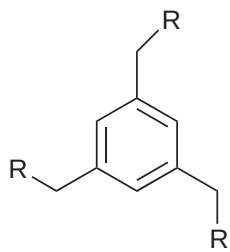
nutrients such as iron are dealt with in the main volume.[157] The topic is also dealt with briefly elsewhere.[158,159] Once ingested the iron, often in complexed form, plays many roles in metabolism,[160–163] especially in electron and oxygen transfer (and free radical chemistry[164]) but also in regulatory processes[165] and in combating infection.[166] Molecular mechanisms of metabolism, the transport of iron in cells,[167,168] and the effects of biological ligands on the precipitation of oxides and hydroxides of iron in human metabolism[169,170] have been discussed. Various fragments of iron complex chemistry appear in two long reviews on iron storage and transport[171,172] and a multi-author book on iron transport.[173] The coordination chemistry associated with the acquisition and transport of iron by microorganisms, which involves siderophores such as hexadentate tripodal tris-catecholates, e.g., (**18**) or (**19**), or tris-hydroxamates, e.g., (**20**) or (**21**), has been reviewed.[174]



(**18**)

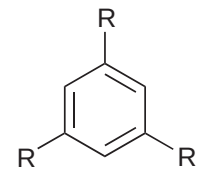


(**19**)



$R = NHCOCH_2CH_2N(O^-)COPh$

(**20**)



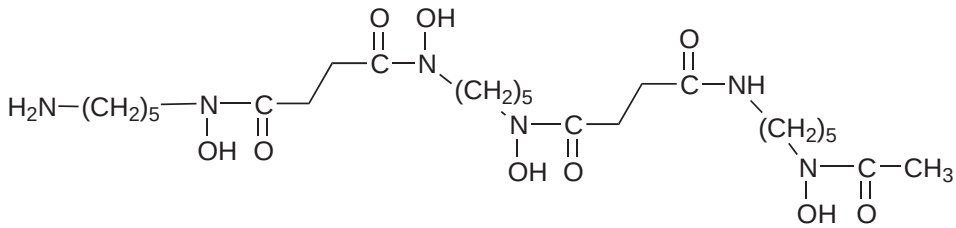
$R = -CONHCH_2CH_2CONHOH$

(**21**)

A healthy human on a normal diet ingests sufficient iron; a slight deficiency or mild anemia can be treated with iron supplements. Since simple Fe^{2+}aq and Fe^{3+}aq are poorly absorbed from the gastrointestinal tract—they are too hydrophilic—supplements generally contain the element in the form of a salt of an organic carboxylic acid, e.g., citrate, fumarate, gluconate, succinate, or orotate (uracil-6-carboxylate).[175] These anions can aid absorption in the gastrointestinal tract through significant ion-pairing or complexation giving one or more species with at least some lipophilic character. Phospholipid complexation and encapsulation of iron(II) sulfate is claimed to improve iron availability.[176] The use of iron supplements dates back to Ancient Egypt; they have maintained their reputation as remedies and tonics ever since, as for example documented for the time of Louis XV.[177]

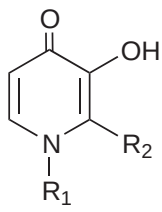
For many years the only fully approved drug for reducing iron levels in the body has been desferrioxamine, (**22**). This has several disadvantages, the main one being that oral administration is not successful—desferrioxamine is metabolized readily, albeit to iron-binding products.[178] Much effort has therefore been devoted to finding a substitute that can be administered orally. General overviews[179–185] include one dealing with the development of iron chelators for the treatment of Cooley's anemia. This reviews the design and testing of 41 compounds of varying types (including edta analogues, pyridoxyl derivatives, macrocyclic ligands with various pendant arms, hydroxamates, catechols), and compares their affinities for Fe^{3+}.[186] A concise account of iron chelators for thalassemia[187] is complemented by a generously referenced review which ranges from inorganic coordination chemistry to biology and medicine.[188] The status of oral iron chelators is reviewed periodically, as for instance in 1990[189] and in 2001,[190] and the prospects

for removal of iron, and of aluminum, from the brain by hydroxypyridinones assessed recently (2002).[191]

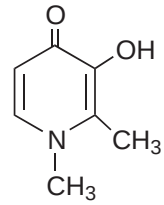


(**22**)

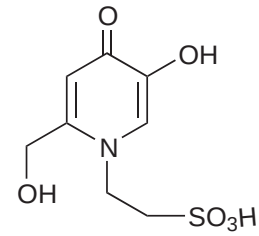
The most promising chelators for treating iron overload are hydroxypyridinones.[192] These are the main candidates[184] for oral administration to facilitate iron removal in the treatment of, e.g., thalassemia, hemochromatosis, siderosis, or severe iron poisoning[156] and, conversely, for administration of iron[193,194] in treating anemia[181,195] and sickle cell disease.[196] The most investigated series of hydroxypyridinones comprises numerous 3-hydroxy-4-pyridinones and their bidentate anions (**23**), with 1,2-dimethyl-3-hydroxy-4-pyridinone, (**24**), also known as CP20, L1, and Deferipron, the most studied.[197] 1-Hydroxy-2-pyridinones, early candidates for treatment of iron overload,[198] have proved less promising than 3-hydroxy-4-pyridinones for the control of iron levels, both in deficiency and in overload. 1,2-Dimethyl-3-hydroxy-4-pyridinone was first assessed for the treatment of iron overload in rats—where it was found to be of comparable effectiveness to desferrioxamine, but with the great advantage of oral efficacy[199]—then humans,[200] with the pharmacokinetics being established.[201] Long term clinical trials have assessed its value for the treatment of iron overload and of Cooley's anemia[202] and have investigated side effects.[203] It is now possible to document the progress, and disease complications where relevant, of patients treated with Deferipron for up to 25 years.[204] Recent reviews of its clinical effectiveness and status[190,205,206] have been complemented by multi-center assessments of its safety profile.[207] Despite all this activity on Deferipron there is good evidence that its mono-[208] or diethyl analogues may well be preferable[209]—for one thing they do less harm to certain enzymes. Carboxylate, sulfonate (e.g., the taurine/kojate ligand (**25**)),[210] or imidazolate[211] functionalized derivatives are potentially useful, the last particularly so since properties of the ligand and its complexes can readily be tuned by pH variation. The incorporation of basic groups such as NR_2, piperidyl, or imidazolyl as substituents on the ring nitrogen makes the hydroxypyridinones more appropriate for targeting lysosome iron.[212] The generally higher affinity of hexadentate ligands in comparison with tris-bidentate analogues has inspired a search for effective iron chelators of this type, e.g., by linking three bidentate chelating groups through units such as (**26**), (**27**), or (**28**) to form a tripodal ligand or using two such capping units to form an encapsulating or cage ligand (cf. Section 5.4.1.9). The requirements for appropriate solvation properties (cf. Section 5.4.1.7)—a balance between the opposing requirements of reasonably high water solubility for oral administration and sufficient lipophilicity for crossing membranes—and to avoid too much interference with the body's normal iron metabolism[213] always need to be borne in mind when developing new chelators. Suitable analytical methods, such as HPLC, have been developed for the estimation of levels of hydroxypyridinone ligands and complexes in human samples.[214]



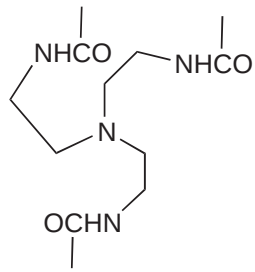
(**23**)



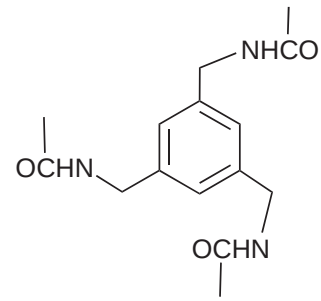
(**24**)



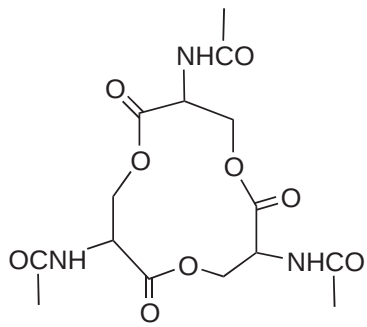
(**25**)



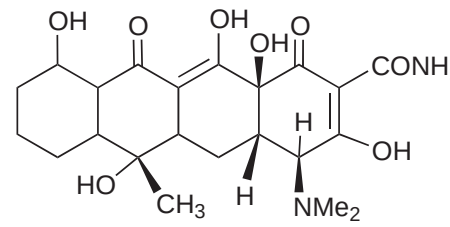
(**26**)



(**27**)



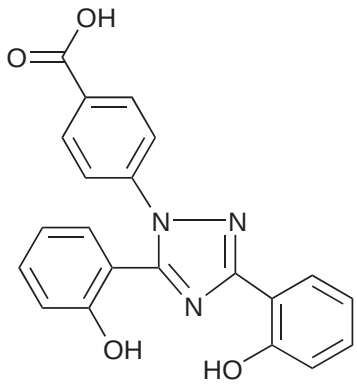
(**28**)



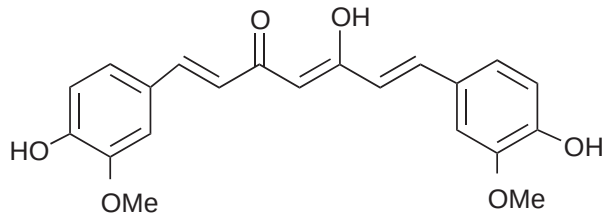
(**29**)

Turning to other types of potential iron chelators, tetracycline (**29**) and its derivatives form moderately stable complexes with Fe^{3+} and with Fe^{2+}, tetracycline probably acting as an *O*,*O*-donor ligand.[216] Several tetracyclines can remove iron from $Fe^{III}{}_2$-transferrin;[217] conversely $FeCl_3$ has been shown to reduce the antibiotic activity of tetracyclines.[218] 2,3-Dihydroxybenzoic acid was tested in the 1970s for decreasing iron overload (it is very specific for Fe^{3+}, particularly in relation to Mg^{2+} and Ca^{2+}),[219] then abandoned, but interest has recently been reawakened in connection with proposals for combination therapy; the administration of two iron chelators may be more efficient than of just one.[190] Bis-hydroxyphenyl-triazoles, e.g., (**30**), are a new class of iron chelators (terdentate, *O*,*N*,*O*-),[220] slightly more effective than desferrioxamine for removing iron. Their stability and selectivity (log $K_1 = 23.3$ for Fe^{3+}, 7.6 for Mg^{2+}, and only 5.5 for Ca^{2+}) make them promising candidates for trials for iron overload treatment.[221] Other proposed chelators include *N*,*N*′-bis(2-hydroxybenzyl)ethanediamine-*N*,*N*′-diacetate (which, like desferrioxamine, is hexadentate),[222] curcumin (**31**),[223] and several diimine derivatives of 2,2′-bipyridyl, (**32**) with R = e.g., —COMe, —CO(*n*-nonyl), —CO(C_6H_5X)[224] and (**33**) with R = e.g., phenyl, *o*-tolyl or 2-pyridyl,[225,226] and of 1,10-phenanthroline, (**34**) with R^1 = e.g., phenyl or —C_6H_4X and R^2 = H or Bu and (**35**) with R = e.g., phenyl or —C_6H_3-3,4-Cl_2. Of all these potential ligands only one, (**33**) with R = CH_2-2-C_5H_4N, shows effectiveness comparable with desferrioxamine and the hydroxypyridinonates as an iron chelator and shows potential as an inhibitor of cell growth.[227] These diimines presumably target iron(II) rather than the more important (in this context) iron(III).

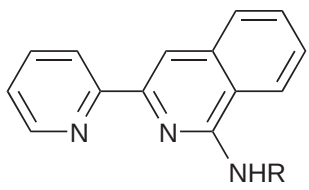
The removal of iron from such species as transferrin or ferritin by hydroxypyridinones, siderophores, and other chelators is of considerable relevance to the control of iron levels in the body, and indeed to iron metabolism in a range of life forms. Methods and mechanisms for such removal are referenced in Sections 5.4.5.2, 5.4.5.5.2, 5.4.5.6.1, and 5.4.5.6.2 below. Interestingly cyanide, one of the most powerful ligands for iron, appears to prefer to bind to iron–transferrin, at the C-terminal Fe^{III}, rather than to remove the iron. This adduct is believed to contain the iron in an octahedral environment of three cyanide ligands (*mer*) and nitrogens from two tyrosine residues and a histidine.[228]



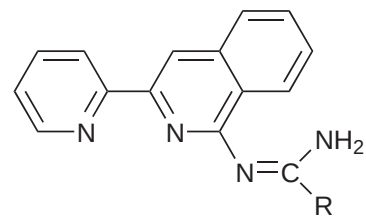
(**30**)



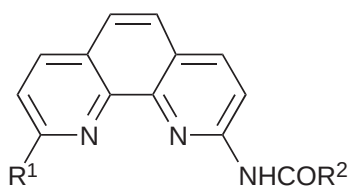
(**31**)



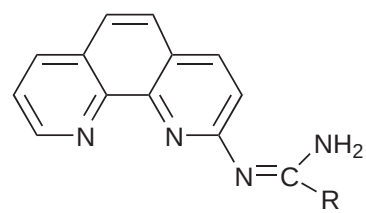
(**32**)



(**33**)



(**34**)



(**35**)

Iron compounds and complexes are returning to favor as contrast agents for use in magnetic resonance imaging (MRI). Iron(III) chloride was the first inorganic contrast agent used in a human, administered orally for gastrointestinal tract imaging. Salts such as iron(III) ammonium citrate (the main ingredient in Geritol, an iron supplement for anemia) and iron(II) sulfate were subsequently assessed as contrast agents.[229,230] Iron(III)–ethylene-bis-(2-hydroxyphenylglycine) has been used for hepatobiliary imaging,[231,232] replacing gadolinium complexes in certain circumstances. Iron is much less toxic than gadolinium, and although gadolinium complexes generally have considerably more favorable relaxivities[214,233] relaxation properties of ternary aqua-iron(III) complexes can be varied considerably by varying the ligand. Thus the residence time for a water molecule on Fe^{3+} is 10^5 times shorter in an iron(III)–aqua-porphyrin complex than in Fe^{3+}aq. Ferritin has also been assessed as an MRI contrast agent.[234] However most recent authors refer to iron oxide nanoparticles, e.g., coated with dextran,[235] as contrast agents.[236] Water-soluble complexes, perhaps of the hydroxamate type considered earlier for imaging,[237] will presumably be required for the current extension of MRI to MRM, magnetic resonance microscopy.[238] A polynuclear $FeGd_3$ species, which is effectively $Fe(phen)_3^{2+}$ with a dota-Gd^{3+} substituent at the five-position, has been synthesized and assessed.[239]

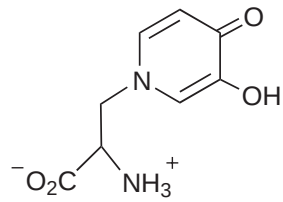
Iron-52 has been considered for use in positron emission tomography.[240] Iron porphyrins and phthalocyanines[241] have been assessed for use in photodynamic therapy. It has been suggested that photolytic release of nitric oxide from Roussin's salts (Section 5.4.5.9.2) or nitrosyl porphyrin complexes may sensitize tissues to radiotherapy.[242] The role of iron biominerals in medicine has been discussed.[243]

5.4.1.11.4 Geochemical and environmental aspects

As life evolved on Earth photosynthetic processes released molecular oxygen into the atmosphere and made it increasingly oxidizing. Since iron(II) salts in aqueous solution are readily oxidized by molecular oxygen, increased oxygen levels led to the formation of highly insoluble iron(III) hydroxide species in lakes and oceans that in time became vast oxide ore deposits. The principles underlying the chemistry of iron in natural waters have been presented in Stumm and Morgan's long-established text[247] and in Pankow's more recent book.[248] Chester gives a more geologically oriented treatment.[249] Kinetic aspects have been the subject of detailed discussion, with iron one of three elements singled out for major coverage,[250] and the role of iron in the more specific environment of estuaries mentioned.[251] Complexes of iron make several brief appearances in books on environmental chemistry in general,[252,253] in groundwater in particular,[254] and very specifically in Botswana savanna.[255] The first three references in the previous sentence are concerned both with natural systems and with pollution. Today iron is not a significant contaminant in the sea but it has come to prominence as a result of dumping "red mud" from the extraction of aluminum from bauxite—this waste material contains between 5 and 40% iron[256]—and acidic iron(II) sulfate from the traditional production of titanium dioxide. In Western Europe several million tons of acidic iron(II) sulfate solution were discharged each year into the sea directly or via rivers. As the Fe^{II} becomes oxidized it is precipitated as complex hydroxo-iron(III) species that drift as a suspension before settling on solid objects. Cases of contamination of shellfish and of the gills of fish have been reported, but there does not appear to have been major ecological damage. Nevertheless, the disposal of iron(II) sulfate waste in this way has been markedly reduced in recent years. However, it has been suggested[257,258] that $FeSO_4$ be dosed into ocean at very low concentration to stimulate plankton growth, thus to encourage them to absorb CO_2, convert it into $CaCO_3$, and so deposit excess of greenhouse gas on the ocean floor. Early experiments to test this idea fell foul of the high affinity of Fe^{3+} for hydroxide and oxide ligands, as the added Fe was deposited on the ocean floor before it could have significant effect.

Alterobactin A, a hydroxycarboxylate–catechol siderophore from an oceanic bacterium, has an extremely high affinity for iron(III) (see Table 12 below).[259] Photolysis of iron(III) siderophore (hydroxycarboxylate–hydroxamate) complexes in the surface ocean produces iron(II), increasing iron availability for plankton.[260] There is a copious literature on iron biominerals in the environment,[243,261] on oxidation of iron(II) species[262] and on the precipitation of iron(III) in environmental systems,[263,264] both in natural waters and in manmade systems such as mine drainage, to which the references cited here provide points of entry. The effects of biological ligands on the precipitation of oxides and hydroxides of iron in marine environments have been considered.[169,170] Much more specific is a consideration of iron(III)–fulvic acid interactions.[265–267] A review of model compounds for iron–oxygen aggregation and biomineralization links fairly simple complexes to metalloproteins such as ferritin and hemerythrin; carboxylate bridges support simple oxo bridges throughout the range.[268]

Iron(II) salts are generally believed toxic to plant life, as for example in the use of iron(II) sulfate as a moss killer, but conversely iron complexes are used to make hydrangeas blue. Iron(II) sulfate is used as a detoxicant in cases of mimosine (**36**) poisoning of sheep and cattle[269]—alopecia may thus result from consuming a certain shrub in northern Australia,[270,271] while the use of mimosine as a defleecing agent[272] may result in accidental poisoning. Iron toxicity in asbestos chemistry and carcinogenicity has been reviewed.[273] As in the preceding section, it appears that iron occupies a middle position, between the comparably unfavorable consequences of deficiency and of excess.



(**36**)

5.4.2 GROUP 14 DONORS

5.4.2.1 Cyanide—Hexacyanoferrates

5.4.2.1.1 Mononuclear hexacyanoferrates

Solubility data (pK_{sp}) for two dozen hexacyanoferrate(II) and hexacyanoferrate(III) salts, and Pourbaix (pe/pH) diagrams for iron–cyanide–water, iron–sulfide–cyanide-(hydr)oxide, iron–arsenate–cyanide-(hydr)oxide, and iron–copper–cyanide-sulfide-(hydr)oxide, are given in a review ostensibly dedicated to hydrometallurgical extraction of gold and silver.[274] The electrochemistry of Prussian Blue and related complexes, in the form of thin films on electrodes, has been reviewed.[275]

(i) Hexacyanoferrate(II)

Hexacyanoferrate(II) can act as the intercalating counterion in several layered double hydroxides, including $Mg(OH)_2/Cr(OH)_3$, $Mg(OH)_2/Al(OH)_3$, and $Cu(OH)_2/Al(OH)_3$.[276,277] $K_4[Fe(CN)_6]$ has been used to photosensitize TiO_2.[278]

The acidity constants for $H_4[Fe(CN)_6]$ are $pK_1 = 2.54$, $pK_2 = 1.08$, $pK_3 = 2.65$, $pK_4 = 4.19$.[279] Association constants have been published for alkali metal cations ion pairing with hexacyanoferrate(II).[280]

Substitution at hexacyanoferrates(II) is very difficult, though it can be catalyzed by metal ions such as Hg^{2+}. Such catalysis can be augmented by surfactants such as sodium dodecyl sulfate (SDS), and indeed SDS-catalysis of Hg^{2+}-catalyzed replacement of cyanides in $[Fe(CN)_6]^{4-}$ by 1,10-phenanthroline has been proposed as an analytical method for the determination of mercury.[281]

(ii) Hexacyanoferrates(III)

The structure of $Bi[Fe(CN)_6]\cdot 4H_2O$ has been elucidated,[282–284] and $Ce[Fe(CN)_6]\cdot 5H_2O$ and $Gd[Fe(CN)_6]\cdot 4H_2O$ studied by X-ray crystallography and Mössbauer spectroscopy.[285] See Section 5.4.2.1.1 above for an estimate of the volume of $[Fe(CN)_6]^{3-}$.

(iii) Hexacyanoferrate(II)/(III) electron exchange

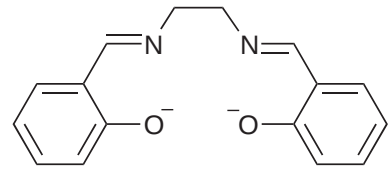
The hexacyanoferrate(II)/(III) electron exchange reaction is strongly catalyzed by cations such as K^+. However if the K^+ is complexed by, e.g., 18-crown-6 or the cryptand [2.2.2] then the rate constant k_{uc} for the uncatalyzed reaction can be determined. Carbon-13 NMR spectroscopy has established that k_{uc} is 240 $M^{-1}\,s^{-1}$ (at 298 K), with $\Delta V_{uc}^{\ddagger} = -11.3\,cm^3\,mol^{-1}$.[286] Pressure effects on the kinetics of the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ electrode reaction have been studied.[106] Factors controlling electron diffusion in electroactive polymer films have been probed by studying the dynamics of incorporated $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$.[287]

(iv) Kinetics of hexacyanoferrate reductions and oxidations

Rate constants for many $[Fe(CN)_6]^{3-}$ oxidations and $[Fe(CN)_6]^{4-}$ reductions have been collected and tabulated.[288]

Kinetic and mechanistic studies of hexacyanoferrate(II) reductions include those of hypochlorite,[289] of peroxodisulfate (for which activation volumes were determined),[290] and of *trans*-$[Co(salen)(H_2O)_2]^+$ (salen = *N*,*N*′-ethylenebis(salicylideneaminate), (**37**)).[291] Peroxonitrite oxidation of hexacyanoferrate(II) is first-order in peroxonitrite, zeroth-order in hexacyanoferrate(II). The inference that the rate-limiting step in this reaction is decomposition of the oxidant is supported by activation volume data – the value of $\Delta V^{\ddagger}$ for oxidation of hexacyanoferrate(II), $+11\,cm^3\,mol^{-1}$, lies within the range established for peroxonitrite decomposition but is very different from the value of $\Delta V^{\ddagger}$, $-7\,cm^3\,mol^{-1}$, for bimolecular peroxonitrite oxidation of $[Ni(cyclam)]^{2+}$.[292] Activation volumes of between $+27\,cm^3\,mol^{-1}$ and $+34\,cm^3\,mol^{-1}$ for $[Fe(CN)_6]^{4-}$

reduction of several cobalt(III) complexes $[Co(NH_3)_5X]^{n+}$ reflect hydrational changes around the iron as the electron is transferred within the reacting ion pair.[293]



(**37**)

Studies of medium effects on hexacyanoferrate(II) reductions have included those of dioxygen,[294] iodate,[295] peroxodisulfate,[296–298] $[Co(NH_3)_5(DMSO)]^{3+}$,[299] and $[Co(en)_2Br_2]^+$.[300] Rate constants for reaction with dioxygen depended strongly on the electron-donor properties of the organic cosolvent. Rate constants for reduction of peroxodisulfate in several binary aqueous media were analyzed into their ion association and subsequent electron transfer components. Rate constants for reduction of $[Co(en)_2Br_2]^+$ in methanol–water and dioxan–water mixtures were analyzed by a variety of correlatory equations (dielectric constant; Grunwald-Winstein; Swain; Kamlet-Taft).

Kinetic studies of hexacyanoferrate(III) oxidations have included the much-studied reaction with iodide[301] and oxidation of the $TlCl_2^-$ anion,[302] of hydrazine and hydrazinium,[303] and of phenylhydrazine and 4-bromophenylhydrazine.[304] These last reactions proceed by outer-sphere mechanisms, and conform to Marcus's theory. Catalyzed $[Fe(CN)_6]^{3-}$ oxidations have included chlororuthenium-catalyzed oxidation of cyclohexanol,[305] ruthenium(III)-catalyzed oxidation of 2-aminoethanol and of 3-aminopropanol,[306] ruthenium(VI)-catalyzed oxidation of lactate, tartrate, and glycolate,[307] and osmium(VIII)-catalyzed oxidation of benzyl alcohol and benzylamine.[308]

Studies of medium effects on hexacyanoferrate(III) oxidations have included those of iodide and of sulfite,[297,298,309,310] in aqueous salt solutions as well as in binary aqueous solvents.

5.4.2.1.2 Polynuclear and mixed valence complexes

(i) Polynuclear complexes

Complexes containing Fe—C—N—Fe or Fe—C—N—M^1 units, indeed M^2—C—N—M^1 units in general, have become of great interest in recent years in relation to their structures, to their magnetic and magneto-optic properties, and to the study of intramolecular electron transfer. Structures include a range of 1D, 2D, and 3D arrangements; metal–metal interactions also cover a wide range, tunable by varying the metal and the other ligands present. Table 4 gives a selection of species of established structure.

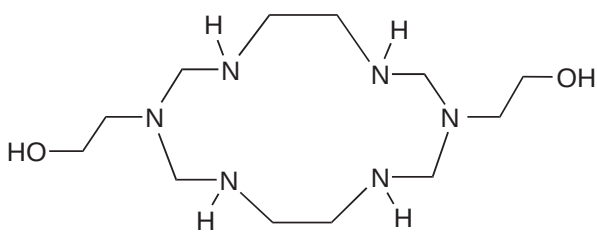
Two iron atoms are bridged by diphenylphosphinopropane, dppp, and by two —CN—Zn—NC— units in $[(C_5H_5)Fe(\mu\text{-}CN)_2ZnI(THF)]_2(\mu\text{-dppp})$.[319] Fe—CN—Zn bridging is also found in $Zn[Fe(CN)_5(NO)]$.[320]

In $[Fe(py)_2M(CN)_4]$, M = Ni, Pd, Pt, cyanide-bridging results in a 2D structure;[321] in $[Fe(pz)M(CN)_4]$, pyrazine-bridging orthogonal to cyanide-bridging gives an infinite 3D structure.[322] These are all spin cross-over complexes. Aniline analogues of $[Fe(py)_2Ni(CN)_4]$ are high-spin species,[323] as is $[Fe(H_2O)_2Ni(CN)_4](dioxan)_2$.[324] The structure of $[Cu(en)(H_2O)]_2[Fe^{II}(CN)_6]\cdot 4H_2O$ comprises a cyanide-bridged bimetallic assembly, of a 1D chain (**39**) with inter-chain links to form 2D polymeric sheets, whereas $[Cu(en)_2][KFe^{III}(CN)_6]$ consists of a 3D network of K^+ and $[Fe(CN)_6]^{3-}$ with the $[Cu(en)_2]^{2+}$ in holes.[325] $[Cu(pn)_2]_2[Fe^{III}(CN)_6]ClO_4\cdot 2H_2O$, where pn = 1,3-propanediamine, has a 2D network structure.[314] Fe^{III}—C—N—Ln^{III} bridging occurs in the complexes prepared from $K_3[Fe(CN)_6]\cdot Ln(NO_3)_3\cdot 6H_2O$ plus DMA. For Ln = Sm, Gd, Ho three different products and structures have been obtained.[326] The salts $CsLn[Fe(CN)_6]\cdot nH_2O$, with Ln = La → Lu and Y, and $n = 4$ or 5, continue studies of double salts of this type.[327] IR spectra indicate significant Fe^{n+}–anion interaction in the double salts $KFe[M(CN)_8]\cdot nH_2O$, $n = 7$ or 8, prepared from octacyanomolybdate-(IV) or -(V) or the tungsten analogues.[328] Fe^{2+}–$[Co(CN)_6]^{3-}$ interactions have been compared with interactions of $[Co(CN)_6]^{3-}$ with other cations through the respective stretching frequencies for the coordinated cyanide.[329]

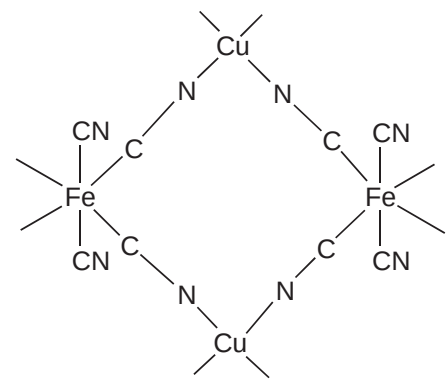
Table 4 Some cyano-bridged binuclear complexes of established structure.

Fe—C—N—M unit	*Compound*	*Structure*	*References*
Fe^{III}—C—N—Rh^{II}	[a]	1D linear chain	311
Fe^{II}—C—N—Mn^{IV}	β-Mn[Fe(CN)$_6$]	Two interpenetrating 3D networks	312
Fe^{II}—C—N—Cu^{II}	[Cu(tn)]$_2$[Fe(CN)$_6$][b]	2D layers[c]	313
Fe^{III}—C—N—Cu^{II}	[Cu(tn)]$_2$[Fe(CN)$_6$]ClO$_4$·2H$_2$O[b]	2D network	314
Fe^{III}—C—N—Cu^{II}	[Cu(hehct)]$_x$[Fe(CN)$_6$]$_y$[d]	1D zigzag chain	315
Fe^{II}—C—N—Ni^{II}	[Ni(hehct)][Fe(CN)$_6$]·4H$_2$O[d]	3D vat-like	315
Fe^{III}—C—N—Ni^{II}	[Ni(cyclam)]$_3$[Fe(CN)$_6$]$_2$·nH$_2$O[e]	2D honeycomb	316
Fe^{III}—C—N—Fe^{III}	[Fe(cyclam)][Fe(CN)$_6$]·6H$_2$O	1D linear chain	317
Fe^{III}—C—N—Fe^{III}	[{Fe(salen)}$_2${Fe(CN)$_6$}]$^-$	2D (cation and solvent dependent)	318

[a] Aqua-K(18-crown-6) salt of {[–Rh$_2$(-benzoate)$_4$–NCFe(CN)$_4$CN–]$^{3-}$}$_n$. [b] tn = 1,3-diaminopropane. [c] Contains Cu_4Fe_3 (defect) cubane units. [d] hehct = 3,10-Bis(2-hydroxyethyl)-1,3,5,8,10,12-hexaazacyclotetradecane (**38**). [e] Prepared from [Ni(cyclam)]$^{2+}$ plus a large excess of [Fe(CN)$_6$]$^{3-}$



(38)



(39)

Metal–metal interactions in [(C$_5$H$_5$)(dppe)Fe—CN—Ni(cyclam)—NC—Fe(dppe)(C$_5$H$_5$)]$^{2+}$ and [(OC)$_5$Cr—CN—Fe(cyclam)—NC—Cr(CO)$_5$]$^+$ were probed by electrochemical and spectroscopic techniques,[330] and intervalence charge-transfer (IVCT) within [(NC)$_5$Fe^{II}CNPt^{IV}(NH$_3$)$_5$] and [(NC)$_5$Fe^{II}CNPt^{IV}NCFe(CN)$_5$]$^{4-}$ analyzed.[331]

Cyanide-bridged complexes involving iron–diimine–cyanide complexes are discussed in Section 5.4.3.5.8.

(ii) Mixed valence complexes

These are of particular interest as pigments and in relation to kinetics and mechanisms of intramolecular electron transfer. Prussian Blue is mentioned in a review of photoswitchable coordination compounds.[332] Three aspects of Prussian Blue and related compounds, viz their structures, their electrochemical behavior (electrodes; batteries), and their uses in medicine (treatment of ^{137}Cs and of thallium poisoning), are mentioned in a review of cyanide complexes of transition metals.[333] The first authentic example of a Turnbull's Blue, i.e., an iron(II)–hexacyanoferrate(III) combination, has been reported. It is a valence-trapped (Robin and Day class I[334,335]) compound.[336] In cobalt–iron Prussian Blue analogues $Na_xCo_yFe(CN)_6 \cdot zH_2O$ electronic and spin states are controlled by temperature and the ligand field strength around the Co^{2+} ions, which in turn is determined by the Co:Fe ratio. The range of compositions studied is summarized in Table 5.[337]

Table 5 Compositions and iron oxidation states in cobalt–iron Prussian Blue analogues $Na_xCo_yFe(CN)_6 \cdot zH_2O$.[325]

Na	*Co*	*z*	*Fe^{II}*	*Fe^{III}*
0.07	1.50	6.3	0.07	0.93
↓	↓	↓	↓	↓
0.94	1.15	3.0	1.0	0

5.4.2.2 Cyanide—Pentacyanoferrates

5.4.2.2.1 Introduction

Advances in the chemistry of $[M(CN)_5L]^{n-}$ complexes, for M = Fe, Ru, and Os, have been reviewed.[338] There has been rather little activity in the preparation of novel complexes, but considerable activity in studying the properties, especially solvatochromism and various aspects of kinetics of substitution, of known complexes. However there has been an attempted preparation of $[Fe(CN)_5(C_{12}H_{25}NH_2)]^{3-}$, in the hope of generating micelles or lyotropic liquid crystals. This preparation appeared to yield $[Fe(CN)_4(H_2O)(C_{12}H_{25}NH_2)]^{2-}$, whose alkali metal salts gave a hexagonal mesophase in water, but were also readily hydrolyzed to $[Fe(CN)_4(H_2O)_2]^{2-}$.[339] Heterobinuclear complexes of the form $[(NC)_5FeL^1ML^2_5]^{n\pm}$ have been much studied, especially in relation to intramolecular electron transfer (see Section 5.4.2.2.5).

5.4.2.2.2 Solvatochromism and piezochromism

Solvatochromism and piezochromism of a range of pentacyanoferrates(II) have been examined in binary aqueous solvent mixtures,[340] and their solvatochromism in micelles and reversed micelles.[341] The solvatochromism of $[Fe(CN)_5(\text{nicotinamide})]^{3-}$ has been established in several ranges of water-rich binary solvent mixtures,[342] of $[Fe^{II}(CN)_5(\text{2,6-dimethylpyrazine})]^{3-}$ in acetonitrile–water mixtures.[343] The solvatochromism of $[Fe(CN)_5(4Phpy)]^{3-}$ and $[Fe(CN)_5(4Bu^tpy)]^{3-}$ has been proposed as an indicator of selective solvation in binary aqueous solvent mixtures.[344]

The piezochromism of $[Fe(CN)_5(4CNpy)]^{3-}$ and $[Fe(CN)_5(pz)]^{3-}$ (and of the biferrocenium cation) was included in a wide-ranging solvatochromism/piezochromism correlation for metal-to-ligand (and ligand-to-metal) charge-transfer bands of a variety of inorganic and organometallic complexes.[345]

The solvatochromism of the ligand-to-metal charge-transfer bands of $[Fe^{III}(CN)_5L]^{2-}$ with L = (substituted) imidazoles and pyrazoles has been described.[346]

5.4.2.2.3 Formation and dissociation kinetics

(i) Aqueous media

Reviews[288,347] of pentacyanoferrate substitution kinetics have included a detailed consideration of high-pressure studies of thermal and photochemical substitution and electron transfer reactions of pentacyanoferrates-(II) and -(III).[348] Photochemical activation can result in the loss of L or of CN^-. The best way to study the latter is through photochemical chelate ring closure in a pentacyanoferrate complex of a potentially bidentate ligand LL: $[Fe(CN)_5(\underline{LL})]^{n-} \rightarrow [Fe(CN)_4(\underline{LL})]^{(n-1)-} + CN^-$.[349]

Kinetic parameters (k, often also $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, occasionally $\Delta V^{\ddagger}$) for formation and dissociation of several pentacyanoferrate(II) complexes $[Fe(CN)_5L]^{n-}$ have been established. Ligands L include several *S*- and *N*-donor heterocycles,[350] 4-methyl- and 4-amino-pyridines,[351] a series of alkylamines,[352] 3- and 4-hydroxy- and 3- and 4-methoxy-pyridines,[353] several amino acids,[354] nicotinamide,[342] 4-pyridine aldoxime,[355] 3-Me and 3-Ph sydnones,[356] several bis-pyridine ligands,[127] neutral, protonated, and methylated 4,4′-bipyridyl, 1,2-bis(4-pyridyl)ethane and *trans*-1,2-bis(4-pyridyl)ethene,[357] pyrazine- 4,4′-bipyridyl- and bis(4-pyridyl)ethyne-pentaamminecobalt(III),[358] edta–ruthenium(III),[359] and pentaammineruthenium-(II)and-(III) complexes of

cyanopyridines[360,361] and of pyrazine.[362] Selections of kinetic parameters are given in Table 6 for dissociation and Table 7 for formation; comparative values from earlier work for many other ligands L are tabulated elsewhere.[74] Both formation and dissociation rate constants for the sydnones are very much lower than for most other uncharged ligands. This exceptional behavior may arise from the mesoionic nature of these ligands (formation), and from considerably more π-bonding than in, e.g., pyridine–pentacyanoferrate(II) complexes (dissociation). Formation of the 4-hydroxypyridine complex is also exceptionally slow, because 4-hydroxypyridine exists almost completely in the *keto* form ($K(keto/enol) = 1{,}310$). The bis-pyridine species were investigated in relation to the generation of $[Fe(CN)_5L]$-capped rotaxanes based on cyclodextrins. Kinetics and mechanisms of the formation, dissociation, and interconversion of linkage isomers of pentacyanoferrate(II) complexes of ambidentate ligands have been discussed in detail.[373]

Equilibrium constants for formation of complexes $[Fe(CN)_5L]$ can be derived from kinetics and independently from spectroscopic determinations. Values are given in many of the papers cited above; stability constants for several pentacyanoferrate(II) complexes have been compared with those for their pentacyanoruthenate(II) analogues.[374]

Rate constants for the sequence of reactions in which successive $[Fe(CN)_5(H_2O)]^{3-}$ complexes react with the peripheral nitrogens of $[Ru(bipz)_3]^{2+}$, bipz = (**40**), decrease from 3,500 $dm^3\,mol^{-1}\,s^{-1}$ for attachment of the first $Fe(CN)_5^{3-}$ to 0.3 $dm^3\,mol^{-1}\,s^{-1}$ for the sixth.[375] Rate constants decrease as the

Table 6 Kinetic parameters[a] for dissociation of pentacyanoferrates(II), $[Fe(CN)_5L]^{n-}$, in aqueous solution at 298.2 K.

L	10^3k (s^{-1})	$\Delta H^{\ddagger}$(kJ mol^{-1})	$\Delta S^{\ddagger}$(J K^{-1} mol^{-1})	$\Delta V^{\ddagger}$(cm^3 mol^{-1})
Ammonia	22	102	+63	+16
Aliphatic amines	2.8 to 22.7	92 to 107	+29 to +71	+16 to +24
Pyridines :				
Unsubstituted	1.1	104	+46	
4-methyl	1.2	100	+38	
4-*t*-butyl	0.92			+11.4
4-butylpentyl	0.37			+16[b]
4-amino	2.5	90	+5	
4-cyano	1.0	105	+50	+20
4-hydroxy	1.1	92	+7	
4-methoxy	2.1	93	+16	
4-phenyl	0.7			+10.4
4-(4′-pyridyl)	0.62	111	+67	+13.5
4-X-(4′-pyridyl)[c]	0.59 to 0.80	115 to 123	+82 to +108	
4-X-(4′-pyridyl.cd)[d]	0.03 to 0.70	112, 116	+42, +76	
4-aldoxime	0.45	134	+140	
3-carboxamide[e]	3.4	107	+130	
Piperidine	7.5	91	+15	
Pyrazine	0.42	110	+59	+12.5
2-Methylpyrazine	0.77	114	+44	+19.4
N-Methylpyrazinium	0.28	115	+75	+0.9
N-*n*-Pentylpyrazinium	0.20			+9.6
Thiourea	13	88	+21	+20.9
Nitro	10			+20.1
3-Me-, 3-Ph-sydnones	0.014, 0.047			
—pz—$Rh^{III}(NH_3)_5$	1.1			
—pz—$Ru^{III}(NH_3)_5$	2.9			
—pz—$Ru^{II}(NH_3)_5$	0.72			
—(4,4′-bipy)—$Ru^{II}(NH_3)_5$	2.5			
—(3-,4-NHCOpy)—$Ru^{II}(NH_3)_5$	2.6 to 2.8			
—(3-,4-NCpy)—$Ru^{II}(NH_3)_5$	2.5 to 5.0			
—(3-,4-NCpy)—$Ru^{III}(NH_3)_5$	8 to 10			
—(L)—Ru^{III}(edta)[g]	2 to 154			

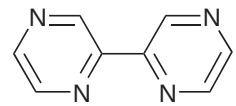
[a] References to the rate constants and activation parameters in this table are cited in the text. [b] In 20% MeOH. [c] X = CH_2, CH_2CH_2, $CH_2CH_2CH_2$, CH=CH, C≡C; when $Co(NH_3)_5$ is coordinated to the 4′-pyridyl rate constants are in the range (1–4) × 10^{-3} s^{-1}. [d] cd = cyclodextrin. [e] i.e., nicotinamide. [f] L = pz; 4,4′-bipy; 3,3′-Me_2-4,4′-bipy; *trans*-py–CH=CH–py; py–$(CH_2)_3$–py.

Table 7 Kinetic parameters for formation reactions from aquapentacyanoferrate(II), $[Fe(CN)_5(H_2O)]^{3-}$+L, in aqueous solution at 298.2 K.

	k_f ($dm^3\,mol^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}$ ($kJ\,mol^{-1}$)	$\Delta S^{\ddagger}$ ($J\,K^{-1}\,mol^{-1}$)	$\Delta V^{\ddagger}$ ($cm^3\,mol^{-1}$)
L^{3+}				
–pz–$M^{III}(NH_3)_5^{3+}$[a]	5,500 to 8,800			
L^{2+}				
–(3-,4-NCpy)–$Ru^{II}(NH_3)_5^{2+}$	5,700; 4,600			
–pz–$Ru^{II}(NH_3)_5^{2+}$	3,700			
–bipz–$Ru^{II}(bipz)_2^{2+}$	35,000			
–pzc–$Co(NH_3)_4^{2+}$	27,300	77	+98	
L^{+}				
N-methyl-4,4′-bipyridylium	2,820	68	+50	
N-methylpyrazinium	2,380	70	+42	
4,4′-bipyridylium	1,610			
L				
4,4′-bipyridyl	586	64	+21	
Methionine	535	70	+42	+18
Pyrazine	380	64	+21	
Pyridine	365	67	+29	
3-CN-, 4-CN-pyridine	413, 383			
Pyridine-4-aldoxime	302			
Histidine	315	64	+21	+17
Imidazole	240	64	+13	+16
2,7-diazapyrene	180			
L^{-}				
Glutathionate	219	76	+54	
β-alaninate	57	60	−10	+14
Pyrazine carboxylate	47			+17
4-nitroimidazolate	45			
Cyanide	30	77	+42	+14
Glycinate	28[b]	61	−13	+16
Ru(edta)L[c]	140 to 180			

References to the rate constants and activation parameters in this table are cited in the text. [a] M = Co, Rh, Ru. [b] Between 18 $dm^3\,mol^{-1}\,s^{-1}$ and 30 $dm^3\,mol^{-1}\,s^{-1}$ for other singly charged amino acid ligands. [c] L = pz; 4,4′-bipy; 3,3′-Me_2-4,4′-bipy.

formal charge on the ruthenium-centered moiety goes from 2+ to 13−, with the consequent change in the notional charge product for the reactants from a favorable 6− to a very unfavorable 39+.



(**40**)

The volume profile has been established for the reaction

$$[Fe(CN)_5(H_2O)]^{3-} + NH_3 \rightleftharpoons [Fe(CN)_5(NH_3)]^{3-} + H_2O$$

$\Delta V^{\ddagger} = +14\,cm^3\,mol^{-1}$ for both the forward and the reverse reaction. That this $\Delta V^{\ddagger}$ value is markedly less than the partial molar volumes of water and of ammonia ($25\,cm^3\,mol^{-1}$ and $18\,cm^3\,mol^{-1}$, respectively) indicates limiting dissociative (*D*) activation,[376] as do the $\Delta S^{\ddagger}$ values of close to $+70\,J\,K^{-1}\,mol^{-1}$ in both directions. Overall the current situation with regard to thermal substitution at pentacyanoferrates(II) appears to be that the I_d mechanism probably operates for $[Fe(CN)_5(H_2O)]^{3-}$, the *D* mechanism for all other $[Fe^{II}(CN)_5L]^{n-}$ complexes.[338] The role of ligand size in determining $\Delta V^{\ddagger}$ for substitution at pentacyanoferrates has been investigated,[377] with a plausible $\Delta V^{\ddagger}$ vs. ligand size correlation, plus a correlation of dissociation rate constants with ligand pK_a values.[378]

Reaction of $[Fe(CN)_5(4CNpy)]^{3-}$ with a wide range of ligands (in 40% MeOH) has been used, along with analogous reactions of molybdenum(0) complexes $[Mo(CO)_5L]$, to illustrate the variety of rate constant vs. incoming ligand concentration dependences in a limiting *D* mechanism.[379]

(ii) Medium effects

Medium effects on reactivity have been established for reaction of $[Fe(CN)_5(4CNpy)]^{3-}$, of $Fe(CN)_5(4,4'\text{-bipy})]^{3-}$,[380] and of $[Fe(CN)_5(4Phpy)]^{3-}$ with CN^- in binary aqueous systems with various hydroxylic solutes—MeOH, Bu^tOH, glycol, glycerol, and sucrose. A multiparameter correlation has been developed for the $[Fe(CN)_5(4Phpy)]^{3-}$ results[381] and also applied to ligand replacement in $[Fe(CN)_5(4,4'\text{-bipy})]^{3-}$ in binary aqueous media.[382] Both solvent (ROH, acetone, MeCN; k, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as a function of solvent composition) and salt effects on reactivity have been studied for dissociation of $[Fe(CN)_5(\text{nicotinamide})]^{3-}$;[342] salt effects were also reported for the reaction of $[Fe(CN)_5(4Phpy)]^{3-}$ with cyanide. The latter case included derivation of activation volume via surface area of activation.[383] Activation volumes obtained directly from high pressure kinetics and indirectly via surface areas of activation from salt effects have been compared for four $[Fe(CN)_5L]^{3-}$ complexes.[384]

Reactivities of pentacyanoferrates(II) in micelles and reversed micelles have been studied.[341] The hexadecyltrimethylammonium cation causes a modest increase in rate constant for the anion–anion reaction $[Fe(CN)_5(4\text{-CNpy})]^{3-} + CN^-$. This can equally well be interpreted according to the pseudophase model developed from the Olson-Simonson treatment of kinetics in micellar systems or by the classical Brønsted equation.[382,386]

Rate constants for reaction of $[Fe(CN)_5(H_2O)]^{3-}$ with pyrazine 3-carboxylate have been obtained in a series of isodielectric aqueous mixtures with hydroxylic cosolvents and solutes.[387]

(iii) Pentacyanoferrates(III)

Activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$) for solvolytic dissociation of $[Fe^{III}(CN)_5(NO_2)]^{3-}$ in water,[388] methanol, dimethyl sulfoxide and dimethylformamide[389] cover a wide range of values, as do $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for reaction of $[Fe^{III}(CN)_5(H_2O)]^{2-}$ with cytosine, cytidine and cytidine-5′-monophosphate.[390] The patterns revealed contrast with those for pentacyanoferrates(II) and suggest that pentacyanoferrate(III) complexes undergo substitution by an interchange mechanism (I_d), as for $[Co^{III}(CN)_5(H_2O)]^{2-}$,[391] rather than the *D* mechanism favored by the iron(II) complexes.

5.4.2.2.4 Redox chemistry

Redox potentials of pentacyanoferrates are often determined in association with kinetic and stability constant determinations.[392,393] They are also available for 4-methyl- and 4-amino-pyridine pentacyanoferrates,[351] and for $[Fe(CN)_5(2,6\text{-dimethylpyrazine})]^{3-/2-}$ in acetonitrile–water mixtures.[343] Oxidation potentials of $[Fe(CN)_5L]^{3-}$ complexes correlate with the electron-withdrawing or -releasing properties of the ligands L.[338]

The activation volume for peroxodisulfate oxidation of $[Fe(CN)_5(\text{pentylpz})]^{3-}$, $0 \pm 2\,cm^3\,mol^{-1}$, suggests, as do the close-to-zero values for analogous reactions of $[Fe(CN)_6]^{4-}$ and of $[Fe(\text{diimine})(CN)_4]^{2-}$, compensation between intrinsic and solvational contributions.[290]

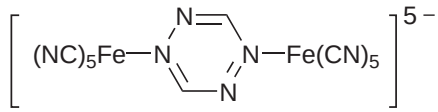
The kinetics of formation of nitroprusside from $[Fe^{III}(CN)_5(H_2O)]^{2-}$ indicate a mechanism of complex formation in which outer-sphere reduction to $[Fe^{II}(CN)_5(H_2O)]^{2-}$ precedes substitution.[394] Reduction of the dimeric pentacyanoferrate(III) anion $[Fe_2(CN)_{10}]^{4-}$ by thiourea is a multi-stage process; the first step is one-electron transfer to give $[Fe_2(CN)_{10}]^{5-}$, which dissociates to give $[Fe(CN)_5(tu)]^{2-}$ and $[Fe(CN)_5(H_2O)]^{3-}$.[395]

5.4.2.2.5 Formation of, and electron transfer within, binuclear species

Binuclear complexes of the type $[(NC)_5Fe^{II}(\mu\text{-}L^2)Co^{III}L^1{}_5]$ or $[(NC)_5Fe^{II}(\mu\text{-}L^2)Ru^{III}L^1{}_5]$ are valuable for monitoring kinetics of intramolecular electron transfer as the Fe^{II} and Co^{III} or Ru^{III} moieties are substitution-inert, as in the classic $[L^1{}_5Ru^{II}(\mu\text{-}L^2)Ru^{III}L^3{}_5]$ systems. A dissociative

mechanism for formation of pyrazine carboxylate (pzc) bridged $Fe^{II}Co^{III}$ species is indicated by activation volumes between $+23\,dm^3\,mol^{-1}$ and $+28\,dm^3\,mol^{-1}$.[396] Salt effects on formation and dissociation kinetics of $[(en)_2Co(\mu\text{-pzc})Fe(CN)_5]^-$ have been studied,[397] with $\Delta V^{\ddagger}$ for dissociation estimated by the indirect "surface area of activation" route (see *Medium effects* part of Section 5.4.2.2.3 above), while k, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for reaction of $[Fe^{II}(CN)_5(H_2O)]^{3-}$ with $[Co(NH_3)_4(pzc)]^{2+}$ have been determined in binary aqueous mixtures.[398]

Kinetics of reaction between $[Fe^{II}(CN)_5(H_2O)]^{3-}$ and $[Co(NH_3)_5(pz)]^{3+}$ permit the estimation of a rate constant for water loss from low-spin iron(II), since the large charge product for this pair of reactants results in a curved plot of k_{obs} vs. incoming ligand concentration, whence the required rate constant can be separated from the association constant for the two reactants. The rate constant of $24\,s^{-1}$ (at 298 K) is much higher than for dissociation of other $[Fe^{II}(CN)_5L]^{3-}$ complexes (cf. Table 6), consistent with the low affinity of the $[Fe^{II}(CN)_5]^{3-}$ moiety for water – the subsequent electron transfer is very much slower.[399] Rate constants and activation volumes have been obtained in water and in methanol–water mixtures,[400] and rate constants in SDS and CTAC micelles,[401] for the relatively slow electron transfer within binuclear $[(en)_2Co(\mu\text{-pzc})Fe(CN)_5]^-$, itself considerably more rapidly formed from $[Fe^{II}(CN)_5(H_2O)]^{3-}$ and $[Co(en)_2(pzc)]^{3+}$. Salt effects[402] and solvent effects (water plus hydroxylic cosolvents or solutes)[403] were also probed for kinetics of intramolecular electron transfer in $[(H_3N)_4Co(\mu\text{-pzc})Fe(CN)_5]^-$. Electron transfer in these Co(pzc)Fe systems (in water, in the dark) has $\Delta V^{\ddagger}$ between $+24\,dm^3\,mol^{-1}$ and $+38\,dm^3\,mol^{-1}$,[400,404] but when photochemically induced $\Delta V^{\ddagger}$ is close to zero. This large difference may be ascribed to the differing hydrational contributions associated with the electron transfer. In thermal electron transfer the large difference in hydration between $-Fe^{II}(CN)_5$ and $-Fe^{III}(CN)_5$ is reflected in the overall observed $\Delta V^{\ddagger}$ value, whereas in the photochemical reaction the rate-limiting step is the orbitally forbidden transfer of the electron from the bridging ligand to the cobalt, a process with only very small intrinsic and hydrational volume changes.[396] The small variation in rate constants for electron transfer within $[(NC)_5Fe^{II}(\mu\text{-}L^2)Co^{III}L^1(NH_3)_4]$ with bridging L^2 = 3,3′-dimethyl-4,4′-bipyridine, 4,4′-bipyridylethyne, 1,4-bis(4-pyridyl)butadiyne, 2,7-diazapyrene, and 3,8-phenanthroline correlates with Fe ⋯ Co distances and with MLCT frequencies.[358] The tetrazine-bridged mixed valence anion (**41**) exhibits a high intensity IVCT band in the near IR. Its comproportionation constant (K_c) is $\sim 10^8$ in water, $\sim 10^{19}$ in acetonitrile – a remarkable solvent effect on K_c. IR and Mössbauer spectra indicate this anion to be Class III,[334,335] i.e., completely delocalized $Fe_2^{2.5+}$.[405]



(**41**)

5.4.2.2.6 *Pentacyanonitrosylferrate(II)*

$Zn[Fe(CN)_5(NO)]$ contains Fe—CN—Zn bridging.[320] The lack of reactivity of $M^{II}[Fe(CN)_5(NO)]$, M = Fe, Co, Ni, is demonstrated by the absence of reaction of these salts with a variety of *N*- and *S*-donor ligands.[406] Pentacyanonitrosylferrate(II) (nitroprusside) reacts with RS^- or RNH_2,[288] e.g.,

$$[Fe(CN)_5(NO)]^{2-} + RS^- \rightarrow [Fe(CN)_5(NOSR)]^{3-} \quad (1)$$

Kinetic parameters have been determined for reaction of pentacyanonitrosylferrate(II) (nitroprusside) with secondary amines, which takes place by parallel reactions:

$$[Fe(CN)_5(NO)]^{2-} \overset{OH^-}{\rightarrow} [Fe(CN)_5(NO_2)]^{4-} \overset{R_2NH}{\rightarrow} [Fe(CN)_5(NHR_2)]^{3-} \quad (2)$$

$$[Fe(CN)_5(NO)]^{2-} + 2R_2NH \rightarrow [Fe(CN)_5(NHR_2)]^{2-} + R_2NNO \quad (3)$$

The mechanism of equation (3) is claimed to involve concerted binding of one amine molecule to the nitrosyl ligand with base-catalyzed proton removal.[407] Kinetic parameters for decomposition of

nitroprussides of several copper(II) aqua-amine cations have been determined thermogravimetrically.[408,409] Equilibrium and kinetic parameters (K, ΔH°, ΔS°; k, $\Delta H^\ddagger$, $\Delta S^\ddagger$) have been reported for the three stages in the reduction of nitroprusside by cysteine and the concomitant NO release.[410]

The nitroprusside ion, $[Fe(CN)_5(NO)]^{2-}$, and related complexes, figure largely in a review of photoswitchable coordination compounds.[332] Examination of the photolability of nitroprusside as a function of wavelength revealed significant release of cyanide only below 480 nm; above 480 nm there is almost exclusively loss of nitric oxide.[411] Synthesis of ^{57}Fe-enriched $[Fe(CN)_5(NO)]^{2-}$ may facilitate mechanistic studies by permitting readier Mössbauer examination of metastable states and intermediates.[412] ESR and relativistic density functional calculations suggest that although $[Fe(CN)_5(NO)]^{2-}$ is, as usually assumed, best regarded as an NO complex of iron(II), there is substantial electron transfer from metal to ligand in the ground state.[413]

$[Fe(CN)_5(NO)]^{2-}$ makes several appearances in a recent symposium volume dedicated to nitric oxide in biosystems, for example in connection with iron(II) citrate-induced oxidative stress.[414] Nitroprusside is the only metal nitrosyl complex in clinical use, where it is important as a rapidly acting agent for the lowering of exceptionally high blood pressure.[235]

5.4.2.3 Other Cyano-complexes

5.4.2.3.1 Tetracyanoferrates and dicyanoferrates

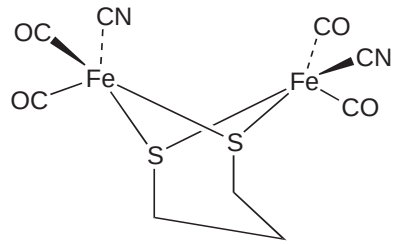
Rate constants and activation parameters for $\delta \leftrightarrow \lambda$ interconversion for the chelate rings in $[Fe(CN)_4(diamine)]^-$ anions with diamine = 1,2-ethanediamine, (2*R*,3*S*)-butanediamine, and (1*R*,2*S*)-*cis*-cyclohexanediamine have been determined from line shape analysis of variable temperature NMR spectra. $\Delta H^\ddagger$ values are 25 kJ mol^{-1}, 30 kJ mol^{-1}, and 43 kJ mol^{-1}, $\Delta S^\ddagger$ values 0 J K^{-1} mol^{-1}, −3 J K^{-1} mol^{-1}, and −8 J K^{-1} mol^{-1}, respectively.[415] Ternary diimine–cyanoferrate complexes appear in Section 5.4.3.5.8.

5.4.2.3.2 Carbonyl cyanides

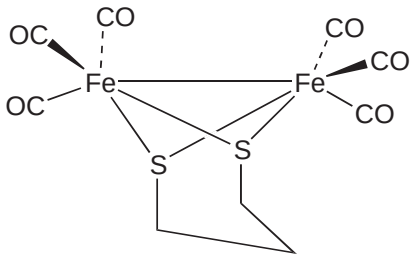
It has been known since the 19th Century that hexacyanoferrates(II) react with concentrated sulfuric acid to give carbon monoxide. The preparation of $[Fe(CN)_5(CO)]^{3-}$ from these reagents was reported in 1913. It now seems likely that the conversion of coordinated —CN into —CO proceeds through —$CONH_2$, here as in certain iron-containing hydrogenases.[416] The stereospecific formation of *fac*-$[Fe(CN)_3(CO)_3]^-$ then *cis*-$[Fe(CN)_4(CO)_2]^{2-}$ from $[Fe(CO)_4I_2]$, as well as the stereospecific production of *trans*-$[Fe(CN)_4(CO)_2]^{2-}$ from iron(II) chloride plus cyanide in an atmosphere of CO, appears to be under kinetic control. *cis*-$[Fe(CN)_4(CO)_2]^{2-}$ decomposes in minutes in aqueous solution, whereas the *trans* isomer, first reported in 2001,[417,418] decomposes considerably more slowly. *fac*-$[Fe(CN)_3(CO)_3]^-$, prepared as its K^+ and PPh_4^+ salts, and *cis*-$[Fe(CN)_4(CO)_2]^{2-}$, have IR spectra characteristic of their C_{3v} and C_{2v} geometries. The carbonyl stretching frequencies are modestly solvatochromic.[419] Crystal structures have been determined for *cis*- and *trans*-$[Fe(CN)_4(CO)_2]^{2-}$ salts. *Trans*-$[Fe(CN)_4(CO)_2]^{2-}$ reacts with cyanide by a dissociative reaction to give $[Fe(CN)_5(CO)]^{3-}$; methylation of $[Fe(CN)_5(CO)]^{3-}$ gives solely *cis*-$[Fe(CN)_4(CNMe)(CO)]^{2-}$.[420] The limiting member of the carbonyl cyanide series is the hexacarbonyl anion $[Fe(CO)_6]^{2+}$, long elusive[421] but eventually prepared and fully characterized as its $[Sb_2F_{11}]^-$ salt.[422] Crystal structures of this and the $[SbF_6]^-$ salt have been published.[423] Other quaternary carbonyl cyanides include the 1,4,7-trimethyl-1,4,7-triazacyclononane complex $[Fe(tmtacn)(CN)_2(CO)]$,[424] and the cyclopentadienyl complexes $K[(cp)Fe(CN)_2(CO)]$ and $Zn[(cp)Fe(CN)_2(CO)]_2$.[310]

The presence of both cyanide and carbonyl bonded to iron is a feature of iron–nickel[425] and iron-only hydrogenases.[426] The former contain an Fe_3S_4 subunit, in which each iron is coordinated by a cysteine, and two Fe_4S_4 subunits, in one of which each iron is again coordinated by a cysteine while in the other three irons are cysteine-coordinated but one is bonded to a histidine. The iron-only hydrogenases feature an Fe_4S_4 cubane linked to an Fe_2S_2 active site in which the iron atoms are bonded to CO, CN^-, and sulfur. The dithiolate bridge is a cysteinate thiol in the hydrogenase from *Clostridium pasteurianum*,[427] 1,3-propanedithiol in that obtained from *Desulfovibrio desulfuricans*.[428] A XRD study of a CO-inhibited iron-only hydrogenase showed an iron site with one CO and two CN^- coordinated to the metal.[429] The hydrogenase model complex (**42**)[430,431] can be obtained from (**43**).[432] (**44**) catalyzes the reduction of protons to dihydrogen,

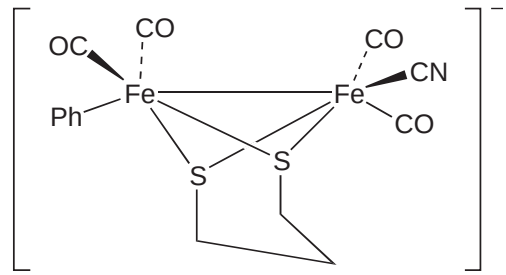
perhaps via an intermediate such as (**45**).[433] It has been structurally characterized, as has $(Et_4N)_2$-$[Fe(SPh)_2(CN)_2(CO)_2]$ (*cis*-CN,*cis*-SPh,*trans*-CO).[420] Density functional theory (DFT) calculations have been carried out on the closely related species (**46**).[434] An alternative approach to modeling the active site is provided by carbonyl cyanide derivatives derived from (**47**), where sulfur-bridging is provided by a tripodal thioether. (**47**) reacts with cyanide in two stages, the sulfur tripod becoming bidentate in the second stage, which produces (**48**).[435]



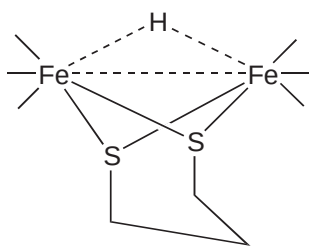
(**42**)



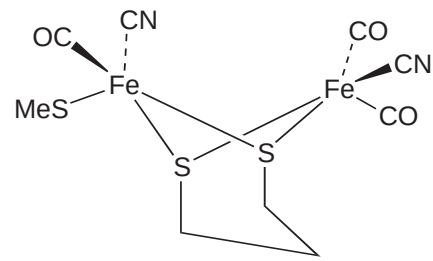
(**43**)



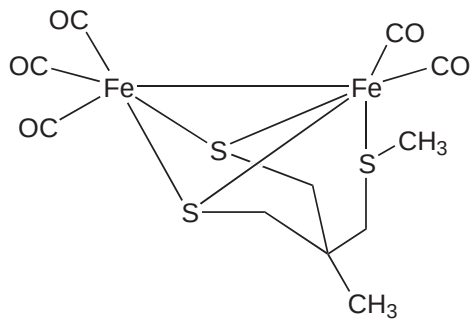
(**44**)



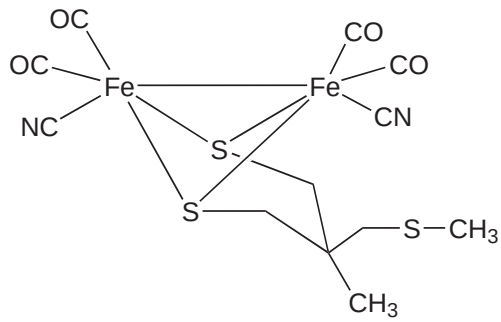
(**45**)



(**46**)



(**47**)

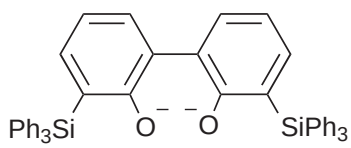


(**48**)

5.4.2.4 Other Ligands

$FeCl_3$ reacts with $Li[C(SiMe_3)_3]$, in toluene at 55–60 °C, to give the red violet iron(II) complex $[Fe\{C(SiMe_3)_3\}_2]$. This is monomeric, with linear C—Fe—C and an Fe—C bond distance of 2.05 Å.[436]

The isocyanide complex $[Fe^{II}(\mathbf{49})(2,6\text{-xylylNC})_2]$ is low-spin, despite the tetrahedral stereochemistry of the Fe^{II}, thanks to the high ligand field strength of the isocyanide ligands.[437] The particularly strong π-acceptor properties of the Bu^tNC ligands cause a change of ground state of the iron in bis(*t*-butyl isocyanide)tetraphenyldihydroporphinato-iron(III) from the normal $(d_{xz}, d_{yz})^3(d_{xy})^2$ to $(d_{xz}, d_{yz})^4(d_{xy})^1$.[438] For isocyanide coordinated to iron bearing an NS_3 tripod ligand see Section 5.4.4.2.



(**49**)

5.4.3 GROUP 15 DONORS

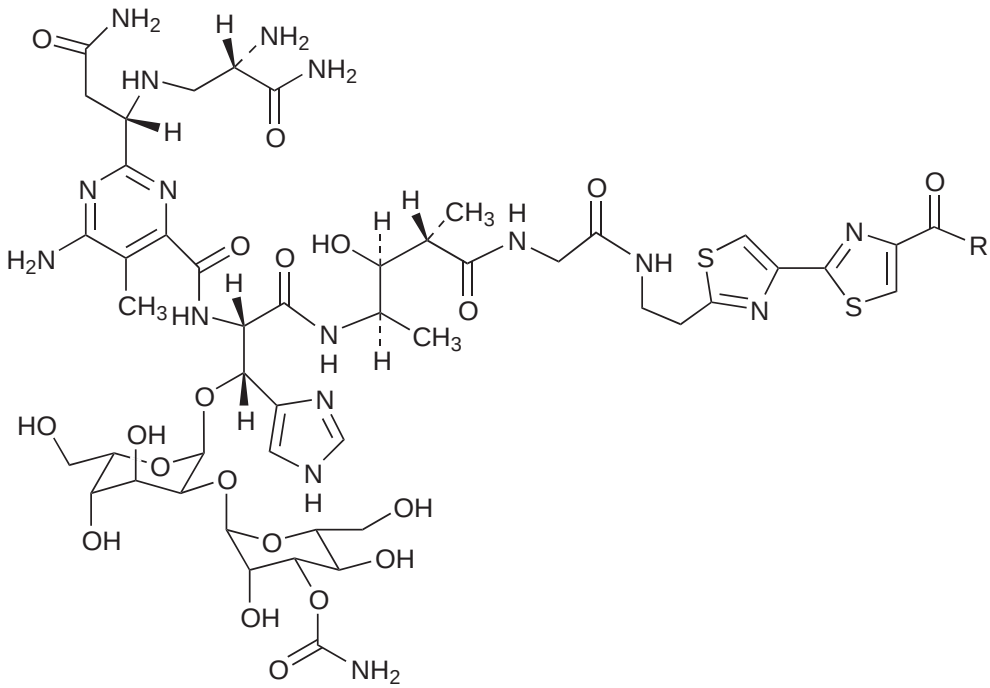
5.4.3.1 Dinitrogen, Ammonia, and Amines

Dinitrogen is η^1-bonded in $[Fe(N_2)(depe)_2]$, in which the iron is in trigonal bipyramidal coordination. The nitrogen can be replaced by CO, CS_2, or H_2 and displaced by protonation.[439]

$[Fe(NCS)_2(NH_3)_2]$ is the product of evolution of ammonia, at room temperature, from the various ammines of iron(II) thiocyanate, $Fe(NCS)_2 \cdot nNH_3$ ($n = 5$, 7, or 8).[10]

$[Fe(NH_3)_6]^{2+}$ and $[Fe(en)_3]^{2+}$ proved useful counterions for crystallization of salts of the $[AgAsS_4]^{2-}$, $[AgSbS_4]^{2-}$, and $[Cu_8Sb_3S_{13}]^{2-}$ anions,[440] and of the open framework chalcogenide anion $[Sb_2Se_5]^{4-}$. The average Fe—N bond distance in the $[Fe(en)_3]^{2+}$ salt is 2.192Å.[441] The combination of the bulky ligand *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and two iodides forces the Fe^{2+} in $[Fe(tmen)I_2]$ to be tetrahedral; the Fe^{2+} in $[Fe(dienm)Cl_2]$ (dienm = bis(2-dimethylaminoethyl)-methylamine) is five-coordinated. Both complexes are mononuclear with no halide bridging in the solid state.[442]

The bleomycins (**50**) are hardly simple amines, but they do have two NH_2 groups and a $CONH_2$ group at the N-terminal domain, as well as potential donor nitrogens in pyrimidine and imidazole, which can complex metal ions.[443] The complexing of iron to bleomycin[444] has a significant effect on bleomycin–DNA interactions—metal complexes can mediate strand scission—and on alkene oxidation. Both may involve hydroperoxide intermediates.[445,446]



Bleomycin A_2 R = $NHCH_2CH_2CH_2\overset{+}{S}Me_2$

Bleomycin B_2 R = $NHCH_2CH_2CH_2CH_2NHC(=NH)NH_2$

(**50**)

5.4.3.2 Thiocyanate

The frequent occurrence of thiocyanate in spin cross-over complexes is documented, in Section 5.4.1.4 above and in connection with diimine and with triazole ligands in Sections 5.4.3.5.9 and 5.4.3.6.3 below, while complex formation with iron(III) appears in Section 5.4.5.1.4.

$Fe(NCS)_2$ dissolves in liquid ammonia to form a series of ammoniates $Fe(NCS)_2 \cdot nNH_3$ ($n = 5$, 7, or 8). These evolve ammonia at room temperature to give $[Fe(NCS)_2(NH_3)_2]$, which has a tetragonal structure with bridging thiocyanates.[10]

$[Fe(isoquinoline)_2(NCS)_4]^-$ forms charge-transfer salts with tetrathiafulvalene and with bis(ethylenedithio)tetrathiafulvalene(**51**).[447] The latter shows long-range ferrimagnetic ordering.[447]

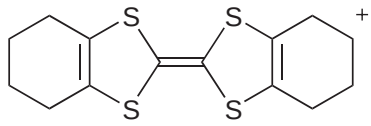
5.4.3.3 Azide

5.4.3.3.1 Iron(II)

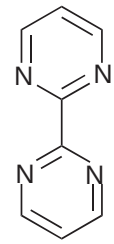
The binuclear complex $[Fe_2(bipym)(N_3)_4]$, prepared in a one-pot reaction from $FeCl_2$, NaN_3 and bipym (2,2′-bipyrimidine, (**52**)), in aqueous solution, has a honeycomb layered structure. It exhibits ferromagnetic interactions through the bridging azide ligands, antiferromagnetic through the bridging bipym ligands.[448]

5.4.3.3.2 Iron(III)

$[Fe(N_3)_5]^{2-}$ is, at least in its Ph_4As^+ salt, trigonal bipyramidal.[449,450] Binuclear $[Fe_2(N_3)_{10}]^{2-}$ has been characterized in its $[Fe(bipym)_3]^{2+}$ salt—now the iron(III) is octahedral. There is significant



(51)



(52)

Fe^{III}—Fe^{III} coupling across the bridging (1,1-μ) azides, but negligible interaction between the high-spin Fe^{III} and the low-spin Fe^{II} centers in the cations. The $[Fe_2(N_3)_{10}]^{2-}$ anion is stable in solution.[451] Both azide (1,1-μ) and pyrazine are bridging, along the *c* and *b* axes, respectively, in $[Fe(pz)_2(N_3)_2]$.[452] Azide forms both 1,1- and 1,3-bridges in $[Fe(4,4'\text{-}Me_2bipy)(N_3)_2]$.[453] The ternary complex anion with hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $[Fe\{HB(3,5\text{-}Me_2pz)_3\}(N_3)_3]^-$, can be prepared from $[Fe\{HB(3,5\text{-}Me_2pz)_3\}Cl_3]^-$ or, unexpectedly, directly from $[Fe_2OCl_6]^{2-}$.[454]

The structure of the ternary bioinorganic complex metazido myohemerythrin, from sipunculan worms, is outlined in (**53**).[455]

5.4.3.4 Pyridines, Pyrazines, and Triazines

Crystal structures have been reported for the iron(II) complexes $[Fe(py)_2(H_2O)_4](O_2CMe)_2$ and for $[Fe(py)_4(O_2CMe)_2]$.[456] Reaction of anhydrous iron(III) chloride with pyridine (py) gives $[Fe(py)_3Cl_3]\cdot py$, which can be obtained in orthorhombic and monoclinic modifications, with a structural phase transition temperature ~200 K. $[Fe(py)_3Cl_3]$ has Fe–N = 2.168(5)Å and 2.274(6)Å for N *trans* to N and N *trans* to Cl, respectively. Mössbauer parameters were recorded.[457] Pyridine and picolinate (pcl) complexes $[Fe(pcl)_2(py)_2]$, $[Fe(pcl)_3]$, $[Fe_2O(pcl)_4(py)_2]$ and $[Fe_2(OH)_2(pcl)_4]$ are involved in Gif-type oxidations of hydrocarbons by hydrogen peroxide.[458] Pyridine, and substituted pyridines, appear as ligands in pentacyanoferrates (Section 5.4.2.2) and in oxotri–iron complexes (Section 5.4.5.4.2); pyridylthiazoles and 2,6-bis(benzimidazol-2′-yl)pyridine appear in Section 5.4.3.5.3).

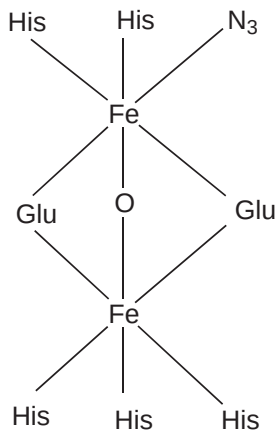
2-Aminomethylpyridine (picolylamine) is an important ligand in respect to spin cross-over, $[Fe(2\text{-}pic)_3]Cl_2$ being the key compound.[45] Heat capacity measurements on $[Fe(2\text{-}pic)_3]Cl_2\cdot EtOH$ gave values of 6.14 kJ mol^{-1} and 50.59 J K^{-1} mol^{-1} for the spin cross-over entropy; the determined entropy was analyzed into a spin contribution of 13.38, an ethanol orientational effect of 8.97, and a vibrational contribution of 28.24 J K^{-1} mol^{-1}.[459] This compound exhibits weak cooperativity in the solid state.[460] The heat capacity of $[Fe(2\text{-}pic)_3]Cl_2\cdot MeOH$ is consistent with very weak cooperativity.[460] $[Fe(2\text{-}pic)_3]Br_2\cdot EtOH$ shows a lattice expansion significantly different from that expected in comparison with earlier-established behavior of $[Fe(2\text{-}pic)_3]Cl_2\cdot EtOH$.[461]

The N_3-terdentate ligand bis(2-pyridylcarbonyl)amine, Hbpca = (**54**), is also a β-diketone, and can therefore act as a bridging ligand. In the complexes $[Fe(bpca)_2][M^2(hfac)_2]_2$, where $M^2 = Fe^{II}$, Mn^{II}, or Ni^{II}, the central iron, in its high ligand field N_6 environment, is low-spin, while the iron coordinated to hfac in the first complex is, as expected for its tris-β-diketonate environment, high-spin.[462]

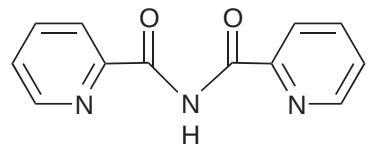
$Fe(bpe)_2(NCS)_2\cdot MeOH$, bpe = *trans*-1,2-bis(4-pyridyl)ethene, is a supramolecular coordination polycatenane, consisting of two interlocked 2D networks.[39] Bis-pyridylethane and bis-pyridylethene also appear elsewhere as bridging ligands in binuclear complexes (e.g., pentacyanoferrates (Section 5.4.2.2)).

The 2-pyridylmethyl unit is an important component of many ligands, both garland (straight chain) and tripodal. Iron(II) complexes of the hexadentate ligands (**55**) with R = OMe or OEt have been prepared from iron(III) complexes of 1,9-bis(2′-pyridyl)-2,5,8-triazanonane by a mechanism involving oxidative coordinated ligand dehydrogenation by the iron(III). The C=N bond generated forms a diimine chelating unit with one of the 2-pyridyl groups; a combination of this diimine group with the multiple chelate effect of ligand hexadenticity is sufficient to assure the stability and substitution-inertness of low-spin iron(II) in these products.[463] Iron(III) complexes of tris(2-pyridylmethyl) derivatives of ethane-1,2-diamine appear in Section 5.4.5.1.6, in relation to peroxo derivatives.

The structures of the bis-ligand iron(II) complexes of the tripodal ligands tris(pyridin-2-yl)methane and tris(pyridin-2-yl)phosphine oxide have been determined.[464] The tetradentate tripodal ligand

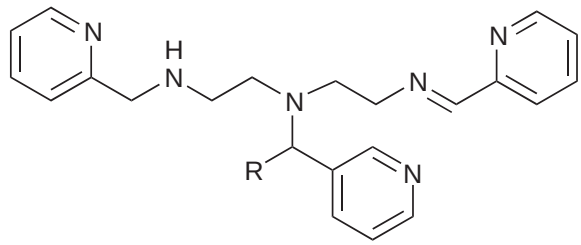


(**53**)

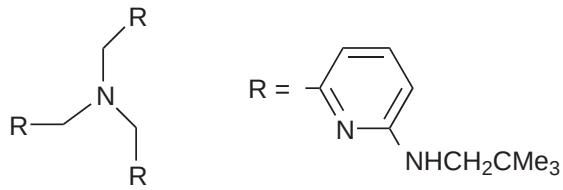


(**54**)

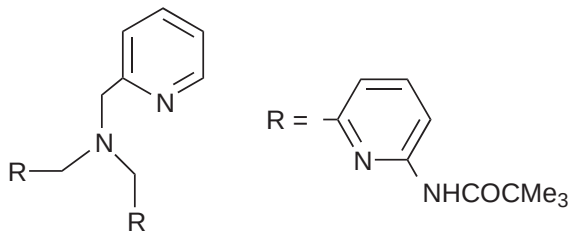
tris(6-neopentylamino-2-pyridylmethyl)amine, tnpa = (**56**), is present in the hydroxide-benzoate complex $[Fe^{III}(tnpa)(OH)(OOCPh)]^{+}$.[465] The very similar ligand bis(6-pivalamido-2-pyridylmethyl)-(2-pyridylmethyl)amine, bppa = (**57**), stabilizes $OOBu^{t}$[466] and even OOH[467] coordinated to Fe^{III}.



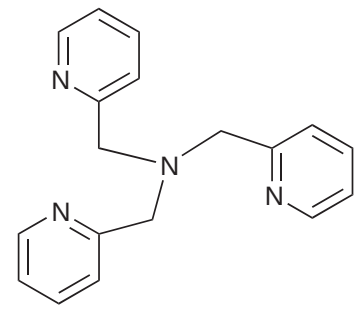
(**55**)



(**56**)

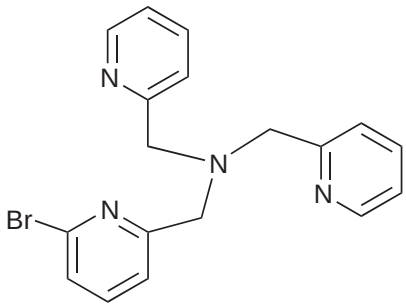


(**57**)

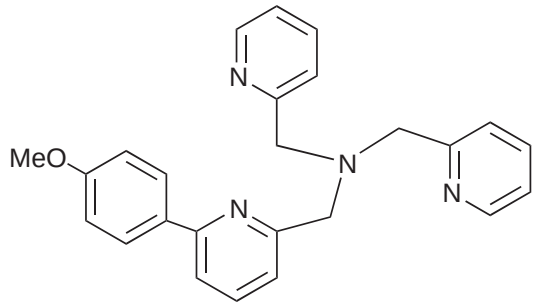


(**58**)

Two iron(III) complexes of unsymmetrically substituted tris(2-pyridylmethyl)amine (tpa, (**58**)) tripodal ligands, [Fe(**59**)Cl_3] and [Fe(**60**)Cl_3], have been synthesized and structurally characterized.[468] The crystal structure, magnetic susceptibility, Mössbauer spectroscopy and photomagnetism of the iron(II) complex [Fe(bpmae)(2,2′-bisimidazole)]$(ClO_4)_2 \cdot \frac{1}{2}H_2O$, where bpmae is the unsymmetrical tripod $N\{CH_2(2\text{-pyridyl})_2\}(CH_2CH_2NH_2)$, have been established.[469]



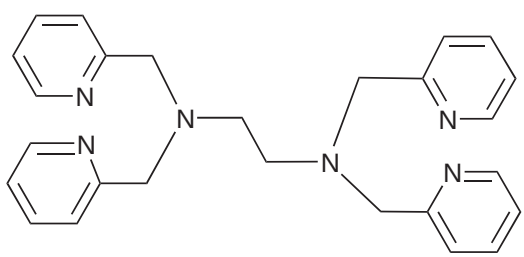
(**59**)



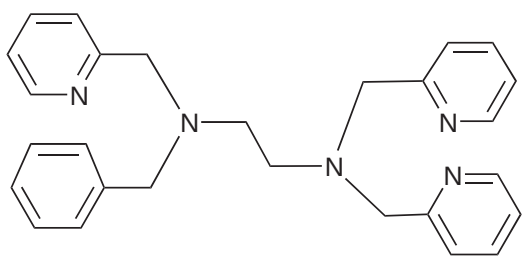
(**60**)

Several iron(III) complexes of tripodal and tetrapodal pentadentate and hexadentate ligands with three or four pendant 2-pyridylmethyl groups have been claimed to show superoxide dismutase activity.[470] Functional and structural influences of tetradentate N_4-donor tripodal ligands—apical nitrogen with 2-pyridylmethyl, quinolylmethyl, and imidazolylmethyl pendant arms variously—on base-promoted intra-diol cleavage of catechols have been assessed. There is a correlation between rate constants for cleaving the coordinated catechol and reduction potentials of the respective iron(III) complexes, models for catechol 1,2-dioxygenase, over a range of 300-fold in rate constants.[471]

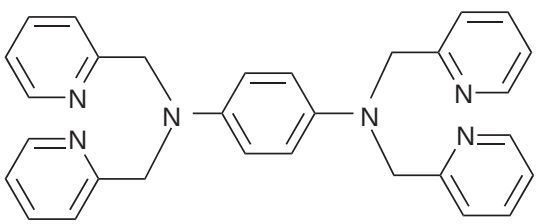
The kinetics of formation of the dinuclear iron(III) complex $[(tpa)Fe(\mu\text{-}O)(\mu\text{-urea})Fe(tpa)]^{3+}$ were investigated in relation to the suggestion that urease action *in vivo* involves an intermediate containing –Ni(μ-OH)(μ-urea)Ni–. The mechanism of formation of the di-iron species from $[(tpa)(H_2O)Fe(\mu\text{-}O)Fe(OH)(tpa)]^{3+}$ is proposed to involve three reversible steps.[472] The tetrapodal analogue of tpa, viz *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethane-1,2-diamine (tetpen, (**61**)), is hexadentate in [Fe(tetpen)]$(ClO_4)_3$, its close relation (**62**) is pentadentate, as in the $[Fe(\mathbf{62})Cl]^{2+}$ cation.[473] Its benzene-1,4-diamine analogue (**63**) is expected to be terdentate – earlier reports of a yellow 1:1 complex were unable to distinguish between a mononuclear complex or a 1D coordination polymer, but it is now known that [Fe(**63**)Cl_2] is the former, containing five-coordinate Fe^{2+}.[474]



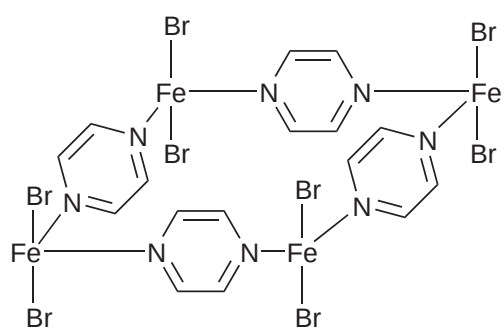
(**61**)



(**62**)



(**63**)

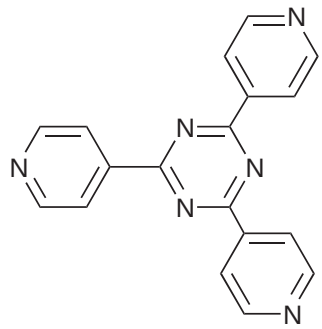


(**64**)

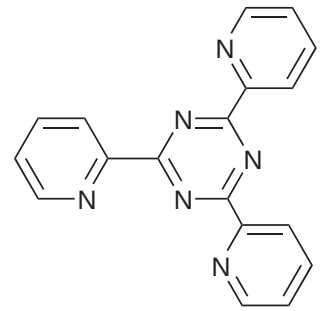
(i) Pyrazines and triazines

Pyrazine is an important bridging ligand, both in binuclear species of the $L^1{}_5M^1$–pz–$M^2L^2{}_5$ type (see, e.g., Section 5.4.2.2.5 for Fe^{II}—pz—Co^{III} → Fe^{III}—pz—Co^{II}) and in forming infinite chains ⋯ M—pz—M—pz—M ⋯, as in $[Fe(pz)_2Br_2]$, $[Fe(pz)_2(N_3)_2]$, and $[Fe(pz)M(CN)_4]$, M = Ni, Pd, Pt. $[Fe(pz)_2Br_2]$ has a 2D layer structure, with pyrazines bridging pairs of Fe ions, each of which has a pair of *trans* bromide ligands, (**64**).[475] In $[Fe(pz)_2(N_3)_2]$ both pyrazine and azide are bridging.[452] In $[Fe(pz)M(CN)_4]$ pyrazine bridging orthogonal to cyanide bridging gives an infinite 3D structure.[322]

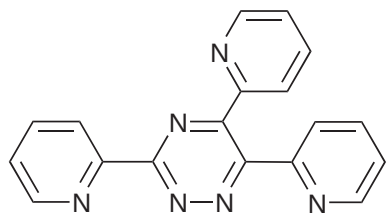
2,4,6-Tris-(4-pyridyl)-1,3,5-triazine, (**65**), links this section to the preceding section, with its bridging properties giving rise to a 2D bimetallic oxide network structure for $[Fe(\mathbf{65})_2]Mo_4O_{13}$ (Section 5.4.5.2).[476] 2,4,6-Tris-(2-pyridyl)-1,3,5-triazine, ^{2,4,6}tptz (**66**), was formerly of considerable analytical importance;[132,477] its iron(II) complex occasionally features in kinetic studies (Section 5.4.3.5.5). 3,5,6-Tris-(2-pyridyl)-1,2,4-triazine, ^{3,5,6}tptz (**67**), another spectrophotometric reagent for iron(II), can bridge iron(II) to molybdenum(0) or rhenium(I) complexes $Mo(CO)_4$(3,5,6-tptz)[478] or $ReCl(CO)_3$(3,5,6-tptz).[479]



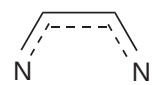
(**65**)



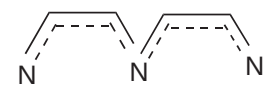
(**66**)



(**67**)



(**68**)



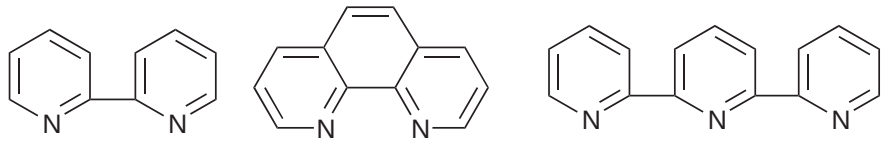
(**69**)

5.4.3.5 Diimine and Related Ligands

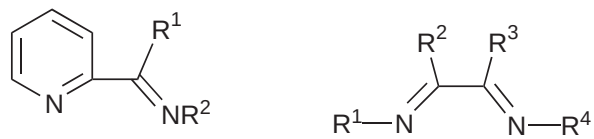
5.4.3.5.1 General

The diimine (**68**) and terimine (**69**) chelating moieties generally bind very strongly to Fe^{2+}, moderately strongly to Fe^{3+}, giving stable and, for Fe^{2+}, substitution-inert complexes. The history and extensive chemistry of these complexes has been surveyed in the first edition of this treatise.[1,2] The most familiar diimine ligands are 2,2′-bipyridyl (**70**) and 1,10-phenanthroline (**71**), the most familiar terimine 2,2′:6′,2″-terpyridyl (**72**). A large number of substituted derivatives of these parent compounds have been prepared, and the range of diimine species greatly extended by the synthesis, either directly or on Fe^{2+} templates, of numerous bidentate Schiff base (**73**) and diazabutadiene (**74**) ligands. The choice of appropriate methods and precursors permits the synthesis of ligands of higher denticity, especially tetradentate and hexadentate ligands containing two or three diimine units, not to forget the series of quater-, quinque-, and sexadentate polypyridyls. Thus over the past few decades a very wide range of diimine ligands and complexes has been built up, of varying

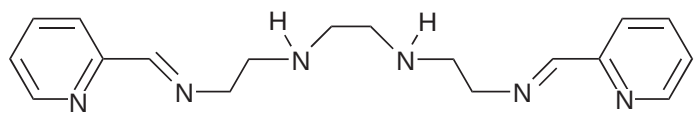
structure, bulk, denticity, base strength, and solvation properties (HLB[97,99,100]), especially for iron(II) analysis, for the study of spin cross-over, and for kinetic and mechanistic investigations, both of substitution and of redox reactions. In recent years these complexes have been used for probing solvation and reactivity of complexes in various media – water, salt solutions, binary aqueous mixtures, and nonaqueous solvents. In the following pages we shall try to document the iron coordination chemistry of a generous selection of this family of complexes, with the coverage divided mainly according to properties and reaction types. However we shall for the most part maintain a division between di-, tri-, and hexadentate ligands on the one hand, and tetradentate bisdiimine ligands on the other. The former can, through the formation of tris-, bis-, and mono-ligand complexes, complete the coordination shell of Fe^{2+} or Fe^{3+}. Bisdiimine ligands cannot achieve this and thus usually either form bi- or polynuclear binary complexes or ternary complexes with one bis-diimine and two other ligands to complete an octahedral coordination shell.



(**70**) (**71**) (**72**)



(**73**) (**74**)



(**75**)

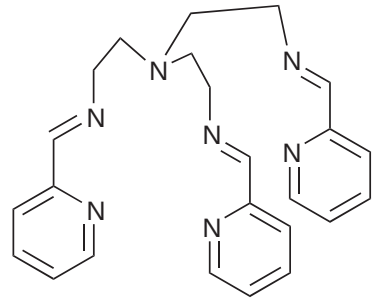
The synthesis of hexadentate tris-diimine ligands, e.g., (**75**), has resulted in Fe^{2+} complexes which are very inert to substitution, especially when the ligand is tripodal, e.g., (**76**), even more so when it is encapsulating. Such extremely inert complexes are particularly valuable for studies of electron transfer or of solubilities and solvation. Fe^{2+} complexes of several encapsulating tris-diimine ligands,[130] for example the cage ligands (**77**), (**78**) and (**79**), show the expected extreme substitution inertness.[480]

There is a brief but comprehensively referenced section on iron in a review of homoleptic 2,2-bipyridyl complexes;[481] iron–terpy (3 pages) and iron–quaterpy (1/2 page) complexes have also been briefly reviewed.[482] Absorption spectra and photochemistry of appropriate iron diimine complexes are included in a text on polypyridyl and porphyrin complexes.[483] A review of the application of chiral 2,2′-bipyridines, 1,10-phenanthrolines, and 2,2′:6′,2″-terpyridines in homogeneous catalysis contains a little material on iron complexes of such ligands.[484]

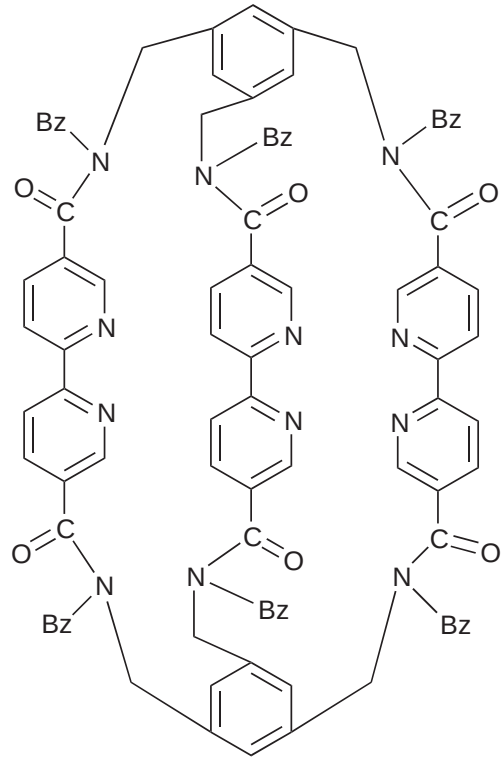
5.4.3.5.2 Preparations, properties, and structures

(i) 1,10-Phenanthroline, 2,2′-bipyridyl, and related ligands

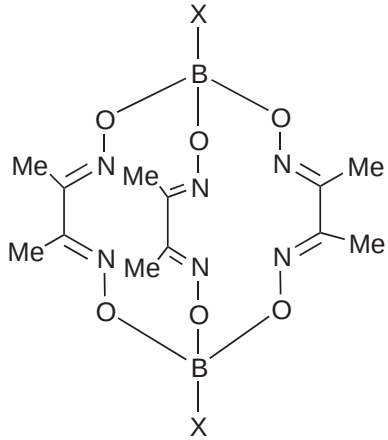
Advances in synthetic methods have made mixed diimine ligand complexes, such as $[Fe(4,7\text{-}Ph_2phen)_n(phen)_{(3-n)}]^{2+}$ [485] whose interaction with DNA is documented below, more accessible. Thus, for example, $[Fe(bipy)_2(MeCN)_2]^{2+}$ (see Section 5.4.5.4.1 below) reacts with diimines, in



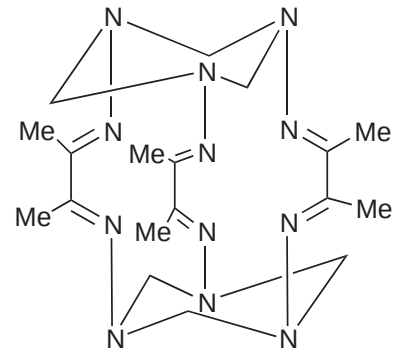
(**76**)



(**77**)

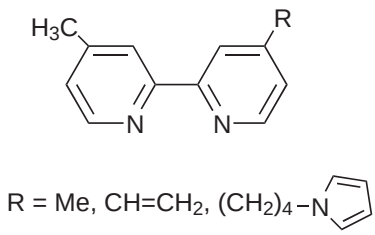


(**78**)

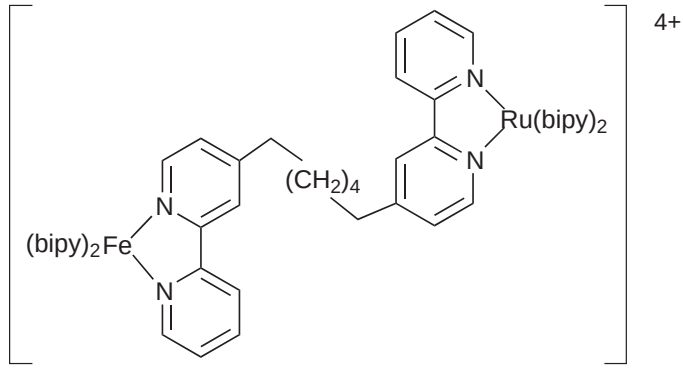


(**79**)

this case (**80**), to give the ternary complexes $[Fe(bipy)_2(diimine)]^{2+}$. It is also the starting material for preparation of the mixed binuclear $Fe^{II}Ru^{II}$ complex (**81**) and its one- and two-electron oxidized $Fe^{III}Ru^{II}$ (class I mixed valence[334,335]) and $Fe^{III}Ru^{III}$ forms.[486]



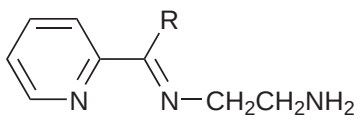
(**80**)



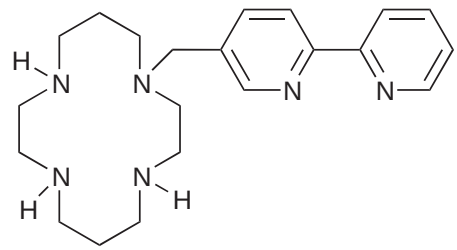
(**81**)

Several tripodal and hexapodal ligands have been prepared with bipy-containing pendant arms. A trimethylamine derivative with three such arms forms a low-spin iron(II) complex in which the six bipy nitrogens are coordinated normally, but with indications of weak interaction between the iron and the amine-nitrogen. The complex has rather low absorption, $\varepsilon_{502} = 1{,}150$, an order of magnitude less than for $[Fe(phen)_3]^{2+}$.[487] A similar tripod based on 1,4,7-triazacyclononane forms a rather short-lived iron(II) complex; a hexaazamacrocycle with six bipy-containing pendant arms forms mono- and binuclear complexes.[488] Presumably all these complexes bind the iron through their bipy moieties; the rather low stabilities of several of their iron complexes may be due to steric constraints imposed by the apex of the tripod or hexapod.

Several ligands combine one or more diimine moieties with other functional groups, as for example in the iron(II) complexes of carboxamide and carbothioamide derivatives of bipy[489] in Sections 5.4.4.1.5 and 5.4.4.2 below, or of the Schiff base ligands (**82**). The combined 2,2′-bipyridyl–tetraazamacrocyclic ligand (**83**)[490] and the carbohydrate-modified bipy ligand (**84**)[491] form stable low-spin Fe^{2+} complexes. The ferrocene-linked bis-2,2′-bipyridyl ligand (**85**) and the similar 1,10-phenanthroline compound (**86**) also form very stable iron(II) complexes, in which the ligands are bonded to the metal through the two diimine groups and two *cis* carbonyl oxygens. Cyclic voltammetry on the free ligands and the complexes suggests that there are strong Fe ··· Fe interactions in the latter. The complex $[Fe(\mathbf{87})_2]^{2+}$ undergoes ligand exchange, which is fast on the NMR time scale.[492] These ferrocene-containing complexes are very lipophilic, as are complexes containing the alkyl-substituted 2,2′-bipyridyl ligands mentioned in connection with solvatochromism of diimine–cyanide–iron(II) complexes (Section 5.4.3.5.8) and the alkoxy complexes $[Fe(\mathbf{8})_3]^{2+}$.[64]

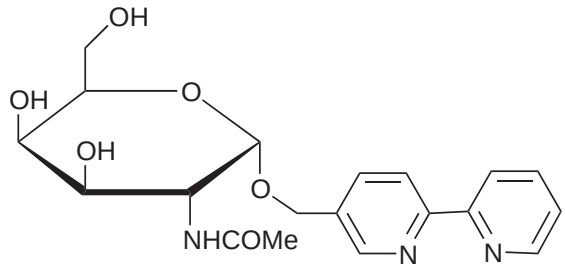


(**82**)

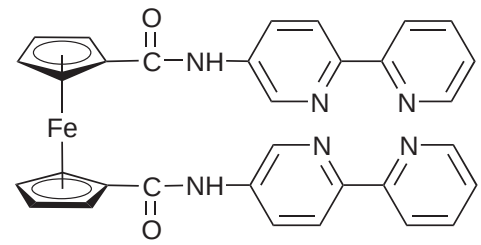


(**83**)

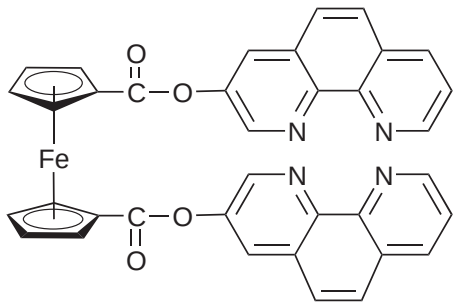
Crystal structures of $[Fe(bipy)_3](ClO_4)_2$,[493] $[Fe(bipy)_3][Fe_2(oxalate)_3]$,[494] and $[Fe(phen)_3](NCS)_2$ have been reported.[495] The crystal structure of $[Fe(phen)_3](sac)_2(sacH)\cdot 6H_2O$ reveals the $[Fe(phen)_3]^{2+}$ residing in channels along the *b*-axis in a hydrogen-bonded network formed by the saccharinate anions, saccharin molecules, and waters of crystallization.[496] Two crystal structure determinations of $[Fe(bipym)_3]^{2+}$ salts involve the ClO_4^- anion[497] and the binuclear $[Fe_2(N_3)_{10}]^{2-}$anion.[498] The structures of $[Fe(phen)_3]I_n$, $n = 14$ or 18, have been established,[499] as has that of a ternary iron(II)–bipy–oxalate complex, which crystallizes as infinite zigzag —Fe—C_2O_4—Fe—C_2O_4—Fe— chains.[500]



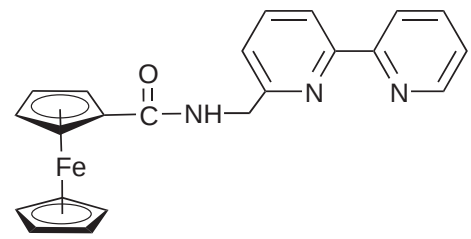
(**84**)



(**85**)

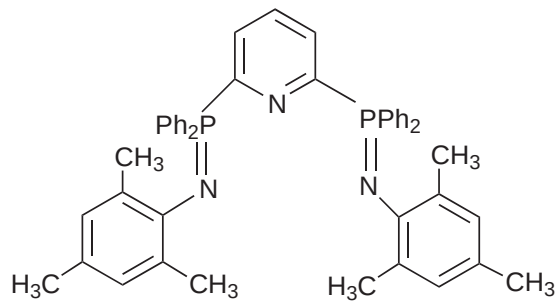


(**86**)

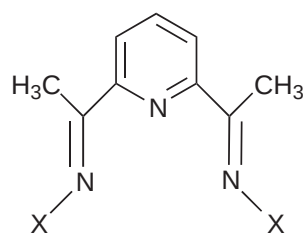


(**87**)

Heat treatment of carbon black impregnated with a salt of $[Fe(phen)_3]^{2+}$ gives an oxygen reduction catalyst.[501] The compounds $[Fe_2(\mathbf{88})Cl_4]$,[502] $[Fe(\mathbf{89})Cl_2]$[503–506] and $[Fe(\mathbf{90})Cl_2]$[507] are potential ethene polymerization catalysts; they all contain five-coordinated iron(II). The chiral terpy ligands (**91**) (R^1, R^2 = all three combinations of H, Pr^i) and the Schiff base analogue (**92**), also



(**88**)

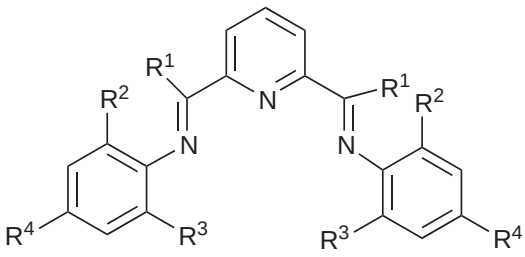


X = NRR', 2,5-dimethylpyrrolyl, 2,6-diisopropylphenyl

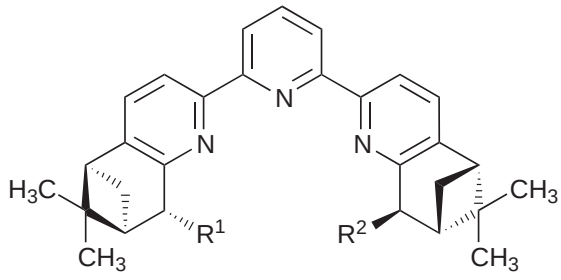
(**89**)

form five-coordinated complexes $[FeLCl_2]$.[508] The pentadentate ligand 2,6-diacetylpyridine-bis-(6-chloro-2-pyridylhydrazone), (**93**), is a terimine derivative which forms a purple complex $[Fe(\mathbf{93})Cl(MeOH)]^+$ in which the iron is believed to be seven-coordinated, with axial chloride and methanol ligands.[509]

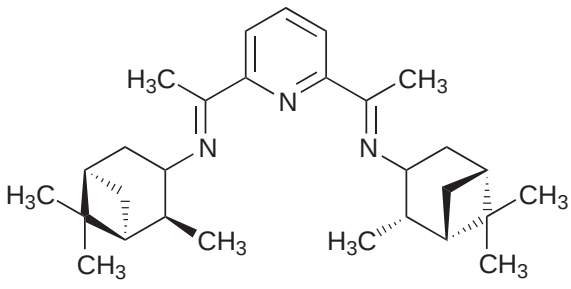
Structures of the ternary iron(III) complexes *mer*-$[Fe(terpy)Cl_3]$ and *mer*-$[Fe(2,4,6\text{-tptz})Cl_3]$ (2,4,6-tptz = (**66**)) have been determined.[510]



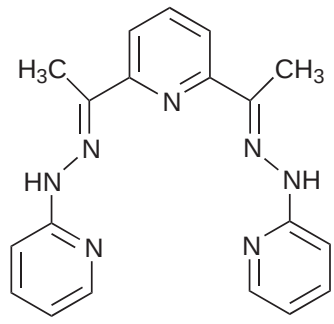
(**90**)



(**91**)



(**92**)



(**93**)

(ii) Schiff base and diazabutadiene complexes

Structures have been determined for $[Fe(gmi)_3](BF_4)_2$ (gmi = MeN=CHCH=NMe),[367] the iron(II) tris-diazabutadiene-cage complex of (**79**) generated from cyclohexanedione rather than from biacetyl,[362] and $[Fe(apmi)_3][Fe(CN)_5(NO)]\cdot 4H_2O$, where apmi is the Schiff base from 2-acetylpyridine and methylamine. Rate constants for *mer* → *fac* isomerization of $[Fe(apmi)_3]^{2+}$ were estimated indirectly from base hydrolysis kinetics, studied for this and other Schiff base complexes in methanol–water mixtures.[370] The attenuation by the —CH_2— spacer of substituent effects on rate constants for base hydrolysis of complexes $[Fe(sb)_3]^{2+}$ has been assessed for pairs of Schiff base complexes derived from substituted benzylamines and their aniline analogues.[511] It is generally believed that iron(II)–Schiff base complexes are formed by a template mechanism on the Fe^{2+}, but isolation of a precursor in which two molecules of Schiff base and one molecule of 2-acetylpyridine are coordinated to Fe^{2+} suggests that Schiff base formation in the presence of this ion probably occurs by attack of the amine at coordinated, and thereby activated, ketone rather than by a true template reaction.[512]

The preparation, characterization, and Mössbauer spectroscopy of the Fe^{3+} complex of the linear hexadentate bis-diimine ligand derived from 1,8-diamino-3,6-diazaoctane (trien) and pyrrole-2-aldehyde have been reported. A crystal structure determination of its PF_6^- salt revealed Fe—N bond distances of 1.915Å, 1.943Å to the pyrrole nitrogens, 1.921Å, 1.930Å to the other diimine nitrogens, and 2.014Å, 2.067Å to the central imine nitrogens.[513]

5.4.3.5.3 Spectroscopy and magnetism

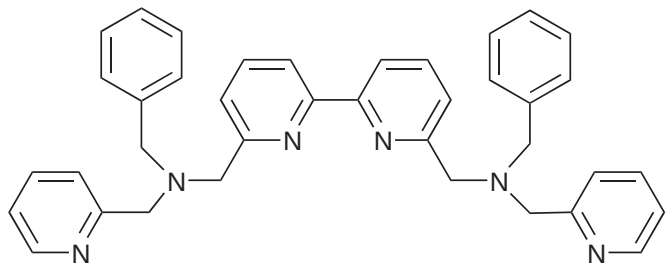
(i) Spectroscopy

A theoretical treatment of the magnetic circular dichroism of $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$, in alcohol glasses at 4 K,[514] and a new theoretical model for the electronic structures involved[515] have permitted yet more detailed analyses of the MLCT bands in the visible absorption spectra of these complexes. The charge-transfer bands in the UV–visible spectrum of $[Fe(bipym)_3]^{2+}$ have been assigned.[516] A standard addition kinetic method for the simultaneous determination of Fe^{II} and Fe^{III} is centered on spectrophotometric $[Fe(phen)_3]^{2+}$ monitoring.[143]

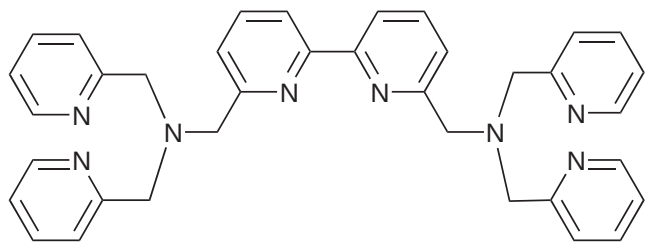
(ii) Magnetism—spin states and spin cross-over

The spin state of iron(II) in substituted 2,2′:6′,2″-terpyridine, (**72**), complexes depends on the position of bulky substituents—phenyl substituents in both the 6 and 6″ positions give a high-spin complex; phenyl substituents in the 4 and 6 positions give a complex which exists both in high-spin and in low-spin forms. Crystal structure determinations gave Fe—N bond distances in both forms of the 4,6-diphenyl complex and of the 6,6″-diphenyl complex. Each ligand in the latter complex has one terminal pyridine very weakly bonded to the iron, with Fe—N = 2.44 Å.[517]

The iron(II) complexes of the hexadentate 2-pyridylmethyl derivatives of bipy (**94**) and (**95**) are spin cross-over compounds, whose light-induced high-spin to low-spin conversion has been monitored in solution by laser flash photolysis. Single exponential kinetics ($k_{H\rightarrow L} = 6.7 \times 10^6$ s^{-1}, at 273 K) were observed for $[Fe(\mathbf{94})]^{2+}$, but for $[Fe(\mathbf{95})]^{2+}$ kinetics were biphasic, with the spin-conversion step ($k_{H\rightarrow L} = 2.5 \times 10^7$ s^{-1}) followed by a slower step ($k = 3.7 \times 10^5$ s^{-1}) involving rearrangement of the pyridylmethyl pendant arms.[518]



(**94**)

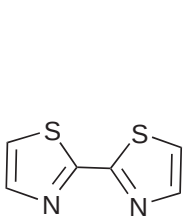


(**95**)

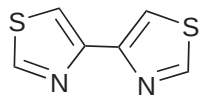
2,9-Bis(2′-methoxyphenyl)-1,10-phenanthroline, bmpphen (**2**), forms a high-spin bis- but not a low-spin tris-ligand iron(II) complex due to interligand repulsion.[16]

2,2′-Bithiazole, 2,2′-btz = (**96**), is a diimine, but it coordinates much less strongly than bipy to Fe^{2+}.[519] $[Fe(2,2'\text{-btz})_3](ClO_4)_2$ exists in two modifications with slightly different magnetic properties.[520] 4,4′-Bithiazole, 4,4′-btz = (**97**), is not a diimine; its iron(II) complex $[Fe(4,4'\text{-btz})_3]^{2+}$ is only weakly colored but its magnetic properties and Fe—N bond distances 1.970–1.973Å suggest that the ligand field effect of 4,4′-btz is not enormously less than that of bipy.[521]

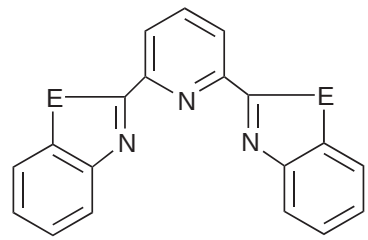
Spin cross-over behavior was investigated for the iron(II) complex of 2,6-bis-(benzimidazol-2′-yl)pyridine, with K, ΔH°, and ΔS° values established in methanol and in propylene carbonate.[522] $[Fe(bzimpy)_2]^{2+}$ (bzimpy = (**98**) with E = NH) is a low-spin complex, but $[Fe(dmbzimpy)_2]^{2+}$ (dmbzimpy = (**98**) with E = NMe) is high-spin. As in, e.g., low-spin $[Fe(phen)_3]^{2+}$ vs. high-spin $[Fe(2,9\text{-}Me_2phen)_3]^{2+}$ interligand Me ··· Me interactions force the ligands sufficiently away from the Fe^{2+} for the resultant ligand field to be insufficient to impose low-spin behavior. When E = S in (**98**) the bis-ligand iron(II) cation is a spin cross-over complex.[523] The sharpness of the spin transition at 403 K for $[Fe(bzimpy)_2](ClO_4)_2 \cdot 0.25H_2O$ is ascribed to inter-ring π-stacking interactions and the resulting high cooperativity in the high-spin state.[524]



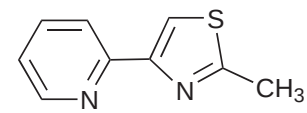
(**96**)



(**97**)

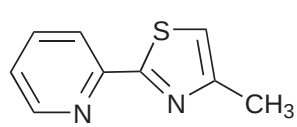


(**98**)

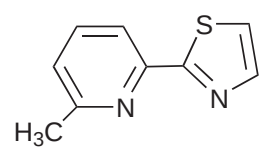


(**99**)

The tris-ligand iron(II) complexes of the isomeric methyl-substituted pyridin-2-ylthiazoles (**99**) and (**100**) have strongly temperature-dependent magnetic moments, consistent with gradual l.s. ⇌ h.s. cross-over; the magnetic moments vary over an unusually long temperature range. Introduction of a methyl substituent ortho to the pyridine nitrogen, to give ligand (**101**), leads to a tris-ligand iron(II) complex in which interligand steric interference is sufficient to make the complex high-spin throughout. The Fe—N bond distances to the pyridine and thiazole moieties of 2.199Å and 2.183Å at 294 K, 2.040Å and 2.028Å at 133 K, are consistent with high-spin and low-spin properties, respectively.[525]

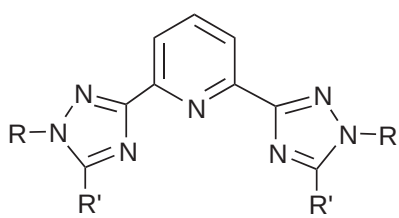


(**100**)

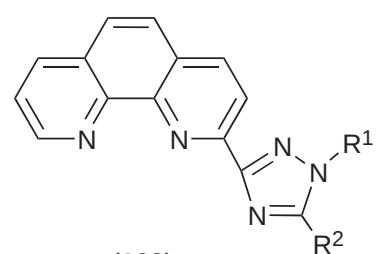


(**101**)

The bis-triazole-pyridine ligands (**102**), with R^1, R^2 = H, Me variously, exert a smaller ligand field than terpy (cf. 2,2′-btz and bipy), as is reflected in their magnetic properties. Those of the hydrates of the bis-ligand complexes with R = H are significantly affected by hydrogen-bonding in the solid state.[526] The triazole-1,10-phenanthroline ligand ((**103**), $R^1 = R^2 = H$) forms a bis-ligand complex with Fe which exists in two polymorphic forms, one low-spin, the other a singlet/quintet mixture.[527] The analogues with $R^1 = R^2$ = Me and the two isomers with R^1 and R^2 = H and Me are all spin cross-over complexes.[528]



(**102**)

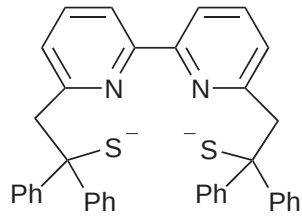


(**103**)

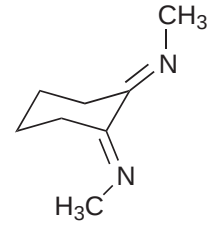
The dianion of 6,6′-bis(2,2′-diphenyl-2-sulfanylethyl)-2,2′-bipyridine (**104**) gives a chloro–iron (III) complex in which the pentacoordinated metal is in the $S = 3/2$ state.[529]

5.4.3.5.4 Solution properties

Partial molar volumes have been determined for $[Fe(phen)_3]^{2+}$, $[Fe(bmi)_3]^{2+}$, and $[Fe(cmi)_3]^{2+}$ (cmi = (**105**)) in water and in methanol–water mixtures, and for $[Fe(bipy)_3]^{2+}$ and $[Fe(Me_2bsb)_3]^{2+}$ in water.[530] Calculations of these partial molar volumes have been compared with the experimentally derived values.[95]



(**104**)



(**105**)

Solubilities, in water, ethanol, and ethanol–water mixtures, have been reported for $[Fe(phen)_3](ClO_4)_2$, $[Fe(phen)_3]_2[Fe(CN)_6]$, and $[Fe(phen)_3][Fe(phen)(CN)_4]$.[531] Solubilities of salts of several iron(II)–diimine complexes have been measured in a range of binary aqueous solvent mixtures in order to estimate transfer chemical potentials and thus obtain quantitative data on solvation and an overall picture of how solvation is affected by the nature of the ligand and the nature of the mixed solvent medium. Table 8 acts as an index of reports of such data published since 1986; earlier data may be tracked through the references cited below Table 8, and through the review of the overall pattern for iron(II) and iron(III) complexes (cf. Figure 1 in Section 5.4.1.7 above) published recently.[96]

Transfer chemical potentials for the low-spin amine–diimine complexes $[Fe(tsba)_2]^{2+}$ with tsba = (**82**) were estimated from the solubilities of their perchlorate salts, in methanol–water mixtures.[532] Solubility and transfer chemical potential data are also available for $[Fe(Me_2bsb)_3]^{2+}$ in several nonaqueous solvents.[533] One of the main purposes in determining transfer chemical potentials for these iron(II)–diimine complexes is to enable dissection of reactivity trends into initial state and transition state components for base hydrolysis (see next section) in binary aqueous solvent mixtures. Systems for which this has been achieved are indicated in Table 8.

Stability constants log K_1 and log K_2 have been determined for iron(II) complexation by 4-X-2,6-bis-(benzimidazol-2′-yl)pyridine, X = H, OH, or Cl, in several methanol-containing solvent mixtures.[534] Redox potentials have been reported for the $[Fe(4,4'\text{-distyrylbipy})_3]^{3+/2+}$ couple and its *p*-methylstyryl analogue (also for Ru, Os analogues).[535]

5.4.3.5.5 Kinetics and mechanisms

(i) Aquation and ligand replacement

Activation volumes for aquation of Schiff base complexes $[Fe(C_5H_4NCH{=}NHR)_3]^{2+}$ (R = Me, Et, Pr^n, Bu^n) in 0.1 M aqueous HCl are between $+11\,cm^3\,mol^{-1}$ and $+14\,cm^3\,mol^{-1}$,[536] and thus within the range established earlier[537] for (substituted) tris-1,10-phenanthroline–iron(II) complexes. These positive values are consistent with dissociative activation, as are those for dissociation of $[Fe(5Brphen)_3]^{2+}$ and of $[Fe(5NO_2phen)_3]^{2+}$ in the presence of edta.[538] $\Delta V^{\ddagger}$ and $\Delta H^{\ddagger}$ values for aquation of $[Fe(5Brphen)_3]^{2+}$ have the subject of isochoric analysis.[539,540] Medium effects on activation volumes have been reviewed for iron–diimine complexes in binary aqueous solvent mixtures.[541]

Salt effects (chlorides and bromides of alkali metal, alkaline earth, and ammonium cations) on rate constants for aquation of $[Fe(bipy_3]^{2+}$ and $[Fe(phen)_3]^{2+}$ in aqueous solution have been interpreted in terms of added cation effects on the activity of the water.[542,543]

Reports on solvent effects on rate constants for aquation of diimine complexes include those on $[Fe(5Brphen)_3]^{2+}$ and $[Fe(4,7\text{-}Me_2phen)_3]^{2+}$ in methanol– and ethanol–water, $[Fe(bipy)_3]^{2+}$, $[Fe(phen)_3]^{2+}$, and $[Fe(5NO_2phen)_3]^{2+}$ in aqueous methyl D-glycopyranosides,[544] and

Table 8 Solvation of iron(II)-diimine complexes in binary aqueous solvent mixtures.[a]

	MeOH	*EtOH*	*Pr^{i}OH*	*Bu^{t}OH*	*Glycol*	*Glycerol*	*DMSO*	*Urea*
Bidentate ligands								
$Fe(bipy)_3^{2+}$	362		363		364	364		
$Fe(phen)_3^{2+}$		363*	363*		364*	364	365	366*
$Fe(gmi)_3^{2+}$		367	367	367	364			366
$Fe(Me_2bsb)_3^{2+}$	368*	368	368		364,368*	368		366,368
$Fe(3OMebsb)_3^{2+}$	369*	369	369	369*			369	
$Fe(pmi)_3^{2+}$	370							
Terdentate ligands								
$Fe(tsb)_2^{2+}$ [b]		363					365*	
Hexadentate ligands								
Fe(**75**)$^{2+}$							365	
Fe(**75′**)$^{2+}$ [c]			369	369			369	
Fe(**79**)$^{2+}$	362							
Fe(Bcage)^0 [d]	371			371			369*	

[a] Numbers given in the body of this table indicate the references in which measured solubilities and derived transfer chemical potentials are reported; an asterisk indicates that the transfer chemical potentials have been used in initial state–transition state analyses of reactivity trends for base hydrolysis. [b] tsb = (**89**) with X = H or Me. [c] (**75′**) = (**75**) with quinolyl in place of pyridyl. [d] Bcage = (**78**) with X = F or OBu^n (also analogues with Ph, Ph in place of Me, Me and X = OBu^n, and with $-CH_2CH_2CH_2CH_2-$ in place of Me, Me (i.e., cyclohexyl moieties) and X = F).

$[Fe(5NO_2phen)_3]^{2+}$ aquation in ternary water–Bu^{t}OH–polyethyleneglycol (PEG400).[545] Kinetic patterns for systems of these types have been the subject of theoretical analyses, as in the application of the Savage–Wood Group Additivity principle to $[Fe(5NO_2phen)_3]^{2+}$ aquation in a variety of water-rich binary aqueous mixtures and in aqueous salt solutions[546] and in the Kirkwood–Buff treatment of preferential solvation of initial and transition states for $[Fe(phen)_3]^{2+}$ aquation in methanol–water[547] and for $[Fe(gmi)_3]^{2+}$ aquation in Bu^{t}OH + water.[548]

Kinetic studies of the reaction of a $CH_2S(CH_2)_3SCH_2$-linked bis-terpyridyl ligand (bterpy) with $[Fe(terpy)_2]^{2+}$ revealed a very slow two-step process. The mechanism suggested consists of slow loss of one terpy, rapid formation of [Fe(terpy)(bterpy)], and finally slow displacement of the second terpy as the partially bonded bterpy becomes hexadentate.[549] Replacement of the 2,4,6-tri(2′-pyridyl)-1,3,5-triazine, 2,4,6-tptz (**66**), in $[Fe(2,4,6\text{-tptz})_2]^{2+}$ by phen or bipy is alleged to occur by an associative mechanism.[550]

Activation volumes for dissociation, base hydrolysis, cyanide attack, and peroxodisulfate oxidation (see following pages) of iron(II)–diimine complexes are collected together in Table 9.

(ii) Base hydrolysis

The long-debated mechanism of hydroxide attack at diimine complexes, i.e., nucleophilic attack at iron vs. attack at the coordinated ligand, is still not unequivocally established.[551–554] A study of $[Fe(ferene)_3]^{4-}$ (ferene = 5,5′-[3-(2-pyridyl)-1,2,4-triazine-5,6-diyl]-bis-2-furansulfonate, (**106**)) base hydrolysis sought further kinetic evidence,[555] as did electron density calculations for coordinated pyridine, 2,2′-bipyridyl and 1,10-phenanthroline.[556,557] Although no firm evidence has been presented recently for hydroxide or cyanide attack at diimines coordinated to iron(II), ligand hydroxylation has been demonstrated for mixed valence copper(I)/(II)/phen or bipy species.[558] There is nonetheless no doubt of the bimolecular nature of the major or sole second-order, $k_{2(OH)}$, term in the rate law for hydroxide attack at iron(II)–diimine complexes. Such $k_{2(OH)}$ values provide a useful probe for medium effects, as can be seen in solute effects of methyl-D-glycopyranosides on $[Fe(bipy)_3]^{2+}$ base hydrolysis kinetics[544] and in salt effects (mainly Et_4NBr and KBr)

Table 9 Activation volumes ($cm^3\,mol^{-1}$) for reactions of iron(II)-diimine complexes, in aqueous solution at (or close to) 298 K.

	Dissociation	*Base hydrolysis*	*Cyanide attack*	*Peroxodisulfate oxidation*
BIS-PYRIDINES				
$Fe(bipy)_3^{2+}$	+12.3, +14.8	+12.8	+12.2	−20.8, −21.9
$Fe(4,4'\text{-}Me_2bipy)_3^{2+}$	+12.5, +15.5	+11.7	+12.3	
$Fe(4,4'\text{-}Et_2bipy)_3^{2+}$	+12.7, +16.9			
$Fe(5,5'\text{-}Me_2bipy)_3^{2+}$	+13.7, +17.4			
$Fe(phen)_3^{2+}$	+15.4	+14.2	+10.5	−27.0
$Fe(4\text{-}Mephen)_3^{2+}$			+10	
$Fe(5\text{-}Brphen)_3^{2+}$	+22.3			
$Fe(5\text{-}NO_2phen)_3^{2+}$	+17.9, +21.7			
$Fe(4,7\text{-}Me_2phen)_3^{2+}$	+11.6			
$Fe(hxsbh)_3^{2+}$		+13.4		
PYRIDINE SCHIFF BASES				
$Fe(X\text{-}bsb)_3^{2+}$		+11.1 to +13.6		
$Fe(py\text{-}2\text{-}CH{=}NR)_3^{2+}$	+11.5 to +14.2			
$Fe(Me_2tsb)_2^{2+}$		+6		
DIAZABUTADIENE				
$Fe(MeNCH{=}CHNMe)_3^{2+}$		+16.7		
DIIMINE-CYANIDE				
$Fe(bipy)_2(CN)_2$				−7.7 to −8.5
$Fe(bipy)(CN)_4^{2-}$				−3.7
$Fe(phen)(CN)_4^{2-}$				−2.1
$Fe(HNCH{=}CHNH)(CN)_4^{2-}$				−10.2
$Fe(Me_2bsb)(CN)_4^{2-}$				+4.6
$Fe(CN)_6^{4-}$				0

References to the activation volumes given in this table are cited in the text.

on base hydrolysis reactivities of low-spin iron(II) complexes of diazabutadiene and Schiff base ligands; ligand hydrophilicity is an important factor.[559] Values for $k_{2(OH)}$ have also been used to assess attenuation of substituent effects on reactivities of low-spin iron(II) complexes of Schiff base ligands.[511] Figure 2 gathers together an illustrative selection of solvent and ligand structural and substituent effects on reactivity for base hydrolysis of low-spin iron(II)–diimine complexes in

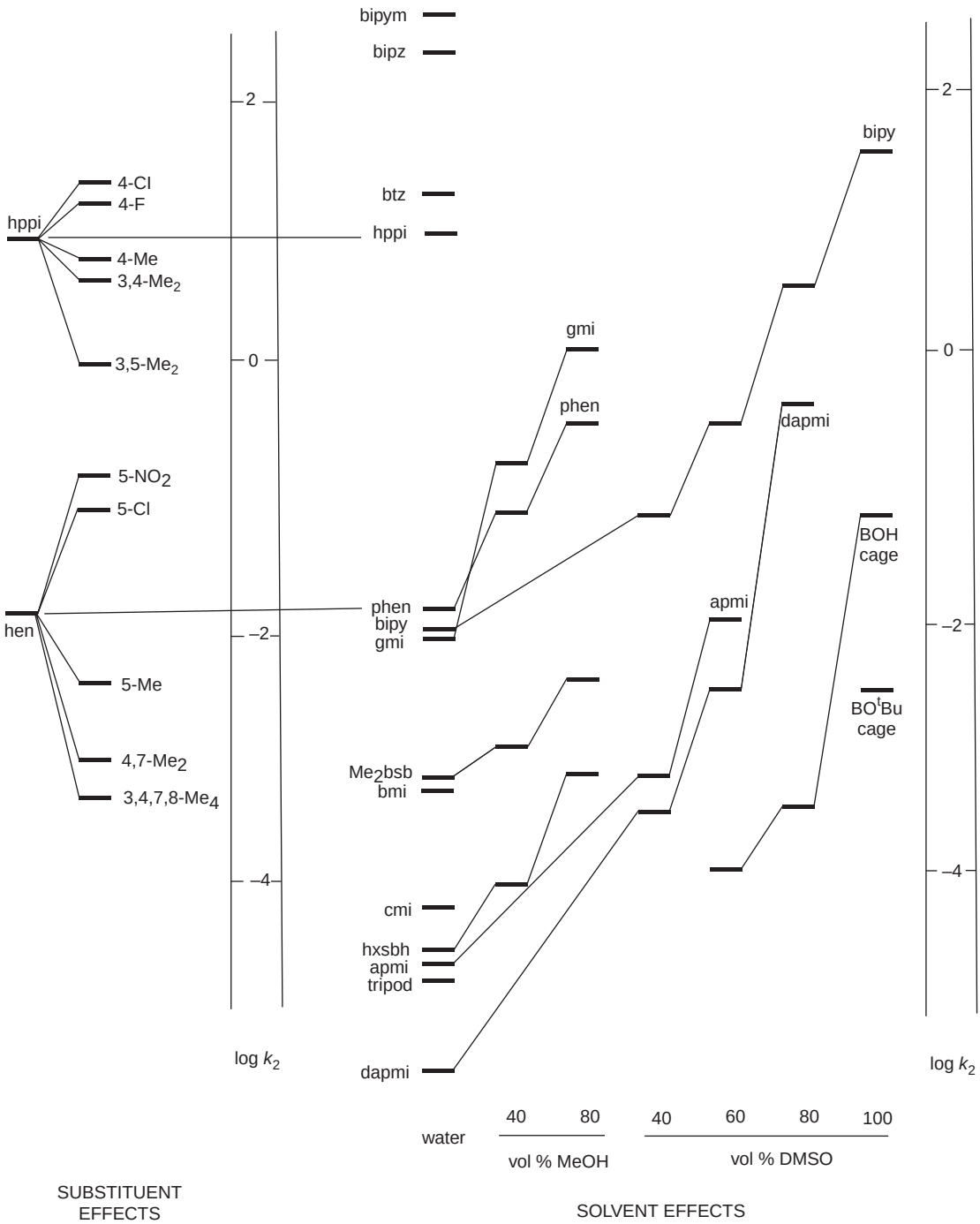
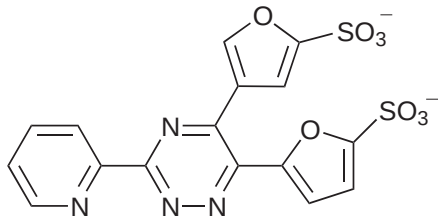


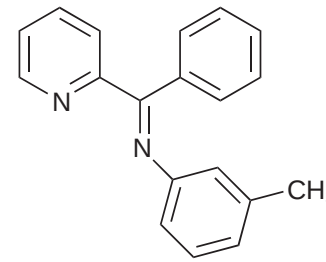
Figure 2 Diagrammatic summary of selected structural, substituent, and solvent effects on rate constants (k_2, at 298 K) for base hydrolysis of low spin iron(II)-diimine complexes. Ligand abbreviations not appearing in the list at the end of this chapter are : apmi = (**73**) with $R^1 = R^2 = Me$; BOH cage = (**78**) with X = OH; $BOBu^t$ cage = (**78**) with $X = OBu^t$; dapmi = (**89**) with X = Me; hppi = (**73**) with $R^1 = H$, $R^2 = Ph$; tripod = (**76**).

methanol–water[560] and in DMSO–water.[561] Further kinetic data are available for $[Fe(phen)_3]^{2+}$ in aqueous diols, where reactivity trends are dominated by (de)solvation of the hydroxide,[562] and for several bidentate, and one terdentate, Schiff base complexes $[Fe(bsb)_3]^{2+}$ and $[Fe(tsb)_2]^{2+}$, in methanol–water media.[371] Systems for which analysis of reactivity trends for base hydrolysis in binary aqueous solvent mixtures into initial state and transition state contributions has been achieved are indicated in Table 8 above.

Activation volumes have been determined for base hydrolysis of $[Fe(phen)_3]^{2+}$, $[Fe(bipy)_3]^{2+}$, $[Fe(4MeObsb)_3]^{2+}$, and $[Fe(3Mebsb)_3]^{2+}$ (3Mebsb = (**107**)). The overall pattern of $\Delta V^{\ddagger}$ and $\Delta H^{\ddagger}$ values for aquation and for base hydrolysis favors dissociative activation for all these reactions.[538] Activation volumes have been also determined for base hydrolysis of several bidentate,[368] and one hexadentate,[563] Schiff base complexes in several binary aqueous solvent mixtures and for $[Fe(gmi)_3]^{2+}$ in glycol–water[364] and a range of other binary aqueous solvent mixtures.[367] These results, along with further results for $\Delta V^{\ddagger}$ for base hydrolysis of $[Fe(phen)_3]^{2+}$ and of $[Fe(bipy)_3]^{2+}$ in alcohol–water mixtures, have permitted the construction of a scheme combining solvent and ligand effects on $\Delta V^{\ddagger}$ for base hydrolysis of a range of diimine–iron(II) complexes.[564]



(**106**)



(**107**)

Substitution reactions of hexadentate diimine complexes of iron(II) are generally slow, thanks to the combination of the strongly binding diimine groups and the chelate effect, even when the ligand contains only two diimine units of the less strongly bonding py—CH=N— type; $k_{2(OH)}$ for $[Fe(hxsbh)]^{2+}$ is ~0.0002 $dm^3\,mol^{-1}\,s^{-1}$.[565] Further diminution of the coordinating strength of the diimine units, by replacing the pyridine ring by quinoline[566] or by pyrrole,[568] results in further increases in $k_{2(OH)}$, whose values are 0.013 $dm^3\,mol^{-1}\,s^{-1}$ and 0.72 $dm^3\,mol^{-1}\,s^{-1}$, respectively (in water at 298 K).

(iii) Cyanide attack

$\Delta V^{\ddagger}$ values for cyanide attack at $[Fe(phen)_3]^{2+}$, $[Fe(bipy)_3]^{2+}$ and $[Fe(4,4'\text{-}Me_2bipy)_3]^{2+}$ in water suggest a similar mechanism to base hydrolysis, with solvation effects dominant in both cases.[567] Cyanide attack at $[Fe(ttpz)_2]^{2+}$, where ttpz is the terdentate ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine, follows a simple second-order rate law; activation parameters are comparable with those for other iron(II)–diimine plus cyanide reactions.[568] Interferences by cyanide or edta in spectrophotometric determination of iron(II) by tptz may be due to formation of stable ternary complexes such as $[Fe(2,4,6\text{-tptz})(CN)_3]^{-}$ (2,4,6-tptz = (**66**)).[569]

(iv) Racemization and isomerization

DNA catalyzes the racemization of $[Fe(phen)_3]^{2+}$—the rate is approximately doubled in the presence of 1,000 μM DNA. DNA also shifts the $\Delta \rightleftharpoons \Lambda$ equilibrium towards a slight enantiomeric excess of the Δ form.[570] The electrostatic and intercalative interactions of $[Fe(phen)_3]^{2+}$ and $[Fe(phen)_3]^{3+}$ with DNA have been probed voltammetrically, and binding constants estimated.[571] The $[Fe(phen)_3]^{2+}$–DNA interaction appears to be primarily electrostatic, $[Fe(4,7\text{-}Ph_2phen)_2(phen)]^{2+}$–DNA interaction to be intercalative.[572] The discussions in these recent publications suggest that early work on the kinetics and mechanism of racemization of $[M(bipy)_3]^{n+}$ and $[M(phen)_3]^{n+}$, M = Ni, Cr as well as Fe,[573–579] is in danger of being overlooked or forgotten. Comparison of k and $\Delta H^{\ddagger}$ values for racemization and dissociation shows that racemization of

$[Fe(phen)_3]^{2+}$ must, at least to a large extent, be intramolecular—in contrast to $[Ni(phen)_3]^{2+}$, where rate constants for racemization and dissociation are identical, indicating an intermolecular mechanism. Molecular modeling predictions of activation energies for the Bailar and Rây-Dutt twists for racemization of $[Fe(phen)_3]^{3+}$ indicate that the latter mechanism should be operative.[580] Added salts have marked effects on rate constants for racemization of $[Fe(phen)_3]^{2+}$ in methanol–water media. From such effects it has proved possible to estimate ion-pairing constants, which are, for example, 11, 18, and 25 for perchlorate, chloride, and thiocyanate, respectively in 80% methanol.[581]

The rate constant for *mer* → *fac* isomerization of $[Fe(3Mebsb)_3]^{2+}$ (3Mebsb = (**107**)) is k_{isomrn} $\sim 10^{-5}$ s^{-1} in aqueous methanol at 298 K.[370]

(v) Redox reactions

A kinetic study of peroxodisulfate oxidation of $[Fe(bipy)_3]^{2+}$ and of $[Fe(phen)_3]^{2+}$ has confirmed the importance of both oxidation and dissociation in determining rate laws and mechanisms.[582] Activation volumes for peroxodisulfate oxidation of $[Fe(phen)_3]^{2+}$ and $[Fe(bipy)_3]^{2+}$ are $-21.9\,dm^3\,mol^{-1}$ and $-27.0\,dm^3\,mol^{-1}$.[290] The role of solvent reorganization free energy in determining solvent effects on rate constants has been probed for peroxodisulfate oxidation of $[Fe(bipy)_3]^{2+}$.[299] Peroxodisulfate oxidation of $[Fe(ttpz)_2]^{2+}$ is kinetically interesting because it is zeroth-order in complex.[568] The rate-determining step here, as in peroxodisulfate oxidations of, e.g., sulfite, Tl^+aq, and $[Co(edta)]^{2-}$, is dissociation of peroxodisulfate into two sulfate radicals. Effects of added salts, up to 4.0 mol dm^{-3} Na_2SO_4 or 5.0 mol dm^{-3} Li_2SO_4, on peroxodisulfate oxidation of $[Fe(phen)_3]^{2+}$ have been reported.[583]

Oxidation of $[Fe(phen)_3]^{2+}$ by concentrated nitric acid is autocatalytic.[584] $[Fe(phen)_3]^{2+}$ reacts with bromate by rate-determining oxidation at high bromate concentration;[585,586] $[Fe(bipy)_3]^{2+}$ and ligand-substituted $[Fe(phen)_3]^{2+}$ cations react with perbromate by rate-limiting dissociation.[587] Reactions of $[Fe(diimine)_3]^{2+}$ with peroxodiphosphate also involve rate-limiting dissociation in the absence of an electron transfer catalyst such as Ag^+.[588] Reaction kinetics and mechanisms for oxidation of $[Fe(diimine)_3]^{2+}$ by peroxoanions have been reviewed.[589]

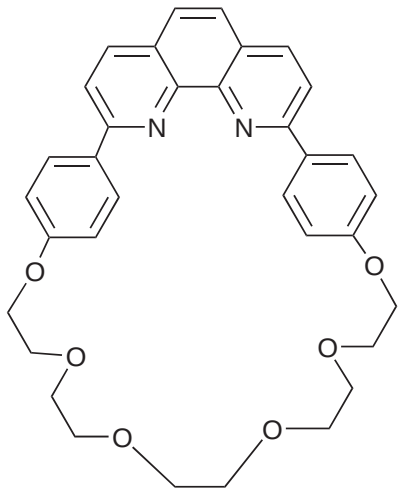
A discussion of the kinetics and mechanisms of one-electron oxidation of thiocyanate and of iodide includes consideration of $[Fe(bipy)_3]^{3+}$, $[Fe(phen)_3]^{3+}$ and ligand-substituted derivatives of the latter as oxidants.[590] Activation parameters for reduction of $[Fe(phen)_3]^{3+}$ by $[Ru_2(\mu\text{-}O)(\mu\text{-}OAc)_2(py)_6]^{2+}$ and by $[Ru_3(\mu\text{-}O)(\mu\text{-}OAc)_6(py)_3]^{+}$, in acetonitrile, are $\Delta H^{\ddagger} = 9\,kJ\,mol^{-1}$, $19\,kJ\,mol^{-1}$ and $\Delta S^{\ddagger} = -100\,J\,K^{-1}\,mol^{-1}$, $-60\,J\,K^{-1}\,mol^{-1}$, respectively, the difference being attributable to a smaller reorganization energy for the trimer.[591] $[Fe(phen)_3]^{3+}$ or $[Fe(bipy)_3]^{3+}$ oxidation of $[Fe(dmf)_6]^{2+}$ involves various mixed solvates, with the observed high order of this outer-sphere redox reaction ascribed to rapid pre-equilibrium between coordinated dimethyl formamide and acetonitrile solvent.[592]

Temperature and pressure effects on rate constants for $[Fe(phen)_3]^{3+}/[Fe(phen)_3]^{2+}$ electron transfer in water and in acetonitrile have yielded activation parameters; $\Delta V^{\ddagger}$ was discussed in relation to possible nonadiabaticity and solvation contributions.[593] Solvation effects on ΔV° for $[Fe(diimine)_3]^{3+/2+}$ half-cells, related diimine/cyanide ternary systems (diimine = phen, bipy), and also $[Fe(CN)_6]^{3-/4-}$ and $Fe^{3+}aq/Fe^{2+}aq$, have been assessed.[105,107] Initial state–transition state analyses for base hydrolysis and for peroxodisulfate oxidation for $[Fe(diimine)_3]^{2+}$, $[Fe(tsb)_2]^{2+}$, $[Fe(cage)]^{2+}$ in DMSO–water mixtures suggest that base hydrolysis is generally controlled by hydroxide (de)hydration, but that in peroxodisulfate oxidation solvation changes for both reactants are significant in determining the overall reactivity pattern.[365]

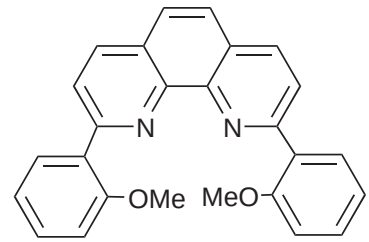
Oxidation of coordinated ligands in complexes $[Fe(diimine)_3]^{3+}$ has been reviewed.[594]

5.4.3.5.6 Lower oxidation states

The polyether–diimine macrocycle (**108**) forms a catenate $[Fe(cat)]^{2+}$ which proved impossible to oxidize to $[Fe(cat)]^{3+}$ but which is readily reducible, electrochemically in dichloromethane solution on a Pt or Hg surface, to $[Fe(cat)]^{+}$ and to $[Fe(cat)]^{0}$.[14] $[Fe(bmpphen)_2]^{2+}$ (bmpphen = (**109**) can be electroreduced to $[Fe(bmpphen)_2]^{+}$ and to $[Fe(bmpphen)_2]^{0}$. The relatively high stabilities of all three bmpphen complexes may be due to their "entwined" character.[16] Here and below one should bear in mind the possibility, outlined in Section 5.4.1.3 above, that it is the ligand rather than the metal which is being reduced.



(**108**)



(**109**)

Reduction potentials of three iron(II)–tris–diazabutadiene complexes, viz $[Fe(gmi)_3]^{2+}$, $[Fe(mmi)_3]^{2+}$, and $[Fe(bmi)_3]^{2+}$, and of two $[Fe(sb)_3]^{2+}$ complexes indicate the relative ease of reduction of these complexes.[595] Reduction of iron(II) chloride in ether in the presence of potential diazabutadiene (dabd) ligands $R^2N{=}CR^1CR^1{=}NR^2$, $R^1 = H$ or Me, R^2 = e.g., Pr^i, Bu^t, Ph, C_6H_4OMe, yields air-sensitive iron(0) complexes $[Fe(dabd)_2]$.[11] These react, with ease or difficulty depending on the nature of R^2, in the presence of an excess of CO to give deep green $[Fe(CO)(dabd)_2]$. They also add nitrosyl chloride, cyanogen, isocyanides, and alkynes ($R^3O_2CC{\equiv}CCO_2R^3$). In the last case the air-stable blue product contains a tetra-(CO_2R^3)-substituted-butadiene coordinated to an octahedral Fe^{II} center.[596] Tetraazadienes also coordinate to iron(0),[597] while monoazadienes, of the form $R^2N{=}CR^1CR^1{=}CR^3{}_2$, provide a link between diazabutadienes and the familiar butadiene "ligands" of organometallic chemistry.[598] Links between the photochemistry, both in solution and in matrices,[599] and spectroscopy of $[Fe(CO)_3$-(dabd)] complexes have been discussed.[600] $[Fe(CO)_3(dabd)]$ complexes are only very slightly solvatochromic.[601–603] $[Fe(CO)_3(bipy)]$ and $[Fe(CO)_3(phen)]$ are considerably more solvatochromic than $[Fe(CO)_3(dabd)]$, and the shifts are in the opposite direction.[604]

The mechanism of replacement of benzylideneacetone (PhCH=CHCOMe, bza) in $[Fe(CO)_3$-(bza)] by diimines is determined by the nature of the incoming ligand, with bipy or diacetyldianil reacting by parallel associative and dissociative pathways, but 2-acetylpyridine anil reacting solely by a limiting dissociative mechanism.[605]

5.4.3.5.7 Binuclear complexes

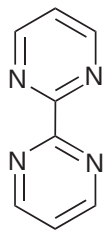
Binuclear complexes with diimine bridges are dealt with here, but those with (hydr)oxide bridges are dealt with, alongside other types of (hydr)oxide bridged complexes, in Section 5.4.5.4 later in this chapter.

(i) Bridging diimines

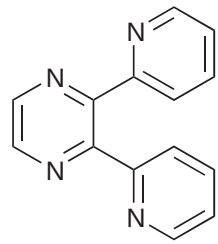
Ligands such as 2,2′-bipyrimidine, bipym (**110**), or 2,3-bis(2-pyridyl)pyrazine, bppz (**111**), can act as bridging ligands, giving ternary binuclear anions such as $[(NC)_4Fe^{II}(bipym)Fe^{II}(H_2O)_4]$[606] and $[(NC)_4Fe^{II}LFe^{II}(CN)_4]^{4-}$ with L = bipym or bppz. These and the corresponding mononuclear anions $[Fe^{II}L(CN)_4]^{2-}$ exhibit strong charge-transfer spectra in the visible region. The binuclear complexes can be oxidized to mixed valence species $[(NC)_4Fe^{II}LFe^{III}(CN)_4]^{3-}$, whose comproportionation constants of 233 (bipym) and 343 (bppz) indicate rather weak Fe ⋯ Fe coupling.[607] Closely related 2,2′-bipyrimidine-dicyanamide (dca,$N(CN_2)^-$) complexes $[Fe_2(dca)_4$-$(bipym)]\cdot H_2O$ and $[Fe_2(dca)_4(bipym)(H_2O)_2]$ form dca- and bipym-bridged 2D networks. In the former compound all dca ligands are bridging, in the latter two dca ligands are bridging, two

nonbridging, with the water molecules occupying the sixth coordination position on each iron. There is antiferromagnetic exchange between the high-spin iron(II) centers.[608]

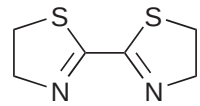
The iron(II) atoms in $[(SCN)_2(bipym)Fe(bipym)Fe(bipym)(NCS)_2]$ are high-spin, and are antiferromagnetically coupled through the bridging 2,2′-bipyrimidine (**110**).[609] $[(SeCN)_2(bipym)Fe(bipym)Fe(bipym)(NCSe)_2]$ is one of the few examples of binuclear spin cross-over complexes of iron(II); it provides an example of synergy between magnetic interaction and spin transition.[610] $[(SCN)_2(btzn)Fe(bipym)Fe(btzn)(NCS)_2]$ (btzn = 2,2′-bi-thiazoline (**112**)) has a two-step spin transition in the range 160–210 K.[611] The interplay between magnetic coupling and spin cross-over in this complex gives rise to unusual photomagnetic behavior.[612] The pyridyltriazine 3,5,6-tptz, (**113**), in its molybdenum(0) and rhenium(I) complexes $Mo(CO)_4(3,5,6\text{-tptz})$[478] and $ReCl(CO)_3(3,5,6\text{-tptz})$[479] can bridge these entities to iron(II) in the shape of its bishexafluoroacetylacetonate, $Fe(hfac)_2$.



(**110**)

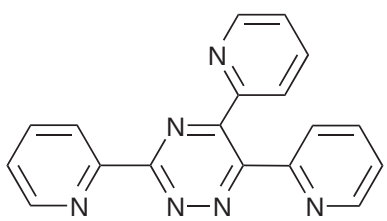


(**111**)

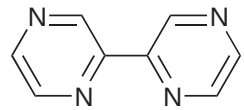


(**112**)

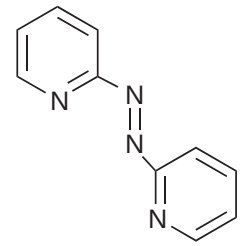
ESR spectroscopy provides evidence for low-lying MLCT states in the $[FeL(CN)_4]^{2-}$ anions with L = 2,2′-bipyrazine (**114**) and 2,2′-azobis(pyridine) (**115**) and suggests that the $[FeL(CN)_4]^{3-}$ anions approximate to Fe^{II} complexes of radical anion ligands.[613] $Na_2[Fe(CN)_4(bipy)]$ and its 4,4′-Me_2 and 4,4′-Ph_2 analogues have been used to sensitize nanocrystalline TiO_2 films to visible light—the solvatochromism of these anions is useful in determining energetics in this type of system.[278]



(**113**)



(**114**)



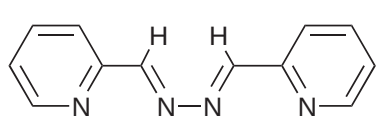
(**115**)

(ii) Tetradentate bis-diimine ligands

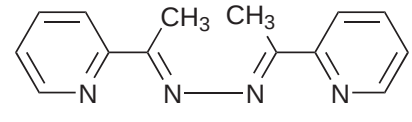
Tetradentate bis-diimine ligands (tbd) may form mononuclear complexes $[Fe(tbd)X_2]$ or, if the tbd ligands have appropriate geometry and are sufficiently flexible, binuclear complexes in which three molecules of diimine span two Fe^{2+} ions, $[Fe_2(tbd)_3]^{4+}$. The latter alternative gives a larger ligand field at each Fe^{2+}. There is the added interest that such an $[Fe_2(tbd)_3]^{4+}$ species may be helical. Alternatively the potentially tetradentate ligands may coordinate through only one diimine unit, in the simplest case giving $[Fe(tbd)_3]^{2+}$.

2-Pyridinaldazine (paa, (**116**)) forms mono- and binuclear complexes with several first-row transition metals, including $[Fe(paa)_3]^{2+}$ and $[Fe_2(paa)_3]^{4+}$ with iron(II).[614–616] The analogous ligand pmk, (**117**), derived from 2-acetyl pyridine, similarly forms $[Fe_2(pmk)_3]^{4+}$. Proton relaxation NMR studies on closely related complexes of the type $[M^1M^2(pmk)_3]^{4+}$ (where M^1, M^2 are Co, Ni, Cu, Zn variously) indicated small but significant interaction between the two metal atoms.[617,618] Several pyridyl azines have been synthesized for analytical procedures.[133] Ligand (**118**), synthesized from di-2-pyridyl ketone and hydrazine, complexes iron(II), though only mononuclear $[Fe(\mathbf{118})_3]^{2+}$ was reported.[619] The bis-3-hydroxy derivative of paa has been proposed as an analytical reagent for several first-row transition metal 2+ cations, including Fe^{2+}.[134] Several bis-diimine analogues have

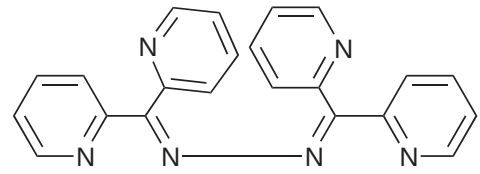
flexible bridges linking the two diimine units. This may be a simple —CH_2CH_2— linkage, as in (**119**),[620] or a peptide-type bridge in which the central =N—N= unit is replaced by =NNHCXNHN=, with X = O, NH, or S.[621,622] Such ligands readily form Fe^{2+} complexes $[Fe_2L_3]^{4+}$.[623,624] The analogous complex from the peptide-linked bis-diimine ligand (**120**) is formed in a metal-directed self-assembly process, which produces a helical $[Fe_2L_3]^{4+}$ complex. The ligand strands are sufficiently rigid to transmit helical information from one Fe^{2+} to the other, imposing homochirality—only the ΔΔ and ΛΛ forms are formed.[625] Of the two most studied bis-iron(II) complexes, $[Fe_2(paa)_3]^{4+}$ is rather labile in aqueous solution[614,615] (though stable in nitromethane),[626] but an aqueous solution of $[Fe_2(pmk)_3]^{4+}$ is much more substitution-inert.[627] Indeed at pH 7 there is no detectable dissociation after several weeks at room temperature.



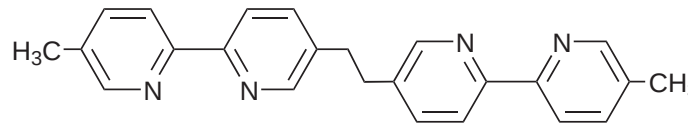
(**116**)



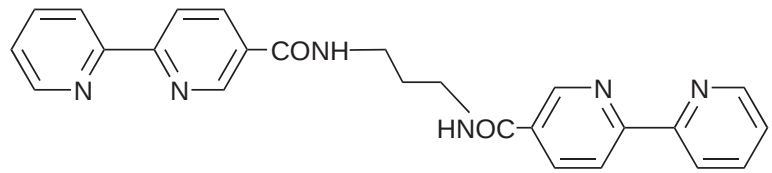
(**117**)



(**118**)



(**119**)



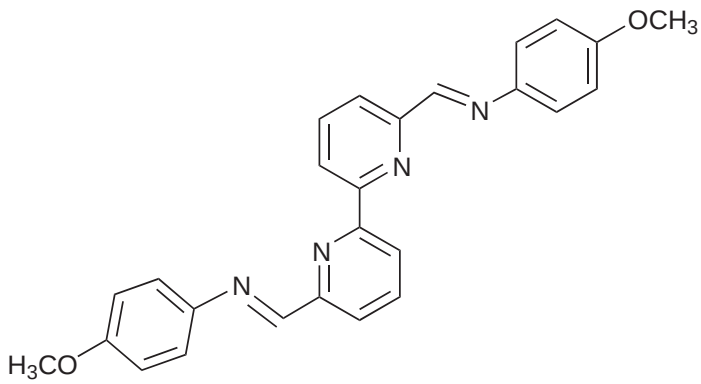
(**120**)

The iron(II) complex of the Schiff base-diimine (**121**) is mentioned briefly in a review more concerned with Cu^+–diimine complexes leading to helicates and catenanes—but which is also concerned with moving from tetrahedral Cu^+ to octahedral metal centers as templates.[119]

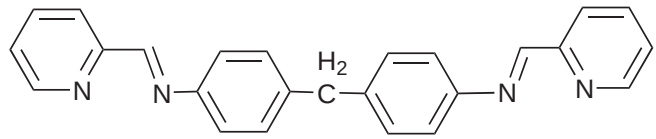
The cylindrical helical binuclear complex $[Fe_2L_3]^{4+}$, where L is the bis-diimine Schiff base (**122**), exists as two enantiomers, whose interactions with DNA differ markedly. The more strongly interacting enantiomer targets the major groove, as also is the case with several ruthenium(II) complexes, and induces dramatic tightening of the DNA coil.[628]

(iii) Quaterpyridyl and hexapyridyl

Quaterpyridyl exhibits several manifestations of steric hindrance in its coordination chemistry to iron. Thus the separation between the middle two rings is too short for the formation of helical



(**121**)

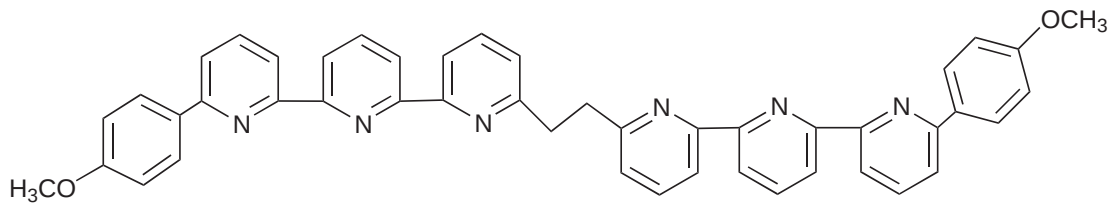


(**122**)

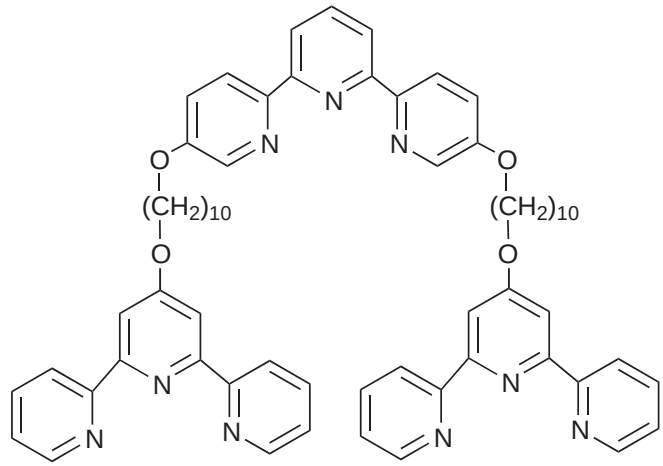
$[Fe_2(quaterpy)_3]^{4+}$, while interligand repulsion makes formation of $[Fe(quaterpy)_2]^{2+}$, which might be expected to be a stable compound, essentially an analogue of the very stable $[Fe(terpy)_2]^{2+}$ with one nonbonded pyridyl group on each ligand, very difficult. However, it would be possible for quaterpy to act as a bidentate ligand to each of two Fe ions, from which a polymeric complex could be built up. Long ago the first report of Fe^{2+}/quaterpy complex formation reported 1:1 stoichiometry,[629] which could result from mononuclear $[Fe(quaterpy)(H_2O)_n]^{2+}$ with $n = 3$ or 2 depending on whether the ligand was tetradentate (unlikely) or terdentate, or from a polymer. Later the determination of log K_1 and log K_2, 8.2 and 6.7, respectively,[630] for the Fe^{2+}/quaterpy system indicated that while the first ligand molecule has a similar affinity for Fe^{2+} to other diimine and terimine ligands, the addition of the second ligand does not occur with the considerable increase in stability normally observed for the formation of low-spin tris-diimine or bis-terimine complexes. $[Fe(quaterpy)_2]^{2+}$ can be generated in, and isolated from, basic solution, but $[Fe(quaterpy)(H_2O)_2]^{2+}$ is obtained from neutral solution. In $[Fe(quaterpy)_2]^{2+}$ each quaterpy is terdentate (and the coordinated nitrogens are, at 2.112(7) Å to 2.207(8) Å, more than 0.2 Å more distant from the metal than in $[Fe(terpy)_2]^{2+}$).[631] In $[Fe(quaterpy)(H_2O)_2](ClO_4)_2$ the coordinated quaterpy is planar and the *trans*-waters make an O—Fe—O angle of 162.3(2)°; $[(ClO_4)(quaterpy)Fe—O—Fe(quaterpy)(ClO_4)]\cdot 8.5H_2O$ has bidentate perchlorate ligands on seven-coordinate Fe^{2+} (∠Fe—O—Fe = 155.2(4)°); in $[Cl(quaterpy)Fe—O—Fe(quaterpy)Cl](ClO_4)_2\cdot 2H_2O$ the Fe—O—Fe unit is linear.[632] Earlier reports on oxo-di-iron–bis-quaterpy complexes provided IR[633] and magnetic[634] data.

$[Fe^{III}(quaterpy)(OH)_2]^+$ anchored to poly-L-glutamate or to poly-D-glutamate acts as a catalyst for the oxidation of epinephrine by H_2O_2.[635] $[Fe(quaterpy)X_2]^{n+}$ interacts with biosubstrates.[636] $[(H_2O)(quaterpy)Fe^{III}—O—Fe^{III}(quaterpy)(H_2O)]^{4+}$ has been prepared as the dihydrate of its perchlorate salt.[637]

Hexapyridine can induce spontaneous assembly of double helical binuclear complexes $[M_2(hexapy)_2]^{4+}$, including M = Fe.[638] The double helix here may be contrasted with triple helices for tetradentate bis-diimine ligand complexes mentioned above. The bis-terimine ligand (**123**) also gives a double stranded helical complex $[Fe_2(\mathbf{123})_2]^{4+}$.[639] The tris-terimine (tris-terpyridyl, tterpy) ligand (**124**) forms a trinuclear complex $[Fe_3(tterpy)_2]^{6+}$ in which the long flexible linkages between the terpy units permit the complex to adopt a doubly looped structure reminiscent of a bow tie.[640]



(**123**)



(**124**)

5.4.3.5.8 Diimine–cyanide complexes

(i) Solutions, solvation, solvatochromism, and piezochromism

Solvent effects on NMR spectra of $[Fe(phen)_2(CN)_2]$ have been detailed,[641] as have ^1H and ^{13}C NMR spectra of $[Fe(bipy)_2(CN)_2]$ in acetone and in dimethyl sulfoxide, and of $[Fe(bipy)(CN)_4]^{2-}$ in D_2O.[642]

Solubilities have been reported for $[Fe(phen)_2(CN)_2]$ and for $[Fe(phen)_3][Fe(phen)(CN)_4]\cdot 8H_2O$, and also for $[Fe(phen)_3](ClO_4)_2\cdot H_2O$ and $[Fe(phen)_3]_2[Fe(CN)_6]\cdot 3\cdot 5H_2O$, in water, ethanol, and ethanol–water mixtures,[531] for $[Fe(bipy)_2(CN)_2]$ and $[Fe(phen)_2(CN)_2]$ in alcohols, MeOH to 1-decanol,[643] of $[Fe(bipy)_2(CN)_2]$ in salt solutions,[644] and of $[Fe(phen)_2(CN)_2]$ in solutions of urea (up to 10 mol dm^{-3}).[645] Solubility ranges of $[Fe(diimine)_2(CN)_2]$ and of $K_2[Fe(diimine)(CN)_4]$, diimine = bipy or the Schiff bases from 2-acetylpyridine and 1-butylamine or 1-decylamine, have been outlined.[646]

Partial molar volumes (V_i) of $[Fe(diimine)(CN)_4]^{2-}$, with diimine = bipy, phen, gmi, *o*-phenylenediimine, or Me_2bsb, correlate with relative molecular masses (RMM), though for a much wider range of inorganic complexes and organic ions (from oxalatometallates to tetraphenylborates) hydrophilic/hydrophobic properties are superimposed on the V_i/RMM trend.[647] Transfer chemical potentials of $[Fe(bipy)(CN)_4]^{2-}$ from water into acetonitrile–water mixtures reflect a balance between solvation of the organic periphery of the coordinated bipy by acetonitrile and hydration of the cyanide ligands, with the former effect slightly larger.[648] Transfer chemical potentials of $[Fe(diimine)(CN)_4]^{2-}$ from water into DMSO–water mixtures are strongly affected by differences in ligand/DMSO interactions.[365] Transfer chemical potentials, to MeOH–water mixtures, have been evaluated for $[Fe(phen)_2(CN)_2]$, several Schiff base complexes $[Fe(sb)_2(CN)_2]$, $[Fe^{III}(bipy)_2(CN)_2]^+$ and $[Fe^{III}(phen)_2(CN)_2]^+$.[649]

The solvatochromism of $[Fe(phen)_2(CN)_2]$ and $[Fe(phen)_2(CN)_2]^+$ has been discussed,[650] with particular reference to solvent hydrogen-bond donor properties.[651] Various solvation models have been applied to solvatochromism of $[Fe(diimine)_2(CN)_2]$,[652] and connections between solvatochromism, electronic absorption spectra, and color perception parameters discussed in relation to $[Fe(phen)_2(CN)_2]$.[653] Solvatochromic properties have been documented for $[Fe(bipy)_2(CN)_2]$,

$[Fe(sb)_2(CN)_2]$, and $[Fe(dab)_2(CN)_2]$ in a variety of solvent media, and for $[Fe(phen)_2(CN)_2]$, $[Fe(bipy)_2(CN)_2]^+$ and $[Fe(phen)_2(CN)_2]^+$ in methanol–water,[649] for $[Fe(bipy)_2(CN)_2]$ and $[Fe(bipy)(CN)_4]^{2-}$ in acetonitrile–water[343] and in 2-ethyl-2-(hydroxymethyl)-1,3-propanediol–water[654] mixtures, and for $[Fe(bipy)_2(CN)_2]$ in DMF–water and 2-butoxyethanol–water.[655] $[Fe(phen)_2(CN)_2]$ can be used to probe solvatochromism in strongly acidic media.[656]

The solvatochromic properties of alkyl-substituted derivatives of $[Fe(bipy)_2(CN)_2]$ are very similar to those of the parent complex, but the lipophilic substituents confer the solubility in nonpolar organic solvents that $[Fe(bipy)_2(CN)_2]$, and $[Fe(phen)_2(CN)_2]$,[657] lacks — the 4-*n*-pentyl-4′-methyl derivative is soluble both in water and in *n*-alkanes,[658] and bis-(4-methyl-4′-pentyl-2,2′-bipyridyl)(dicyano)iron(II) has just the right combination of solvation properties for it to be soluble in the full range of solvents from water to alkanes.[658] Derivatives containing 4,4′-di-isobutyl, 4,4′-di-*n*-pentyl, or 4,4′-di-*n*-heptyl substituents are suitable (as are certain other iron–diimine–cyanide complexes,[659] including $[Fe(bipy)_2(CN)_2]$ itself,[660] but especially $[Fe(sb)_2(CN)_2]$ with sb = a Schiff base ligand from 2-acetylpyridine plus a long chain amine[661] or that from 2-acetylpyridine plus 4-fluoro-3-methylaniline[662]) for probing the properties of organized media such as micelles and microemulsions. Indeed the 4,4′-di-*n*-pentyl and 4,4′-di-*n*-heptyl derivatives show self-aggregating properties,[663] and show these more markedly than the above $[Fe(sb)_2(CN)_2]$ complexes. $[Fe(4,4'\text{-di-}n\text{-nonyl-bipy})_2(CN)_2]$ forms vesicles in certain water-rich solvent mixtures, acting as its own indicator in that there is an abrupt change in λ_{max}, apparent as a red to deep blue color change, at the onset of vesicle formation. Cyclic voltammetry shows this complex to form redox-active films on electrode surfaces.[664] The Schiff base complex from 4-fluoro-3-methylaniline is particularly versatile, for it can also be used to probe a wide range of binary solvent mixtures and aqueous salt solutions. $[Fe(bipy)_2(CN)_2]$ also exhibits halochromism in aqueous salt solutions (Li^+, Na^+, K^+, Mg^{2+}; NO_3^-, SO_4^{2-}, ClO_4^-).[644]

Piezochromism and thermochromism of diimine–cyanide–iron(II) and –iron(III) complexes (diimine = bipy or phen),[665] piezochromism and solvatochromism of dicyano–, tricyano–, and tetracyano– diimine– (terimine–) iron(II) complexes,[666] and piezochromism of $[Fe(bipy)_2(CN)_2]$ in 90% Pr^iOH have been documented.[667]

The solvatochromic behavior of the closely related iron(0) complexes $Fe(CO)_3$(diimine) is mentioned under lower oxidation states (Section 5.4.3.5.6).

(ii) Kinetics and mechanisms

Reaction kinetics and mechanisms for oxidation of $[Fe(diimine)_2(CN)_2]$, $[Fe(diimine)(CN)_4]^{2-}$ (diimine = bipy or phen) (and indeed $[Fe(CN)_6]^{4-}$) by peroxoanions such as ($S_2O_8^{2-}$, HSO_5^-, $P_2O_8^{4-}$) have been reviewed.[668] Reactivity trends have been established, and initial state—transition state analyses carried out, for peroxodisulfate oxidation of $[Fe(bipy)_2(CN)_2]$, $[Fe(bipy)(CN)_4]^{2-}$, and $[Fe(Me_2bsb)(CN)_4]^{2-}$ in DMSO—water mixtures. Whereas in base hydrolysis of iron(II)–diimine complexes reactivity trends in binary aqueous solvent mixtures are generally determined by hydroxide solvation, in these peroxodisulfate oxidations solvation changes for both partners affect the observed pattern.[365]

Activation volumes for peroxodisulfate oxidation of $[Fe(bipy)_2(CN)_2]$ and of $[Fe(diimine)(CN)_4]^{2-}$ with diimine = bipy, phen, Me_2bsb, ein (HN=CHCH=NH) show a large ligand effect, +5 for $[Fe(ein)(CN)_4]^{2-}$ to $-10\,cm^3\,mol^{-1}$ for $[Fe(Me_2bsb)(CN)_4]^{2-}$. This reflects the big difference in solvation properties, from hydrophilic ein to strongly hydrophobic Me_2bsb.[669] There is a moderately good correlation between $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ for peroxodisulfate oxidation of the sequence of complexes $[Fe(diimine)_3]^{2+}$, $[Fe(diimine)_2(CN)_2]$, $[Fe(diimine)(CN)_4]^{2-}$, and $[Fe(CN)_6]^{4-}$ (diimine = bipy or phen).[670] Salt effects ([salt] up to 6 mol dm^{-3}) on $\Delta V^{\ddagger}$ have been established for peroxodisulfate oxidation of this sequence of complexes for bipy as diimine.[644]

$\Delta V^{\ddagger}$ values have been obtained for oxidation of benzenediols by $[Fe(bipy)(CN)_4]^-$, including the effect of pH, i.e., of protonation of the iron(III) complex,[671] and the kinetics of $[Fe(phen)(CN)_4]^-$ oxidation of catechol and of 4-butylcatechol reported.[649] Redox potentials of $[Fe(bipy)_2(CN)_2]$ and of $[Fe(bipy)(CN)_4]^{2-}$ are available.[343] The self-exchange rate constant for $[Fe(phen)_2(CN)_2]^{0/+}$ has been estimated from kinetic data for electron transfer reactions involving, *inter alios*, catechol and hydroquinone as $2.8 \pm 2.5 \times 10^7\,dm^3\,mol^{-1}\,s^{-1}$ (in dimethyl sulfoxide).[672]

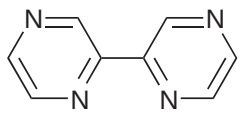
Kinetics of peroxodisulfate oxidation of $[Fe(terpy)(CN)_3]^-$ in water and in binary aqueous solvent mixtures have been analyzed, with the aid of measured solubilities of $[Ph_4As][Fe(terpy)(CN)_3]$, to separate the initial state and transition state contributions to the observed reactivity trend.[673]

(iii) Structures; other properties

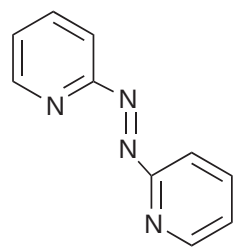
The anions in $[Ph_4As][Fe(terpy)(CN)_3]\cdot 2H_2O$ are stacked so that terpyridyl ligands in adjacent anions lie parallel to each other.[673] Thermogravimetric studies of $[Fe(bipy)_2(CN)_2]\cdot 2H_2O$ show it to decompose immediately on losing its $2H_2O$, at the unexpectedly high temperature of 324 °C. This behavior may be ascribed, according to the reader's predilections or prejudices, either to covalent hydration or to unusually strong hydrogen-bonding.[674]

Coordinated cyanide in $[Fe(phen)(CN)_4]^-$, prepared by chlorine oxidation of $K_2[Fe(phen)(CN)_4]$, can act as a bridging ligand,[675,676] for example in the complexes $[\{Fe(phen)(CN)_4\}_2M(H_2O)_2]\cdot 4H_2O$, where M = Mn or Zn, whose structure is of double zigzag chains,[677] and of bipy analogues.[678] There is similar bridging to ytterbium, as in $(phen)_2Fe\{\mu\text{-}CN—YbCl_3(H_2O)—NC\}_2Fe(phen)_2$, obtained from the reaction of ytterbium trichloride with $[Fe(phen)_2(CN)_2]$.[650]

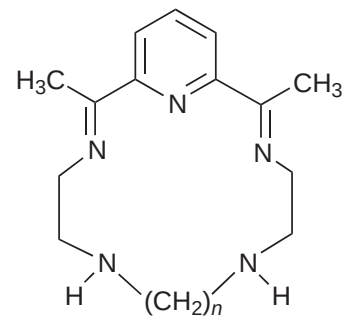
ESR spectroscopy provides evidence for low-lying MLCT states in the $[FeL(CN)_4]^{2-}$ anions, L = 2,2′-bipyrazine, (**125**) and 2,2′-azobis(pyridine), (**126**), and suggests that the $[FeL(CN)_4]^-$ anions approximate to Fe^{II} complexes of radical anion ligands.[613] $Na_2[Fe(CN)_4(bipy)]$ and its 4,4′-Me_2 and 4,4′-Ph_2 analogues have been used to sensitize nanocrystalline TiO_2 films to visible light—the solvatochromism of these anions is useful in determining energetics in this type of system.[278] The IR spectrum of the salt $[Fe(phen)_3][Fe(phen)(CN)_4]$ is very different from that of its isomer $[Fe(phen)_2(CN)_2]$.[641]



(**125**)



(**126**)



(**127**)

In the ternary complexes [Fe(**127**)$(CN)_2$] the normally pentadentate macrocyclic aza-terimine ligand is only tetradentate, thanks to the particularly advantageous combined ligand field of two cyanide ligands and four nitrogen donor atoms in octahedral geometry.[679]

5.4.3.5.9 Diimine–thiocyanate complexes

(i) Spin cross-over

The red form of $[Fe(phen)_2(NCS)_2]$, which Mössbauer spectroscopy suggested was low-spin[680] and whose IR spectroscopy has been detailed,[681] is probably[682] $[Fe(phen)_3]\,[Fe(NCS)_4](NCS)_2\cdot 3H_2O$. This compound readily gives the normal violet form of $[Fe(phen)_2(NCS)_2]$, originally prepared by refluxing $[Fe(phen)_3](NCS)_2$ in CCl_4 for 48 hours.[683] LIESST (light-induced excited spin state trapping) in $[Fe(phen)_2(NCS)_2]$ has been studied by synchrotron X-ray absorption spectroscopy.[684] $[Fe(bipy)(phen)(NCS)_2]$ shows a more gradual spin cross-over than $[Fe(bipy)_2(NCS)_2]$ or $[Fe(phen)_2(NCS)_2]$.[685] Calorimetric heat capacity measurements have given $\Delta H = 10.1$, 9.6 kJ mol^{-1}, $\Delta S = +48$, $+55$ J K^{-1} mol^{-1} for $[Fe(bipy)_2(NCS)_2]$[686] and $[Fe(btzn)_2(NCS)_2]$ (btzn = 2,2′-bi-thiazoline, (**112**)),[687], respectively. The spin transition for $[Fe\{4,7\text{-}(n\text{-}C_{17}H_{35})_2\text{-}5\text{-}(O\text{-}n\text{-}C_{18}H_{37})phen\}_2(NCS)_2]$ has been probed in a Langmuir-Blodgett film.[688]

5.4.3.5.10 Other ternary diimine complexes

$[Fe(diimine)_2Cl_2][FeCl_4]$, diimine = bipy or phen, can be prepared by crystallizing a 1:1 mixture of $FeCl_3$ and the diimine in acetonitrile.[689] Crystal structures have been published for both the bipy

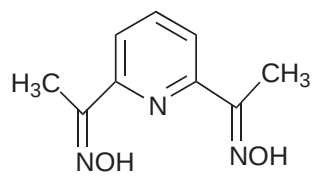
and, earlier,[690] the phen compounds, and for the compounds $[Fe(diimine)_2Cl_2][Fe(diimine)Cl_4]$, again for diimine = bipy or phen. $[Fe(bipy)_2Cl_2]Cl$, with its Ru and Ir and their phen analogues, are potential bifunctional/phase transfer catalysts, as these cations are sufficiently lipophilic to transfer hydrophilic anion reagents into organic media. Thus, for example, $[Fe(phen)_2Cl_2]Cl$ has been tested in this role for reaction of styrene with dichlorocarbene. Although these $[M(diimine)_2Cl_2]Cl$ compounds do act as bifunctional/phase transfer catalysts they are considerably less effective than the usual onium salts of the R_4NX and R_4PX type.[109]

An improved preparation for $[Fe(terpy)Cl_3]$ has been recommended.[510]

5.4.3.5.11 *Dioximes and monoximes*

The UV–visible absorption spectra of a series of complexes $[Fe^{II}(dmgH)_2(X\text{-}py)_2]$ show MLCT bands whose energies correlate with redox potentials; the dmg complexes may be compared with $[Fe^{II}(CN)_5(X\text{-}py)]^{3-}$.[691] The relative amounts of mono- and binuclear products in the reaction of bis(naphthoquinone dioximato)-bis(pyridine)iron(II) with 1,4-diisocyanobenzene are under kinetic control in a limiting dissociative (*D*) mechanism with $[Fe(nqdx)_2(py)]$ as transient intermediate.[692]

The hybrid dioxime/terimine 2,6-diacetylpyridinedioxime, $dapdxH_2$ (**128**), forms stable complexes both with Fe^{2+} and with Fe^{3+}. $[Fe^{II}(dapdxH_2)X_2]$, X = Cl, Br, or I, are high-spin complexes whose magnetic moments and Mössbauer spectra suggest the iron to be five-coordinated, but the Fe^{2+} in dark red $[Fe^{II}(dapdxH_2)](ClO_4)_2$ is octahedrally coordinated. The binuclear iron(III) complexes $[Fe_2(dapdxH_2)_2X_4]$, X = Cl, Br, I, NCS, or NCSe, also form dark red crystals.[693] 5,5′-Dimethyl-1,2,3-cyclohexanetrione-1,2-dioxime-3-thiosemicarbazone, dcdt (**16**), gives an intensely colored tris-ligand complex $[Fe^{II}(N,N'\text{-dcdt})_3]$ (violet, $\varepsilon_{550} = 8{,}900$; $\log \beta_3 = 14.2$) suitable for spectrophotometric determination of iron in foods, wines, and minerals. This ligand acts as an *N*,*N*′,*S*-donor (Section 5.4.4.2) to Fe^{3+}.[135]



(**128**)

Peroxodisulfate oxidation of 3,14-dimethyl-4,7,10,13-tetraazadeca-3,13-diene-2,5-dionedioximatoiron(II) proceeds by electron transfer within a preformed ion pair.[694] The electrochemistry of $[Fe^{II}(dmgH)_2(imH)_2]$, with the kinetics of its autooxidation (catalyzed by Cu^{II} but inhibited by excess of imidazole) and of its oxidation by $[Co(phen)_3]^{3+}$, have been described.[695]

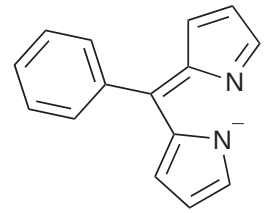
The monoximato-complexes link bipy, Schiff base diimines, and diazabutadienes to dioximes. Aquation kinetics for tris-ligand complexes of 2-pyridinealdoxime, 2-acetylpyridineketoxime, and 2-benzoylpyridineketoxime have been reported, as have the solvatochromism of $[Fe(acpyoxime)_2(CN)_2]$ and of three $[Fe(dioxime)_2(CN)_2]$ complexes. $[Fe(acpyoxime)_2(CN)_2]$ was used to probe solvation in ternary water–Bu^{t}OH–polyethyleneglycol (PEG400) media.[545]

5.4.3.6 Azoles

5.4.3.6.1 *Pyrroles*

Pyrrole units form part of the coordinating entities of Schiff base ligands derived from pyrrole 2-carboxaldehyde,[513] for example in the iron(II) complex of the ligand derived from pyrrole 2-carboxaldehyde and trien, which is low-spin despite the feeble coordinating properties of the pyrrole—CH=N— units.[561] The synthesis, structure, and spectroscopic and electrochemical properties of tris-ligand iron(III) complexes of phenyldipyrromethenate (dipyrrin, (**129**)), and its

4-methoxycarbonyl derivative are an adjunct to the utilization of dipyrrins in supramolecular chemistry.[696]



(**129**)

5.4.3.6.2 Imidazoles and pyrazoles

(i) Imidazoles

Imidazole and the methylimidazoles are important as ligands and incoming groups in several areas of the coordination chemistry of iron. DFT calculations show that whereas imidazole bonds through nitrogen to first-row transition metal cations it might, especially if it contains even modestly bulky substituents, prefer in some circumstances to bond through carbon to second- and third-row transition metal cations, thereby possibly resulting in marked differences between iron and ruthenium complexes.[697]

The structures of *trans*-[Fe(imidazole)$_4$Cl$_2$]Cl·THF·H$_2$O[698] and of *mer*-[Fe(*N*-methylimidazole)$_3$Cl$_3$][510] have been reported. The iron(II) complex of the potentially heptadentate tripodal ligand tris{2-[2-(1-methyl)imidazolyl]methyliminoethyl}amine, an effective superoxide scavenger, is in fact octahedrally coordinated, with three imine-nitrogens at 2.18–2.26 Å and three imidazole-nitrogens at 2.27–2.31 Å.[699] Poly-2,2′-bipyridyltetrakis(imidazolato)iron(II) has a 2D structure containing alternating tetrahedrally and octahedrally coordinated Fe^{2+} ions, differentiated by Mössbauer spectroscopy. The layers are separated by bipy molecules coordinated to the octahedral Fe^{2+} ions.[700] Several bis(benzimidazol-2-yl)pyridine derivatives are of interest in relation to the spin cross-over phenomenon (see Sections 5.4.1.4 and 5.4.3.5.3).[523,524]

(ii) Pyrazoles

Structures of the iron(III) complexes *mer*-[Fe(pyrazole)$_3$Cl$_3$] and *trans*-[Fe(3-methylpyrazole)$_4$Cl$_2$]Cl have been determined.[510] The Fe—N bond distances in the former are 2.119Å for the mutually *trans* ligands, 2.172 Å for Fe—N *trans* to Cl (cf. 2.168 Å, 2.274 Å in *mer*-[Fe(py)$_3$Cl$_3$]py,[457] in the latter 2.137–2.140 Å. The occasional iron complex is mentioned in an extensive review of pyrazole-based ligands.[701]

The hydrotris(3,5-dimethyl-1-pyrazolyl)borate complex [Fe{HB(3,5-Me$_2$pz)$_3$}(N$_3$)$_3$]$^-$ can be prepared from [Fe{HB(3,5-Me$_2$pz)$_3$}Cl$_3$]$^-$ or directly from [Fe$_2$OCl$_6$]$^{2-}$.[454] Generally pyrazolylborates give bis-ligand octahedral complexes [Fe^{II}L$_2$], but sterically demanding 3-*t*-butyl substituents can lead to distorted tetrahedrally coordinated high-spin complexes. Ligands containing the less bulky 3-isopropyl group give mono- or bis-ligand complexes. An example of the former is afforded by [Fe^{II}LCl] with L = hydrotris(3-isopropyl-4-bromopyrazolyl)borate;[702] examples of the latter include the pale green 3-isopropylpyrazolylborates [Fe{HB(3-Pr^{i}pz)$_3$}$_2$] and [Fe{B(3-Pr^{i}pz)$_4$}$_2$].[703] Complexes [FeL$_2$](BF$_4$)$_2$ with L = HC(1-pyrazolyl)$_3$, HC(3,5-Me$_2$-1-pyrazolyl)$_3$, or PhC(1-pyrazolyl)$_2$(py) have been synthesized, characterized, and investigated with respect to their magnetic properties and behavior.[704] A variable-temperature X-ray structural examination of [Fe{HC(3,5-Me$_2$-1-pyrazolyl)$_3$}$_2$](BF$_4$)$_2$ has shown that the thermally induced spin transition accompanies a phase transition. Above 206 K all Fe^{2+} ions are in an identical environment, but below 200 K the mixture of high-spin and low-spin states (50:50) corresponds to Fe^{2+} sites of two markedly different geometries.[705]

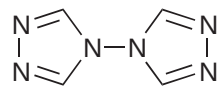
The iron(II) compounds [FeL$_2$](ClO$_4$)$_2$·MeCN, [FeL$_2$](BPh$_4$)$_2$·2MeCN and [FeL$_2$](PF$_6$)$_2$, where L is the terdentate ligand 2,6-bis(3,5-dimethylpyrazol-1-ylmethyl)pyridine, all show temperature-

variable magnetic properties. $[FeL_2](BPh_4)_2 \cdot 2MeCN$ exhibits a clear phase transition at about 200 K, but the other two compounds exist as a mixture of high-spin and low-spin forms whose ratio changes only very slowly with temperature. This unusual behavior is ascribed to structural interconversion between two forms rather than to simple spin cross-over behavior.[706] Light-induced spin transitions in 3,5-bis(2-pyridyl)pyrazolato-bridged di-iron–pyridine–thiocyanate complexes have been monitored by variable temperature laser Raman spectroscopy.[707]

The structures of the bis-ligand iron(II) complexes of the tripodal ligands tris(pyrazol-1-yl)methane and bis(pyrazol-1-yl)(pyridin-2-yl)methane have been determined; the former is a spin cross-over complex.[464] Polybis(pyrazolate)iron(II) has a 1D chain structure with the Fe^{2+} ions doubly bridged by pyrazolates; the Fe^{2+} ions ($S = 2$) are weakly antiferromagnetically coupled.[700]

5.4.3.6.3 Triazoles

Several triazole and ternary triazole–thiocyanate complexes have been examined, usually for their structural or their magnetic properties, especially their spin cross-over characteristics (cf. Section 5.4.1.4 above). The 4,4′-bis-1,2,4-triazole (btrz, (**130**)) compound $[Fe(btrz)_3](ClO_4)_2$ was the first 3D spin cross-over species to be reported. Its dimensions change significantly with temperature, the mean Fe—N distance increasing from 1.99 Å to 2.16 Å, the Fe ⋯ Fe distance from 8.42 Å to 8.62 Å, on increase of temperature from 150 K to 260 K.[708] The properties of tris-btrz complexes may be varied and tuned by such means as substitution (e.g., amino, 2′-hydroxyethyl) at N4 and varying the counterion (halide, nitrate, tetrafluoroborate, tosylate, 3-nitrophenylsulfonate)[40,709] — room temperature cross-over has been achieved, for the 2′-hydroxyethyl/iodide combination.[710]



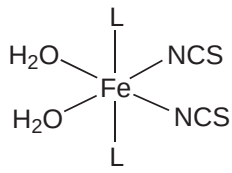
(**130**)

$[Fe(btrz)_2(NCS)_2]H_2O$ has a 2D grid structure, with all Fe^{3+} ions octahedral, all btrz ligands bridging two Fe^{3+} ions, all NCS^- *trans* to each other, and the waters of crystallization hydrogen-bonded to noncoordinating nitrogen atoms of btrz ligands. $[Fe(btrz)_2(NCS)_2]H_2O$ shows sharp h.s. ⇌ l.s. transitions, at 123.5 K on cooling, 144.5 K on warming.[711] At atmospheric pressure anhydrous $[Fe(btrz)_2(NCS)_2]$ is high-spin throughout the studied temperature range, but the low-spin form can be obtained at high pressure.[56] The crystal structure of the selenium analogue $[Fe(btrz)_2(NCSe)_2]H_2O$ has been established, and NMR and ESR spectra of both this and the SCN complex reported.[712] *cis*,*trans*,*cis*-Diaquabis(5-methyl[1,2,4]-triazolo[1,5-α]pyrimidine)-e)bis(thio-cyanato)iron(II) has the geometry shown in (**131**).[713]

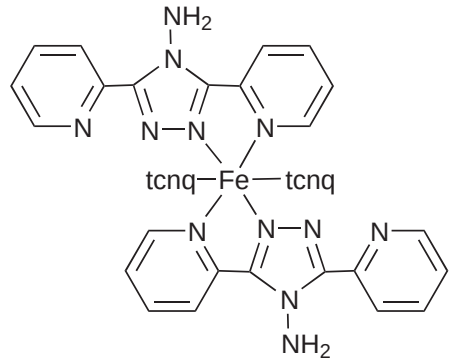
$[Fe(abptrz)_2(tcnq)_2]$ is an iron(II) complex of the triazole 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (abptrz) and the 7,7′,8,8′-tetracyanoquinodimethane (tcnq) radical anion whose structure, (**132**), Mössbauer and IR spectra, and magnetic behavior (thermally induced (280 K) spin cross-over $S = 2 \rightleftharpoons S = 0$) have been established.[714]

In the compound $[Fe_2L_5(NCS)_4]_2[FeL_2(NCS)_2(H_2O)_2]$, where L = 4-(4′-tolyl)-1,2,4-triazole, the dinuclear unit exhibits a spin transition, whereas the mononuclear unit is high-spin throughout.[715] Reaction of Fe^{2+} with 4-(4′-methoxyphenyl)-1,2,4-triazole, mptrz, gave two trinuclear products, viz $[Fe_3(mptrz)_8(H_2O)_4]^{6+}$ and $[Fe_3(mptrz)_6(H_2O)_6]^{6+}$ as their respective BF_4^- and tosylate salts. On heating the latter at 100°C $[Fe_3(mptrz)_6(H_2O)_3](tos)_6$ is obtained. These complexes contain linear Fe_3 units, with triple bridging ligands joining the metal ions. The hexa-mptr compounds undergo spin transitions associated with the central Fe^{2+}, but the octa-mptr compound is high-spin throughout.[716] The 4-isopropyl-1,2,4-triazole complex $[Fe_3(iptrz)_6(H_2O)_3](tos)_6$ has a similar structure and again exhibits a spin transition associated with the central Fe^{2+} ion.[717]

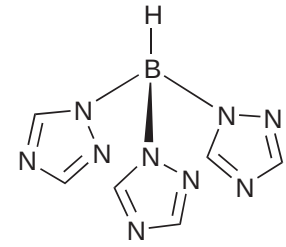
The hydrotris(triazolyl)borate (httazb, (**133**)) ligand gives a bis-ligand iron(II) complex $[Fe(httazb)_2] \cdot 6H_2O$, whose structure consists of layers of complex molecules separated by layers of water molecules.[718]



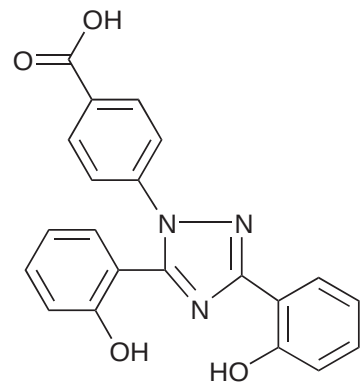
(**131**)



(**132**)



(**133**)



(**134**)

Bis-hydroxyphenyl-triazoles, e.g., (**134**), are a new class of iron chelators. They are *O*,*N*, *O*-terdentate, bonding through a triazole nitrogen and two phenoxide groups; their properties can be pH-tuned by (de)protonation of the carboxy substituents.[220]

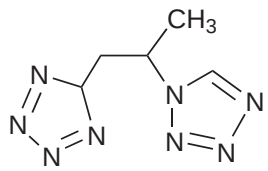
Spin cross-over iron(II)–triazole and –tetrazole complexes have been reviewed.[719,720]

5.4.3.6.4 Tetrazoles

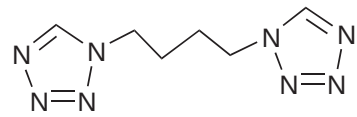
The rapid and reversible change between the dark red low-spin form and the colorless high-spin form of $[Fe(1\text{-propyltetrazole})_6](BF_4)_2$[721] could form the basis of an optically driven switch.[38] $[Fe(btzp)_3](ClO_4)_2$, where btzp is the bis-tetrazolyl ligand (**135**), has a linear chain structure, with an Fe ··· Fe distance of 7.422(1) Å at 200 K, 7.273(1) at 100 K. It exhibits spin cross-over behavior, with a very gradual change in spin properties; irradiation with green light at 5 K causes significant population of the high-spin state.[722] $[Fe(1\text{-methyltetrazole})_6](CF_3SO_3)_2$ undergoes a spin-state change on cooling to below 157 K, though only one third of the Fe^{2+} ions become low-spin.[723] The tris-(bis-tetrazolyl) complex $[Fe(tbtb)_3](ClO_4)_2$, tbtb = 1,4-bis(tetrazol-1-yl)butane (**136**), is a 3D spin cross-over compound with a sharp thermal spin transition at 160 K. It is described as a supramolecular catenane, containing two interpenetrating —Fe—tbtb—Fe— networks, in which there are some fairly short Fe ··· Fe distances, perhaps as little as 8.3 Å.[724]

5.4.3.6.5 Thiazoles

$[Fe^{II}(thiazole)_6]^{2+}$, in the form of its $[Fe^{III}{}_2OCl_6]^{2-}$ salt, is the product of reaction of an excess of thiazole with $FeCl_3$.[725] Several complexes of bithiazole and other thiazole-containing ligands are



(135)



(136)

mentioned in connection with their spin cross-over behavior in Sections 5.4.3.5.3 and 5.4.3.5.9; ferrithiocin is in Section 5.4.4.1.5.

5.4.3.7 Macrocyclic Ligands

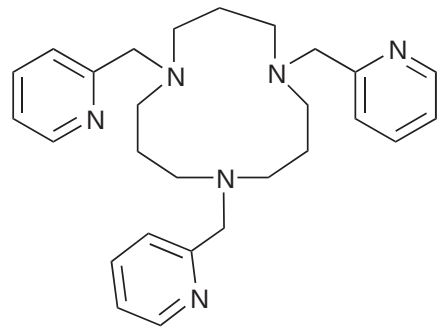
5.4.3.7.1 Triaza-, tetraaza-, and hexaaza-macrocycles

Six pages of a ca. 100 page review of 1,4,7-triazacyclononane (tacn) and related ligands deal with Fe^{2+} and Fe^{3+} complexes.[726] The iron(II)—1,4,7-trimethyl-1,4,7-triazacyclononane complex Fe(tmtacn)Cl_2, which is $[Fe_2(tmtacn)_2Cl_3][Fe(tmtacn)Cl_3]$ in the solid state, reacts in solution with CN^- or a CO/CN^- mixture to give $[Fe(tmtacn)(CN)_3]^-$ and $[Fe(tmtacn)(CO)(CN)_2]$, respectively.[424] 1,5,9-tris(2-pyridylmethyl)-1,5,9-triazacyclododecane (**137**) forms a high-spin Fe^{2+} complex which is markedly more resistant to oxidation than the Fe^{2+} complex of 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane.[727] Its $[FeCl_4]^{2-}$ salt has Fe—N = 2.226(5), 2.257(5) Å.[728] 1,4-Bis(2-pyridylmethyl)-1,4,7-triazacyclononane, bpmtacn (**138**), is a pentadentate ligand forming iron(II) complexes $[Fe(bpmtacn)X]^+$ with X = Cl or NCS. The former is high-spin, the latter low-spin. The binuclear complexes $[Fe_2(\mathbf{139})X_2]^{2+}$, where (**139**) is a related bis-tacn bridging ligand, again with 2-pyridylmethyl pendant arms, are high-spin both for X = Cl and for X = NCS.[729] 1,4,7-Triazacyclononane with three bipy-containing pendant arms has been used as the starting material for the preparation of a hexaazamacrocycle with six bipy-containing pendant arms. The former forms a rather short-lived iron(II) complex, the latter mono- and binuclear complexes.[488]

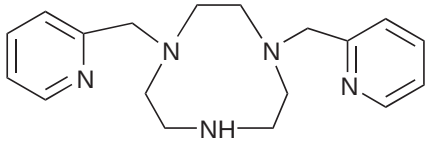
Solid $[Fe(tacn)_2]Cl_2 \cdot 4H_2O$ is low-spin, but solutions of the bromide and trifluoromethylsulfonate salts of $[Fe(tacn)_2]^{2+}$ give indications of the existence of spin equilibria.[52] $[Fe(Me_3tacn)(MeCN)_3](O_3SCF_3)_2$ and $[Fe(Me_3tacn)(MeCN)_3](BPh_4)_2$ are spin-equilibrium compounds, as is the $[Fe(Me_3tacn)(MeCN)_3]^{2+}$ ion in solution. The trifluoromethylsulfonate salt, but not the tetraphenylborate, readily loses coordinated MeCN, giving a high-spin complex.[730]

The triazacyclononane ligand with *o*-aminophenylmethyl pendant arms (**140**) forms a bis-ligand complex with Fe^{2+}, isolated as its perchlorate.[731] Aerial oxidation of this salt gives an uncharged iron(III) complex containing the ligand in triply-deprotonated form.[732]

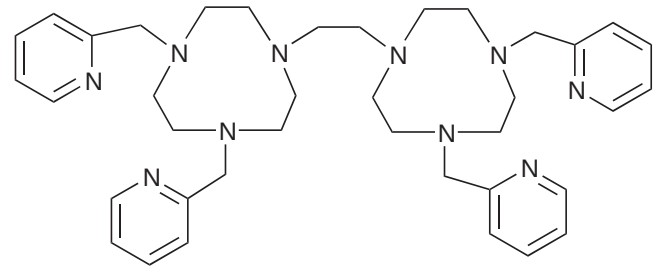
The binuclear iron(II) complex (**141**) has a short C—C bond (1.41 Å, ~40% double bond character) linking its two halves, and an intense absorption band in the near IR ($\varepsilon_{874} = 14{,}000$, in



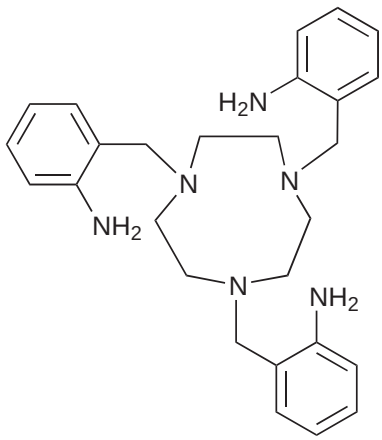
(137)



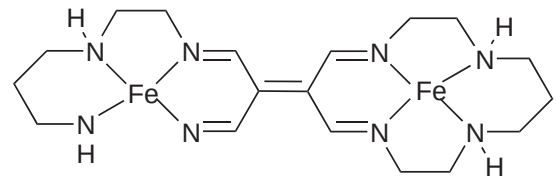
(**138**)



(**139**)

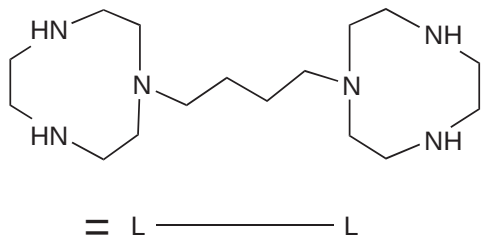


(**140**)

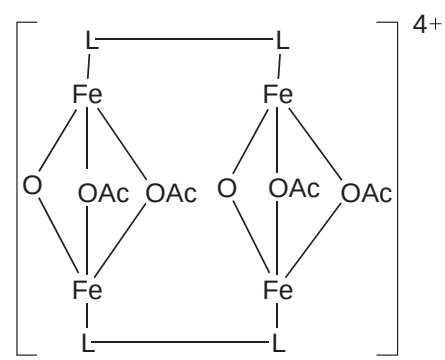


(**141**)

MeCN).[733,734] Its one-electron oxidation ($Fe^{II}Fe^{III}$) product has a comproportionation constant of 10^{11} and near IR absorption band with $\varepsilon_{940} = 27{,}000$, both consistent with Robin and Day[334,335] class III mixed valence character.[735] The bis-triazacyclononane ligand (**142**), btacn, forms a binuclear complex $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2(\mu\text{-btacn})]$[736] and a tetranuclear complex $[Fe_4O_2(btacn)_2(O_2CMe)_4]^{4+}$,[737] both containing iron(III). The structure of the latter is shown as (**143**).



(**142**)



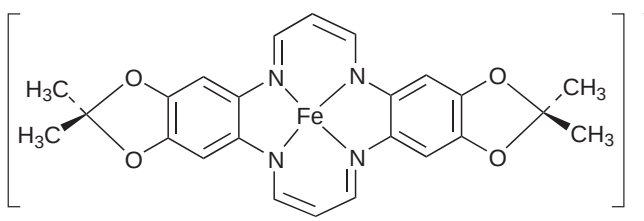
(**143**)

The dibenzotetraaza[14]annulene-iron(III) cation (**144**) shows catalase-like activity, converting hydrogen peroxide into dioxygen under physiological conditions.[738] The iron(II) complex of

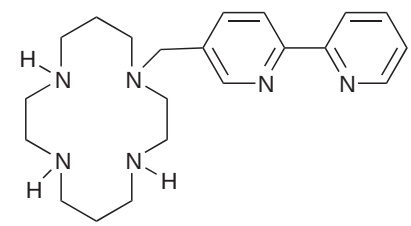
dibenzotetramethyltetraaza[14]annulene [dbtmta; Me_4-(**144**)] can be reduced, by sodium in tetrahydrofuran, to give [Fe(dbtmta)Na(THF)$_3$], in which the Fe—N bond distances of 1.889–1.926 Å are claimed to be not inconsistent with iron in oxidation state 1+.[12]

$[Ni(cyclam)]^{2+}$ reacts with $[Fe(CN)_6]^{3-}$ to give initially the salt $[Ni(cyclam)]_3[Fe(CN)_6]_2 \cdot 6H_2O$. With an excess of $[Fe(CN)_6]^{3-}$ this very slowly gives $[Fe(cyclam)][Fe(CN)_6] \cdot 6H_2O$, which has a cyanide-bridged chain structure.[317] New synthetic routes to *cis*- and *trans*-$[Fe(cyclam)Cl_2]^+$ salts have been reported; *cis*-$[Fe(cyclam)Cl_2]^+$ reacts with 2-aminophenol to give a product, characterized by XRD techniques, containing the quinonoid oxidized form of the coordinated 2-aminophenol.[739] Logarithms of stability constants for a series of five tetraazamacrocyclic complexes of iron(III) range from 24.1 (cyclam) to 27.6.[740] Bis-cyclam–di-iron complexes make a brief appearance in a bioinorganic review.[741] $[Fe(cyclam)Br_2]^+$ reacts with $[Cr(CO)_5(CN)]^-$ to give the trinuclear complex $[(OC)_5Cr—CN—Fe(cyclam)—NC—Cr(CO)_5]^+$, isolated and characterized as its chloride.[330]

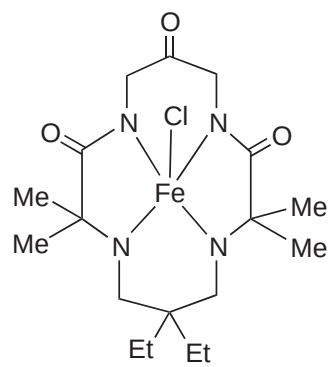
The combined diimine–tetraazamacrocyclic ligand 1-(2′,2″-bipyridyl-5′-yl-methyl)-1,4,8,11-tetraazacyclotetradecane, (**145**), forms a low-spin tris-ligand Fe^{2+} complex in which each ligand coordinates only through its diimine moiety.[490] The stability constant (log K at 308 K) for the Fe^{2+} complex of 3,6,10,13,19-heptaaza-bicyclo[13.3.1]-nonadeca-16,18,19-triene is 10.76.[742] Stability constants (log K at 298 K) for the Fe^{2+} and Fe^{3+} complexes of [15]aneN_4 are 10.61 and 12.62, respectively. This same reference details kinetics of oxidation of $[Fe([15]aneN_4)]^{2+}$ by dioxygen and by hydrogen peroxide.[743]



(**144**)



(**145**)



(**146**)

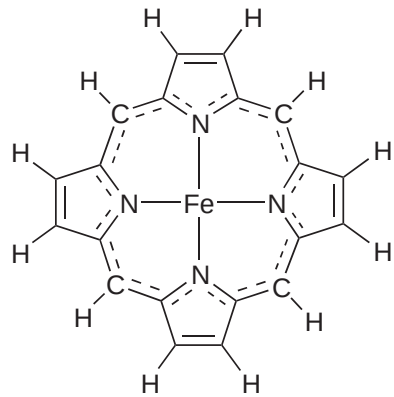
Iron(IV) is stabilized by an amido-tetraazamacrocycle in the complex (**146**).[20]

5.4.3.7.2 Porphyrin complexes

(i) General

This area has been very active in the past 20 years—fortunately most aspects have been reviewed in depth from time to time. A 1996 complete issue of *Chemical Reviews* on metals in biological

systems contains several contributions devoted to, or mentioning, iron porphyrin (**147**) complexes.[744] In relation to porphyrin synthesis and the great variety of picket-fence, capped, and hybrid porphyrins available,[115] reviews have dealt with new synthetic routes,[745] highly halogenated porphyrins,[746,747] multiporphyrins,[748,749] and "superstructured" species,[750] and with applications of such techniques as EXAFS,[751] NMR,[752,753] Mössbauer,[72,754] and resonance Raman[28,755] spectroscopies, and magnetic circular dichroism.[6,756] Electrochemical techniques have been applied to synthesis, characterization, and electron transfer.[757–760]



(**147**)

Interactions and reactions of iron porphyrins with dioxygen species,[115,761–765] with nitric oxide (see Section 5.4.3.8), with nitrite[766] and with nitrate,[767] and also of complexes containing carbon-bonded ligands,[768] have continued to attract considerable interest and be reviewed.

Reviews of kinetics and mechanisms deal with long-range electron transfer[769,770] and with the uptake and release of dioxygen species,[771] especially uptake from organic peroxides.[27,483,772–780] The photochemistry of iron porphyrin complexes has been documented.[483]

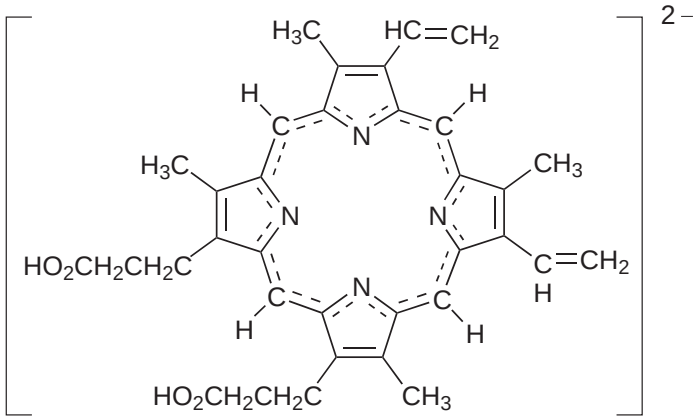
(ii) Synthesis and properties

Single-face hindered porphyrins with one handle and two pivaloyl pickets have been synthesized from 5,10,15,20-tetrakis-(*o*-aminophenyl)porphyrin. Their iron(II) complexes, with 1-methylimidazole as fifth ligand, form stable dioxygen adducts reversibly. Equilibrium and rate constants for dioxygen addition are affected less for these dioxygen adducts than for the corresponding carbon monoxide adducts by steric constraints.[781] Chiral picket fence porphyrins, specifically (+)- and (−)-*meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis[2-[(*p*-menth-3-ylcarbonyl)amino]phenyl]porphyrin, have been prepared.[782] Stability constants for adduct formation between [Fe(ppix)(CO)], $ppix^{2-}$ = the protoporphyrin IX dianion (**148**), and nitrogen bases, in 90:10 DMF:water mixtures at 298 K, have been estimated by means of ^{57}Fe NMR spectroscopy.[69] Stabilities of dioxygen complexes ranging from myoglobin to simple porphyrin derivatives have been documented,[761,783] and theoretical calculations on the latter have been reviewed.[784] Substituent electronic effects have been probed through UV–visible and ^{1}H NMR spectroscopies, ligand binding constants, and redox properties for a series of iron(III) tetraphenylporphyrinates.[785]

Dendritic iron(II) porphyrins[115] with tethered axial ligands have been developed as models for myoglobin and hemoglobin,[786] for cytochromes,[787] and for heme mono-oxygenases.[788] Iron(II)–heme can be alkylated by the anti-malarial peroxide-containing drug artemisinin.[789] Treatment of several iron(II) porphyrins with hydrogen peroxide results in oxygenation of the heme to give oxophlorin complexes.[790]

(iii) Structures

Several hundred crystal structures of iron porphyrin complexes have been solved and published in the past two decades. Interest has centered on nitrosyl complexes, on iron–porphyrin π radical



(**148**)

cations, on the extent of distortion of five-coordinated species from square-pyramidal geometry, and particularly on "saddle-shaped" or "ruffled" deviations of coordinated porphyrins from planarity. 5,10,15,20-Tetrakis(2,6-difluorophenyl)-porphyrinato-iron(III) methoxide provides a recent example of a distorted square-pyramidal structure,[791] *meso*-5,10,15,20-tetraisopropylporphyrinato-bis(tetrahydro-furan)iron(III) perchlorate shows a particularly large deviation from planarity for an "S_4-ruffled" iron–porphyrin complex,[792] and chloro(2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrinato)iron(III), an $S = 3/2$ complex, is distorted square-pyramidal with a slightly ruffled saddle-shaped macrocyclic ligand,[793] thus combining all three of the distortions mentioned. The structural effects of bulky axial bases on the iron-dioxygen portion of hematoporphyrin derivatives have been monitored by ^{17}O NMR and by FTIR spectroscopy.[794] The relative orientations of planar axial ligands and porphyrin rings have received attention,[795,796] with kinetic parameters determined by NMR techniques for rotation of axial ligands in six-coordinate complexes with 2,6-dichloro- or 2,6-dibromo-substituted phenyl ring substituents on porphyrins coordinated to iron(III).[797]

Catalase from *Micrococcus lysodeikticus* provides a rare example of water coordinated directly to heme–iron (Fe—O = 2.28 Å). This ligand water is hydrogen-bonded to another water molecule resident in the heme pocket.[798]

(iv) Spin states

The spin state of six-coordinate iron(III) porphyrins is determined by the number and nature of the axial ligands — two pyridine or imidazole ligands give low-spin complexes ($S = 1/2$), one chloride ligand gives a high-spin complex ($S = 5/2$). Markedly nonplanar complexes with weakly bonded axial ligands can give species of intermediate spin, $S = 3/2$.[799,800] The saddle-shaped octaethylporphyrin complexes $[Fe(oep)L_2]^+$ exhibit the unusual spin cross-over $S = 1/2 \leftrightarrow S = 3/2$, with the proportion of the $S = 3/2$ state correlating with the donor power of L.[801] The tricyanomethide, $[C(CN)_3^-]$, salt of 5,10,15,20-tetraphenylporphinatoiron(III), which contains octahedral Fe^{3+} with anion-nitrogens in axial positions, has $S = 3/2$,[802] while its perchlorate analogue shows a mixed 3/2, 5/2 state.[803] The perchlorate of octaethylporphyriniron(III) has $S = 3/2$,[804] but octaethyltetraphenylporphyrinchloroiron(III), [Fe(oetpp)Cl],[805] occurs in two slightly different forms, one with marked 3/2, 5/2 spin admixture,[806] the other predominantly in the spin 5/2 form.[807] The structures and spectroscopy (NMR, ESR) of the low-spin complexes $[Fe(oetpp)L_2]^+$, L = *n*-methylimidazole, 2-methylimidazole, 4-dimethylamino(pyridine), have been reported.[808]

Bis(*t*-butylisocyanide)tetraphenylchlorinatoiron(III) (chlorin = dihydroporphyrin) is a low-spin iron(III) complex with the unusual ground state $(d_{xz}, d_{yz})^4(d_{xy})^1$. This deviation from normal behavior, viz $(d_{xz}, d_{yz})^3(d_{xy})^2$, is ascribed to the strong π-acceptor properties of the axial Bu^tNC ligands.[438]

The peroxoferrioctaethylporphyrin anion $[Fe^{III}(oep)(O_2)]^-$ has been shown to be high-spin on the basis of its magnetic moment and Mössbauer and ESR spectra.[809]

(v) Solubilization

The solubilization of iron–porphyrin complexes in micelles generally gives rise to monomeric species, which can be studied by techniques such as NMR and Mössbauer spectroscopy. NMR and ESR spectra indicate that $[Fe(ppix)(H_2O)_2]^+$ and $[Fe(ppix)(OH)(H_2O)]$ ($ppix^{2-}$ = the protoporphyrin IX anion, (**148**) above) are monomeric in SDS micelles;[810] Mössbauer spectra of high-spin ppix-iron(III) species in these media are also consistent with six-coordinate $[Fe(ppix)(H_2O)_2]^+$ monomers.[811] NMR, UV–visible spectra and magnetic properties have been reported for four-coordinate [Fe(ppix)], for five-coordinate [Fe(ppix)(2-Meimid)] ($S = 2$), and for six-coordinate $[Fe(ppix)(py)_2]$ ($S = 0$) in aqueous CTAB micelles,[812] and for the high-spin ($S = 2$) 3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,8-dipropionate iron(II) complex $[Fe(porph)(THF)_2]$ solubilized by CTAB.[813] ^1H and ^{15}N NMR studies on low-spin iron(III) porphyrin derivatives $[Fe(ppix)(CN)_2]^-$ and [Fe(ppix)(py)(CN)] in CTAB, SDS, and Triton X-100 micelles (in 18% pyridine in water) again indicate the absence of aggregates in these media.[814] These results contrast with electronic spectroscopy indications that protoporphyrin IX–iron(III) in water exists as aggregates of five-coordinate [Fe(ppix)(OH)].[815]

(vi) Kinetics and mechanisms of substitution and addition

Axial ligand replacement reactions in five- and six-coordinate porphyrin derivatives are generally dissociative in character.[816] Hydrogen-bonding to leaving groups such as imidazole[817] may significantly affect dissociation rates, as in displacement of azide from tetraphenylporphyrinatoiron(III) by imidazole or *N*-methylimidazole,[818] and of chloride from the iron(III) complex of a porphyrin with a $—CH_2CH_2CO_2H$ substituent.[819] Activation parameters for water exchange at three substituted (sulfonated) porphyrin complexes $[Fe(porphs)(H_2O)_2]^{3-}$, $57 < \Delta H^{\ddagger} < 71\ kJ\ mol^{-1}$, $+60 < \Delta S^{\ddagger} < +100\ J\ K^{-1}\ mol^{-1}$, and $+7 < \Delta V^{\ddagger} < +12\ M^{-1}$ indicate dissociative activation for water exchange and, by implication, for complex formation for these complexes and for previously described $[M(porphs)(H_2O)_2]^{3-}$ (M = Cr, Co, Rh as well as Fe) formation reactions.[820] Less rapid reaction than with NO (cf. Section 5.4.3.8 below), and negative $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values, for reaction of sulfonatoporphyrin complexes with CO indicate associative interchange.[821] The kinetics and equilibria of cyanide binding to the iron in the protoporphyrin IX moiety of peroxidase from *Coprinus cinereus* have been studied and compared with those for several other peroxidases. Protonated cyanide attacks the basic form of the enzyme with $k = 7.7 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$, while the rate constant for cyanide dissociation is $0.38\ s^{-1}$.[822] Volume profiles have been established for reactions of a lacunar Fe^{II} complex with CO[823,824] and for myoglobin with O_2 and with CO.[825,826] Detailed kinetic studies of the reaction of Fe^{II} in cyclophane hemes with O_2 and with CO probed polarity and steric effects, with the effects of deformation of the porphyrin skeleton from planarity assessed for one compound.[827]

The kinetics and mechanism for oxygen transfer between 4-cyano-*N*,*N*,-dimethylaniline *N*-oxide and a C_2-capped *meso*-tetraphenylporphyrinatoiron(III)[828] and *meso*-tetrakis(pentafluorophenyl)-porphyrinatoiron(III)[829] have been established. Addition of a copper(II)–porphyrin cap to an iron(II)–porphyrin complex has the expected effect of reducing both the affinities and rate constants for addition of dioxygen or carbon monoxide. These systems were studied for tetradecyl-substituted derivatives solubilized by surfactants such as poly(ethylene oxide) octaphenyl ether.[108]

The incorporation of iron(II) into the protoporphyrin IX ring, the final step in heme biosynthesis, is catalyzed by ferrochelatase. Kinetic parameters were reported both for this process and for the reaction of Fe^{2+} with ferrochelatase, whose kinetics were used to characterize the latter.[830]

(vii) Redox properties and electrochemistry

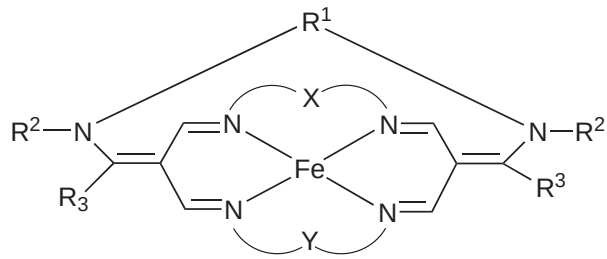
A discussion of redox potentials of a range of iron complexes in relation to the nature of the iron–ligand bonding concentrates on porphyrin complexes.[831] The electrochemistry of iron porphyrin complexes in nonaqueous media has been dealt with at length (~50 pages).[758] Electrochemical oxidation of $[Fe(tpp)F_2]^-$ generates an iron(IV) species,[25] while the first evidence for an iron(V)–porphyrin species was obtained in the course of an investigation of electrocatalytic hydroxylation. This iron(V) species contains an octafluoroporphyrin ligand and is believed to have either two F^- or an F^- and an O^{2-} coordinated to the metal.[26] Weak bridging of $[Fe(oep)]^+$ through F^- to Cu is referenced in Section 5.4.6.1 below.

Cyclic voltammetry of iron(III)–porphyrin-sulfate complexes has been described.[832] Thiosulfate can add to iron(III)–porphyrins to give an adduct which is high-spin at normal temperatures but low-spin at low temperatures. The tetraphenylporphyrin adduct undergoes decomposition slowly in DMF to give [Fe^{II}(tpp)] plus tetrathionate. In DMSO tetraphenylporphyrinatoiron(III) oxidizes thiosulfate by an autocatalytic process.[833] Tetrathiotungstate complexes of iron(III)–tetraphenylporphyrin undergo spontaneous reduction to iron(II) products with a half-life of about 30 minutes at ambient temperature.[834]

The bis-hydroxylamine adduct [Fe^{II}(tpp)(NH_2OH)$_2$] is stable at low temperatures, but decomposes to [Fe(tpp)(NO)] at room temperature.[835] [Fe(porphyrin)(NO)] complexes can undergo one- and two-electron reduction; the nature of the one-electron reduction product has been established by visible and resonance Raman spectroscopy.[836] Reduction of [Fe(porphyrin)(NO)] complexes in the presence of phenols provides model systems for nitrite reductase conversion of coordinated nitrosyl to ammonia (assimilatory nitrite reduction),[837] while further relevant information is available from the chemistry of [Fe^{III}(porphyrin)(NO_3)].[838] Iron–porphyrin complexes with up to eight nitro substituents have been prepared and shown to catalyze oxidation of hydrocarbons by hydrogen peroxide and the hydroxylation of alkoxybenzenes.[839]

Iodide is oxidized rapidly,[840] bromide slowly,[841] by the mono-oxidized form of μ-oxo-di-iron(III) bis-tetraphenylporphyrin. The latter reaction occurs in three kinetically distinct steps; the first, with $k_{298} = 738\ dm^3\ mol^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 59\ kJ\ mol^{-1}$, and $\Delta S^{\ddagger} = +9\ J\ K^{-1}\ mol^{-1}$ leads to the formation of Br_2^- as intermediate. Cyanide reduces iron(III) porphyrins, probably by rate-limiting nucleophilic attack, at least in DMSO (in which CN^- has a very high chemical potential).[842]

The alternative mechanisms for autooxidation of myoglobin, hemoglobin, and a range of lacunar iron(II)-cyclidene (**149**) model complexes—oxidative (electron transfer),[843] dissociative, and nucleophilic displacement[844]—have been discussed at length.[845] Autooxidation mechanisms have also been discussed in relation to lacunar complexes as dioxygen carriers,[764] and as the point where activation and stabilization of dioxygen are in balance.[847] Metmyoglobin catalysis of the decomposition of hydrogen peroxide involves a ferryl ($Fe^{IV}=O^{2+}$) intermediate,[23,24] whose Fe—O stretching frequency has been established by resonance Raman spectroscopy.[848] The kinetics of photoinduced electron transfer between cyt *c* in its oxidized form (Fe^{III}) and modified zinc myoglobin (lysine residues modified with dtpa) suggest that electron transfer takes place from the peripheral dtpa sites to the cyt *c*(III).[849]

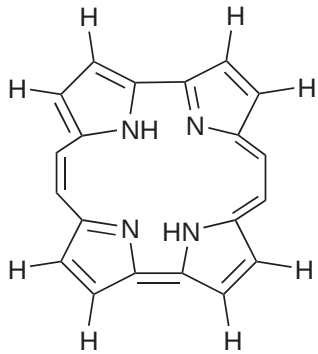


(**149**)

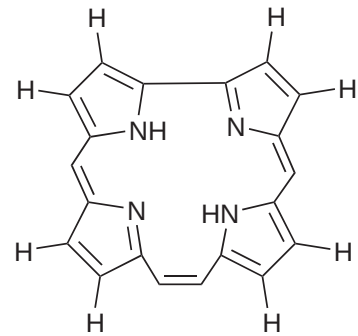
5.4.3.7.3 Porphycene, porphyrazine, and corrole complexes

Porphycenes (**150**) and corrphycenes (**151**) are porphyrin isomers,[850] several of whose iron(III) complexes have been characterized. Examples include distorted square-pyramidal (12,17-diethoxycarbonyl-2,3,6,7,11,18-hexamethylcorrphycenato)iodo-iron(III),[851] [Fe(tprpc)X] (where tprpc = 2,7,12,17-tetra-*n*-propylporphycene) with X = Cl, Br, N_3, O_2CMe, or OPh and [Fe(tprpc)$_2$]O.[852–854] Iron(II)– and iron(IV)–tprpc complexes also exist, as established in an examination of oxygenation of iron(II) porphycene.[855] The structure of chloro(3,6,13,16-tetraethyl-2,7,12,17-tetramethylporphycenato)iron(III), also distorted square-pyramidal, has been compared with those of chloro-iron(III) porphyrin complexes.[856]

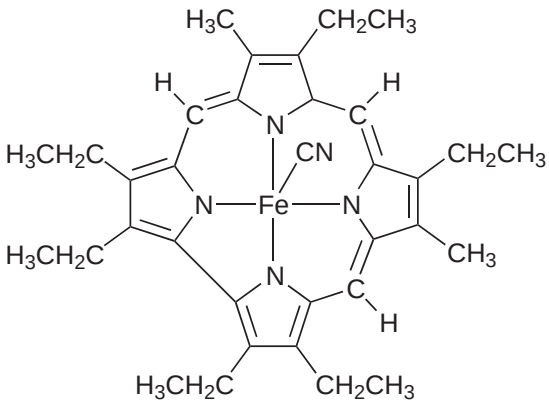
Corroles are porphyrins which lack the 20-methine group. (7,13-dimethyl-2,3,8,12,17,18-hexaethylcorrolato)iron chloride[857] reacts with cyanide to form a low-spin dicyano complex, which is subsequently reduced by excess of cyanide to give (**152**). The iron in the dicyano complex is still in the 3+ oxidation state, with the reduced corrolate as a dinegative radical ligand.[858]



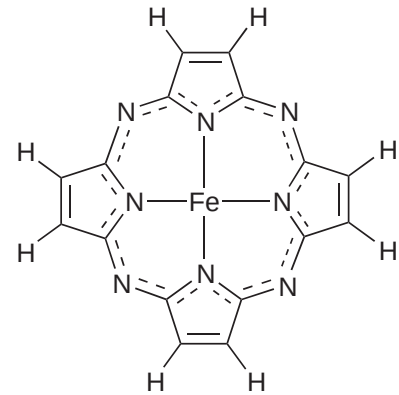
(**150**)



(**151**)



(**152**)



(**153**)

Porphyrazines (**153**) are porphyrins with the four =CH— inter-ring bridges replaced by =N—, thus forming a halfway house between porphyrins and phthalocyanines (next section). The octaethylporphyrazine complexes of iron(II) and of iron(III) have been reviewed.[859]

5.4.3.7.4 Phthalocyanine complexes

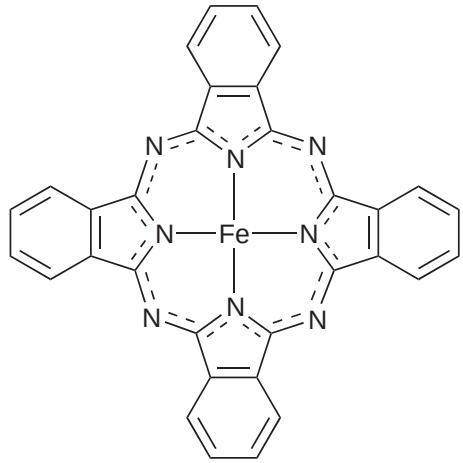
Investigations continue of ligand replacement reactions of the two coordinated solvent molecules of iron(II) phthalocyanine, (**154**), in DMSO.[860,861] It has been confirmed that both steps can be monitored for the incoming ligands pyridine, 4-aminopyridine, or imidazole. Rate and equilibrium constants are presented for both stages for the reactions with all three incoming groups.[862] The relatively weak electron-donating properties of alkylthio-substituents are reflected in the rate constants for addition of a second cyanide (addition of the first is very fast) to octa-*n*-butylthiophthalocyanine–iron(II).[863]

An equilibrium and kinetic study of the iron(II) phthalocyanine/nitric oxide system in DMSO, at 293 K, showed that formation of [Fe(pc)(NO)] obeys a simple second-order rate law, like [Fe(pc)] plus CO but unlike [Fe(pc)] plus dioxygen. A rate constant for dissociation of [Fe(pc)(NO)] was derived from its formation rate and equilibrium constants.[864]

Iron phthalocyanines feature in a review of photodynamic therapy.[241]

5.4.3.8 Nitric Oxide Complexes

The importance of NO is emphasized by the recent appearance of a new dedicated journal. Reactions of metalloporphyrins with NO have been reviewed.[783,865–868] A review of reactions of



(**154**)

nitric oxide with transition metal complexes is dominated by the kinetics and mechanisms of a range of complexes of iron, particularly polyaminocarboxylates, porphyrins, and heme derivatives.[869] A selection of thermodynamic and kinetic parameters for the formation of ternary nitric oxide complexes of iron(II) and of iron(III) is given in Table 10. Rate constants have been determined for the forward and reverse reactions for the interaction of NO with Fe^{2+}aq and with citrate, acetylacetone, and edta complexes of iron(II).[870] Kinetics of formation of NO complexes from iron(II) complexes of edta,[871] nta, dtpa, and related ligands have also been examined.[872] Activation volumes for formation ($\Delta V^{\ddagger}_{f} = +6.0\,cm^3\ mol^{-1}$) and for dissociation ($\Delta V^{\ddagger}_{d} = +1.2\,cm^3\ mol^{-1}$) of $FeNO^{2+}$aq indicate dissociative interchange mechanisms in both directions, though the very small negative values for the activation entropies ($\Delta S^{\ddagger}_{f} = -3\ JK^{-1}mol^{-1}$, $\Delta S^{\ddagger}_{d} = -15\ J\,K^{-1}\ mol^{-1}$) suggest that the character of the interchange process is very close to the dissociative/associative boundary—not altogether unexpectedly for Fe^{2+}. Mössbauer and ESR spectra of the product suggest that a formulation based on Fe^{III}—NO^- (cf. cobalamin(III)—NO^-[873]) is to be preferred to the Fe^{I}—NO^+ form usually given in text books.[874] This conclusion confirms earlier proposals based on X-ray absorption edge and resonance Raman spectra of the Fe–edta–NO complex.[875] Aminocarboxylatoaqua-complexes of iron(II) react somewhat more quickly with nitric oxide than does Fe^{2+}aq;[876] there is good agreement between equilibrium constants for formation of these NO complexes determined from kinetic measurements and values determined spectrophotometrically. Reversible binding of NO to iron(II) in aqueous solution may be tuned by using aminocarboxylate and related ligands.[877] Activation volumes for reactions of most aminocarboxylatoaqua-complexes of iron(II) with NO indicate dissociative interchange, though the negative value of $\Delta V^{\ddagger}$ for reaction of $[Fe(nta)(H_2O)_2]^-$ with NO suggests a mechanism of associative interchange in this case.[878]

Reactions of NO with water-soluble Fe^{II} porphyrin complexes are very fast ($k \sim 10^9\ M^{-1}\ s^{-1}$); diffusion-dominated dissociative interchange is suggested by the k, $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values (Table 10).[821] The Fe^{III} tetra-meso-(4-sulfonatophenyl)porphinate (tpps) complex and its sulfonatomesityl analogue react with NO in aqueous solution with large positive $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values; values for dissociation of the adducts formed are similar. A D mechanism is thus believed to operate for each of these reactions, in modest contrast to similar iron(II)—NO systems. Nitrite catalyzes reductive nitrosylation of $[Fe^{III}(tpps)(H_2O)_2]^{3-}$ to $[Fe^{II}(tpps)(NO)]$.[879] Formation of $Fe(tpp)(NO_2)$ occurs with traces of NO_2; coordinated —NO_2 labilizes the coordinated —NO in the reversibly formed intermediate $[Fe(tpp)(NO)(NO_2)]$.[880] Deoxyhemoglobin binds NO firmly[881–883] and rapidly ($k = 2.2 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$, at 293 K). NO also reacts rapidly with oxyhemoglobin ($k = 3.4 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$) and Fe^{II}–myoglobin ($k = 2.2 \times 10^7\ dm^3\ mol^{-1}\ s^{-1}$), somewhat less rapidly with Fe^{III}–myoglobin ($k = 7.0 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$).[884] These *in vitro* reactions are up to two orders of magnitude slower in the cell as the rate-limiting step there is often diffusion of NO to the complex.[885–887] The effects of NO on cellular iron metabolism,[888] the mechanism of NO-induced oxidation of

Table 10 Kinetic parameters and equilibrium constants for formation and dissociation of ternary nitric oxide complexes (in water, at 298 K).

	k_f	$\Delta H^{\ddagger}_f$	$\Delta S^{\ddagger}_f$	$\Delta V^{\ddagger}_f$	k_d	$\Delta H^{\ddagger}_d$	$\Delta S^{\ddagger}_d$	$\Delta V^{\ddagger}_d$	K°
Iron(II) complexes									
aq	1.6×10^6	37	−3	+6.0	3.2×10^3	48	−15	+1.2	500 or 1,200
nta	2.1×10^7	24	−22	−1.5	9.3	66	−5	−3.5	1.8×10^6
edta	2.4 x10^8	24	−4	+4.1	91	61	−5	+7.6	2.1×10^6
tpps	1.5×10^9	24	+12	+5	< 2				
tmps	1.0×10^9	26	+16	+2					
cytochrome *c*	8.3				2.9×10^{-5}				
nitric oxide synthase	3×10^5 to 2×10^7				~0 to 70				
Iron(III) complexes									
tmps	3.0×10^6	62	+86	+13	730	83	+89	+18	4.1×10^3
tpps	7.2×10^5	70	+100	+8	680	78	+67	+18	1.1×10^3
cytochrome *c*	7.2×10^2				0.044				1.6×10^4
myoglobin	4.7×10^4				37				1.3×10^3
catalase	3.0×10^7				170				1.8×10^5

The kinetic parameters and K° values in this table are from M. Wolak and and R. van Eldik,[869] and references therein.

Mb, Hb,[884] and NO mediation of iron uptake from transferrin[889] have been discussed. In this last case, in contrast to several established cases of Fe—NO interaction at active sites in metalloproteins (e.g., lactoferrin—Fe—NO[890]), there appears not to be direct Fe—NO interaction but an indirect NO effect operating from an Fe-remote site.[891] $HbFe^{II}NO$ has been characterized in blood taken from humans administered hydroxyurea,[892] a currently much-discussed possible treatment for sickle cell disease.[893] NO binds to iron which is itself coordinated by imidazole groups of histidine, thiol groups of cysteine, or carboxylate groups of aspartate or glutamate.[894] The attachment of dioxygen to hemoglobin promotes binding of NO to cysteineβ93; deoxygenation results in an allosteric transition of the S-nitrosohemoglobin which releases NO. This sequence is central to the regulation of blood flow.[895] NO has a direct effect on the Fe_4S_4 cluster of an iron-regulating protein and thence on iron mobilization from cells.[896]

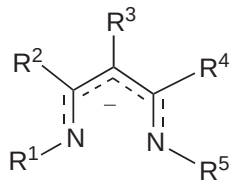
Reaction of the manganese tropocoronand complex [Mn(tc-5,5)(NO)] with [Fe(tc-5,5)] results in complete transfer of the NO to the [Fe(tc-5,5)].[897] Other nitric oxide complexes appear in the sections on nitroprusside (Section 5.4.2.2.6 above), on phthalocyanines (Section 5.4.3.7.4 above), and on polynuclear iron–sulfide complexes (Roussin's salts; Section 5.4.5.9.2 below); Fe–porphyrin–NO redox chemistry has been mentioned in Section 5.4.3.7.2 above.

5.4.3.9 Other *N*-donor Ligands

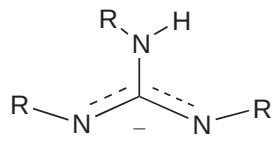
Coordinated nitriles occur in several diphosphine (diphos) complexes *trans*-$[Fe(diphos)_2(NCMe)_2]^{n+}$, $n = 1$ or 2.[898,899] The cyanide stretching frequency for the MeCN solvate of Fe^{2+} has been compared with values for a range of other cations.[329]

A review of complexes of β-diketiminate ligands (**155**) contains little material on iron complexes.[900]

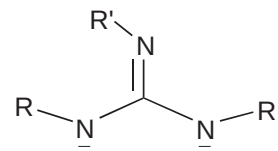
Mononuclear iron(II) and iron(III), and binuclear iron(II), complexes with monoanionic and dianionic trialkylguanidinate ligands, (**156**) and (**157**), have been characterized. The trichloroiron(III) complex of (**156**), R = Pr^i, appears to be five-coordinate; both (**156**) and (**157**) act as bridging ligands in binuclear iron(II) complexes, as also can a related biguanidinate ligand.[901] Binuclear iron(III) complexes $Fe_2L_2(\mu\text{-L})$ where L = *N*,*N*′-diphenylformamidine (dpf) or *N*,*N*′-diphenylbenzamidine have particularly short Fe···Fe distances, at 2.198, 2.232 Å; the iron atoms are in trigonal prismatic coordination. In the iron(II) complex $[Fe_2(dpf)_4]$ the Fe···Fe distance is 2.462 Å.[902,903]



(**155**)



(**156**)



(**157**)

The ternary triazole complex $[Fe^{II}(abptrz)_2(tcnq)_2]$ ((**132**) in Section 5.4.3.6.3 above; abptrz = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) contains the 7,7′,8,8′-tetracyanoquinodimethane (tcnq) radical anion coordinated in *trans*-positions at unusually short Fe—N distances; the tcnq radical ligands are stacked in pairs to give diamagnetic entities.[714]

5.4.3.10 Phosphorus Donor Ligands

The cyclic (D_{5h}) P_5^- anion, which can be generated from white phosphorus by cleaving either with sodium in diglyme or LiH_2P in THF, forms stable $Fe^{II}(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_5)$; there is some evidence for the generation of unstable black $Fe^{II}(P_5)_2$ on treatment of $FeCl_2$ with P_5^-.[904]

The *cis*-1,2-bis(diphenylphosphino)ethene complexes $[Fe(Ph_2PCH{=}CHPPh_2)_2X_2]$, X = Cl or Br, undergo pressure-induced spin-state transitions at about 8 kbar for the chloro complex, about 60 kbar for the bromo complex. The difference is ascribed to the difference in ligand field strengths and lattice cooperativity.[57]

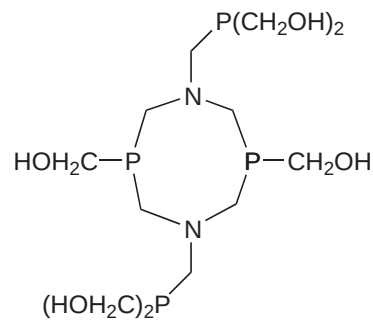
The diphosphine complexes *trans*-$[Fe(H)(X)\{Ph_2P(CH_2)_nPPh_2\}_2]$, $n = 2$ or 3, X = Cl or Br, react with cyanide to give *trans*-$[Fe(H)(CN)\{Ph_2P(CH_2)_nPPh_2\}_2]$,[905] which can be protonated to give, *inter alios*, the *trans*-$[Fe(H_2)(CNH)\{Ph_2P(CH_2)_nPPh_2\}_2]^{2+}$ cation.[906] *cis*-$[Fe\{P(CH_2CH_2PMe_2)_3\}(H_2)]$ reacts with EtNCS, PhNCS, or PhNCO to give *cis*-$[Fe\{P(CH_2CH_2PMe_2)_3\}(SCHNEt)H]$, *cis*-$[Fe\{P(CH_2CH_2PMe_2)_3\}(SCHNPh)H]$ (*cis*-$[Fe\{P(CH_2CH_2PMe_2)_3\}(SCHNPh)_2]$ if PhNCS is in excess), or *cis*-$[Fe\{P(CH_2CH_2PMe_2)_3\}(OCHNPh)H]$. Similar reactions of *cis*-$[Fe(Me_2PCH_2CH_2PMe_2)_2\}(H_2)]$ give more complicated mixtures of products.[907]

A qualitative order of ligand strength towards iron(II) has been established by competition experiments for a series of diphosphines in their complexes $[Fe(diphos)_2Cl_2]$.[908] The tripodal tetradentate phosphorus donor ligand engenders high stability in the hydride/dihydrogen complex *cis*-$[Fe\{P(CH_2CH_2PPh_2)_3\}(H)(H_2)]^+$.[909] The relative stabilizing effects of bidentate and tripodal phosphorus ligands have been compared through determination of rate constants for replacement of acetonitrile by halide in the complexes $[Fe(Ph_2PCH_2CH_2PPh_2)_2(MeCN)_2]$, $[Fe\{P(CH_2CH_2PPh_2)_3\}(MeCN)_2]$, and $[Fe\{N(CH_2CH_2PPh_2)_3\}(MeCN)_2]$. The apical nitrogen in the last of these confers a degree of lability.[910] The tripodal tetradentate ligand $P(CH_2CH_2PMe_2)_3$, tppm, appears in a number of iron(II) complexes, such as $[Fe(tppm)Cl_2]$, [Fe(tppm)HCl] and the $[Fe(tppm)(PPh_3)Cl]^+$ cation.[911] The tetrapodal ligand (**158**) has sufficient hydrophilic centers for the sulfate of its bis-aqua-iron(II) complex $[Fe(\mathbf{158})(H_2O)_2]^{2+}$ to be soluble in water.[912]

There are many phosphine and phosphite complexes of iron(0), sometimes acting as P,C-donors in orthometallated complexes. In general this area is deemed to be organometallic chemistry, so we shall cite just one recent reference to act as a possible point of entry to this area, relating to $[Fe(CO)_2\{P(OPh)_3\}\{P(OPh)_2(OC_6H_4)\}]$ which contains both a P- and a P,C-donor triphenylphosphite ligand.[913]

Monodentate phosphines complete the coordination shells of a number of hydride complexes, e.g., $[FeH_2(PR_3)_4]$ and $[FeH_3(PR_3)_4]^+$.[914] Bidentate bis-phosphine ligands stabilize a number of ternary complexes of small molecule ligands, such as dinitrogen, carbon monoxide, carbon disulfide, dihydrogen,[439,915] and acetonitrile.[898,899] Diphenylphosphinoethane can also act as a bridging ligand, as in the binuclear counterion of the acetonitrile-containing cation in *trans*-$[Fe(dppe)(NCMe)_2][Cl_3Fe(\mu_2\text{-dppe})FeCl_3]$.[916]

Ligand concentration dependences, activation parameters, and solvent effects for reaction of *trans*-$[FeH(H_2)(dppe)_2]^+$ with MeCN in MeCN, THF or acetone present a not altogether consistent mechanistic picture. In particular the large negative activation volumes are unexpected. These reactions cannot be simple dissociative, in contrast to earlier-studied similar reactions of iron(II)–phosphine complexes.[917] The suggestion is that the rate-limiting step is some sort of associative ring closure after easy initial opening of the dppe chelate ring.[918]



(**158**)

5.4.4 GROUP 15/16 DONORS

5.4.4.1 Nitrogen and Oxygen Donors

5.4.4.1.1 Oxines

Tris-(2-methylquinolin-8-olato)iron(III) has three *mer* N and three *mer* O-donor atoms; the 0.2 Å range of Fe—N bond distances is attributed to small but significant steric effects of the methyl substituents.[919] Solubilities of tris-(quinolin-8-olato)iron(III) complexes in methanol–water mixtures are consistent with the expected more favorable solvation by methanol.[920]

The acid-catalyzed aquation of iron(III)–(substituted)oxinate complexes involves iron–oxygen bond breaking and concomitant proton transfer in transition state formation. The latter aspect contrasts with the much slower acid-catalyzed aquation of hydroxamates, where proton transfer seems not to take place in the transition state. Reactivities, with and without proton assistance, for various stages in dissociation of a selection of bidentate and hexadentate hydroxamates, oxinates, and salicylates are compared and discussed—the overall theme is of dissociative activation.[921]

5.4.4.1.2 Schiff bases

The structure and properties of $[Fe^{II}(H_2O)_6][Fe^{III}(tsb)_2]_2 \cdot 2H_2O$, where tsb = the terdentate Schiff base derived from salicylideneglycine, have been described.[922] The detailed 2D structures of salts of $[\{Fe(salen)\}_2\{Fe(CN)\}_6]^-$ depend on the nature of the cation and the solvent used in their preparation.[318] Binuclear iron(III) complexes have been prepared from Schiff bases derived from 2,6-diformyl-*p*-cresol and anilines.[923]

[Bis(5-bromosalicylidene)benzene-1,2-diimine]chloroiron(III) crystallizes with one five-coordinate complex and one six-coordinate (water *trans* to chloride as sixth ligand) in the unit cell.[924] Fe^{3+} complexes of three linear hexadentate (*O*,*N*,*N*,*N*,*N*,*O*) bis-Schiff base ligands derived from trien and 2-hydroxypropiophenone, 2-hydroxybenzophenone, and 1-hydroxy-3-methoxybenzophenone, or pyrrole-2-aldehyde, plus Fe^{3+} complexes of two tripodal $\{N(N,O)_3\}$ ligands derived from tren, have been prepared; their Mössbauer spectra are given.[513] The potentially pentadentate binucleating ligand 2,6-bis(*N*-2-pyridylethyl)iminomethyl)-4-methylphenolate (**159**) forms a mononuclear complex, in which the ligand is *N*,*N*,*O*-coordinated (*mer*) on reaction with iron(III) chloride.[925] The potentially heptadentate (*N*,*O*,*N*,*N*,*N*,*O*,*N*) macrocyclic ligand forms binuclear $Fe^{II}Co^{II}$ complexes with high-spin iron(II) (*O*,*N*,*N*,*N*,*O*)-coordinated.[926]

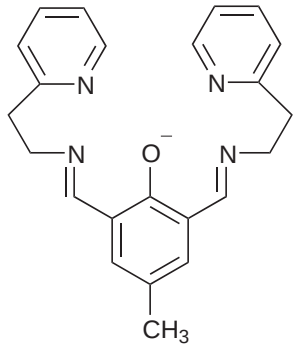
The solubility properties of salen-type complexes can be tailored by employing substituents such as *t*-butyl and triphenylphosphonium-methyl (—$CH_2PPh_3^+$), with its associated chloride, in the aromatic rings.[927] The stability constant for *N*,*N*′-*o*-phenylenebis(salicylideneimine)–iron(III) in 80% (w/w) DMSO–water has been compared with stability constants for complexes of six M^{2+} metal ions with this ligand.[928]

The first step in the reaction of *trans*-$[Fe(salpn)(H_2O)_2]^+$, salpn = *N*,*N*′-propylene-1,2-bis-salicylidiniminate, with sulfur(IV) is the formation of $[Fe(SO_3)(salpn)(H_2O)]^-$, with the pH-rate profile showing greater *trans*-labilization by hydroxide than by water, in that *trans*-$[Fe(salpn)(H_2O)_2]^+$ reacts ten times less rapidly than *trans*-[Fe(salpn)(OH)(H_2O)]. A limiting dissociative (*D*) mechanism is proposed for reaction of the latter; formation of the sulfito complex is followed by a slow intermolecular redox reaction.[929] A similar situation prevails for the analogous *trans*-$[Fe(salen)(H_2O)_2]^+$/sulfur(IV) system (salen = (**160**) with R = H); this paper also deals with the kinetics and mechanism of sulfur(IV) reduction of *trans*-$[Fe(salen)(H_2O)_2]^+$.[930] Mechanisms of photoredox processes of *trans*-[Fe(R-salen)(MeOH)F] (Rsalen = (**160**) with R = F, I, Me, CF_3, OMe, or NO_2) involve the formation of $\cdot CH_2OH$ radicals and their conversion into formaldehyde. The F^- ligand stabilizes the Fe^{3+} in these complexes in comparison with coordinated Cl^-, Br^-, or I^-.[931]

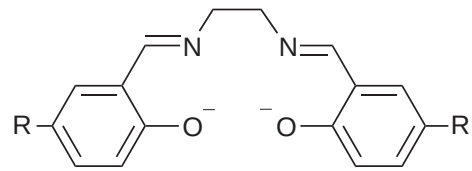
Salicylaldimine complexes of iron(III) catalyze epoxidation of stilbene by hypochlorite.[932]

(i) Spin cross-over

The cyclic Schiff base terimine ligand (**161**) forms a spin cross-over ternary iron(II) complex [Fe(**161**)$(CN)_2$]. This has intermediate magnetic behavior, indicating a 50:50 mixture of high-spin

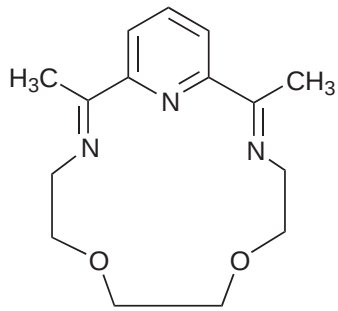


(**159**)

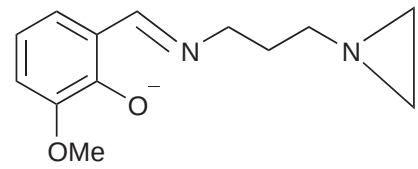


(**160**)

and low-spin forms, over the long temperature range of 150–200 K.[679] The spin mixture form can be obtained by cooling [Fe(**161**)$(CN)_2$] slowly; rapid cooling to low temperature gives the low-spin form. The rate constant for conversion of the seven-coordinate high-spin form to the six-coordinate (one noncoordinated ether–oxygen) low-spin form is 2.3×10^{-3} s^{-1} at 130 K; an Arrhenius plot gives an activation energy of 30 kJ mol^{-1} for the spin cross-over process.[933]

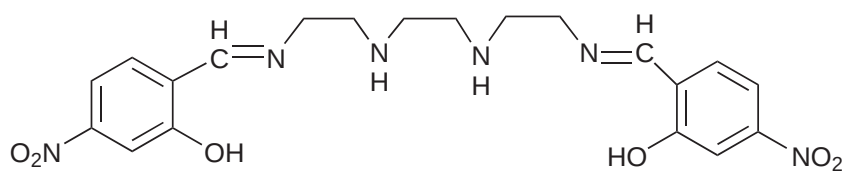


(**161**)



(**162**)

Spin cross-over behavior has been established for a number of Schiff base complexes of iron(III) complexes with N_4O_2-donor sets.[934–936] A two-step spin cross-over in the warming direction for [Fe{*N*-(8-quinolyl)salicylaldiminate}$_2$](NCSe) has been ascribed to intermolecular π-interactions between aromatic rings.[937] Usually spin cross-over in these N_4O_2-complexes is rapid on the Mössbauer timescale ($k > \sim 10^7$ s^{-1}); interconversion has been shown to be rapid on the Mössbauer timescale but slow on the ESR timescale ($k < \sim 10^{10}$ s^{-1}) for the iron(III) complex of the Schiff base (**162**) in the $[Fe^{III}(\mathbf{162})_2]^+$ cation.[938] A thorough variable-temperature study of spectroscopic and magnetic properties of $[Fe^{III}(\mathbf{162})_2]ClO_4 \cdot C_6H_6$ indicated not only a spin cross-over centered on 205 K but also an order–disorder transition ($C2/c$ at high temperatures, $P2_1/c$ at low temperatures) around 180 K.[939] Mössbauer and ESR studies indicate anion control of spin cross-over rates for bis-ligand iron(III) complexes of N_2O-donor Schiff bases derived from, e.g., salicaldehyde and 2-pyridylmethylamine.[935] The iron(II) complex of the garland Schiff base ligand (**163**) provided the first example of spin cross-over behavior in a hexadentate N_4O_2-donor complex. Over the temperature range ~145–175 K there exists an l.s. $\rightleftharpoons$ h.s. equilibrium with $K \sim 1$.[940] The methanol and dichloromethane solvates of the *N*-(8-quinolyl)-salicylaldimine complex [Fe(qsal)$_2$]NCSe exhibit the unusually wide hysteresis loop of 70 K.[941]

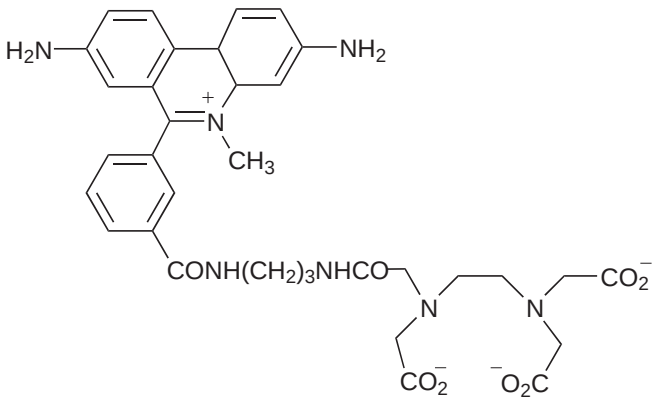


(**163**)

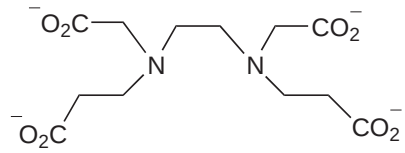
5.4.4.1.3 Acyclic polyaminocarboxylates

Reactions of iron-polyaminocarboxylates with nitric oxide have already been covered, in Section 5.4.3.8; bi- and polynuclear complexes containing polyaminocarboxylate ligands will be found in Section 5.4.5.4 below.

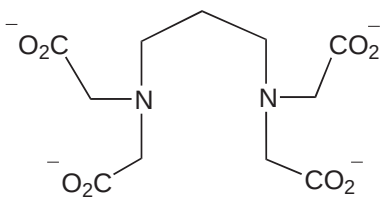
The partial molar volume and heat capacity of $[Fe^{III}(edta)]^-$ have been derived from experimental measurements on its sodium salt, and the thermodynamic constants (K, ΔH, ΔS, ΔC_p, and ΔV) for complexation of Fe^{3+} by H_2edta^{2-} obtained.[942] Formation of the iron(II) complex of the aromatic edta analogue 1,2-$C_6H_4\{N(CH_2CO_2)_2\}_2^{4-}$ has been assessed spectrophotometrically and potentiometrically.[943] Propyl-edta-derivatization of methidium, giving (**164**), allows complexing of iron and thus a study of the effects of this substitution on methidium–DNA interactions (strand scission mediation).[944,945] Molecular mechanics calculations on iron(III)-transferrin models, including the Fe^{3+} complex of 1,4,7-triazacyclononane-1,4,7-triacetate, have been based on force-field parameters derived from published crystal structures of the Fe^{3+} complexes of the ligands (**165**), (**166**), and (**167**).[946]



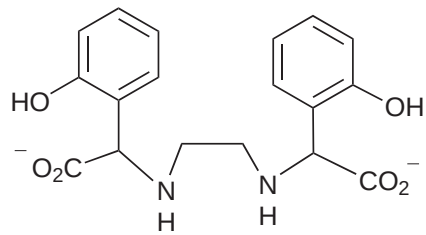
(**164**)



(**165**)



(**166**)

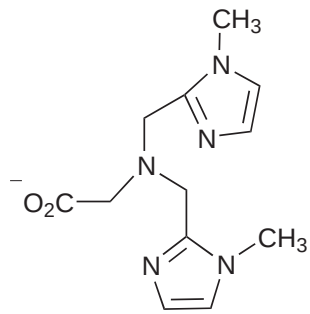


(**167**)

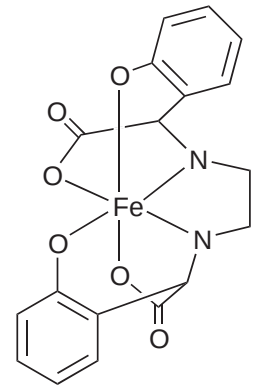
The Fe^{3+} complex of the tetradentate N_3O-donor tripodal ligand (**168**) provides a model for mononuclear nonheme bioactive sites. $[Fe^{III}(\mathbf{168})Cl_2]$, whose chloride ligands are substitution-labile, reacts with O_2^- in DMSO solution to give an $Fe^{III}.O_2^-$ species that may well be identical with the stable $Fe^{II}.O_2$ species obtained from the reaction of the iron(II) complex of (**168**) with O_2.[947]

Site-specific cleavage of a protein has been achieved by attaching a $—CH_2CONHC_6H_4CH_2CH\{CH_2N(CH_2CO_2^-)_2\}_2$ group at a cysteine residue, followed by complexation with Fe^{2+}, then treatment with hydrogen peroxide.[948]

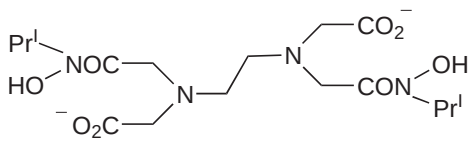
A new aminocarboxylate chelator of potential therapeutic value, *N*-(2-hydroxybenzyl)-*N*′-benzylethylenediamine-*N*,*N*′-diacetate, reacts as LH_4^+ and LH_3 with $FeOH^{2+}$aq by dissociative activation with rate constants of $770\,M^{-1}\,s^{-1}$ and $13{,}300\,M^{-1}\,s^{-1}$, respectively. These rate constants are similar to those for reaction of $FeOH^{2+}$ aq with edta and with nta. These formation reactions are, however, considerably faster than with simple ligands of identical charge thanks to the zwitterionic properties of aminocarboxylates.[949] Iron(III)–ehpg[950] (ehpg = ethylene-bis-(2-hydroxyphenylglycine)), (**169**), is an effective hepatobiliary contrast agent.[231] Dihydroxamate derivatives of edta and of dtpa, (**170**) and (**171**), respectively, are analogues of aerobactin.[951]



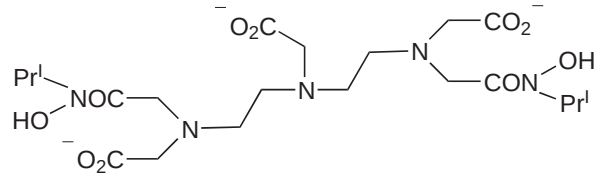
(**168**)



(**169**)



(**170**)

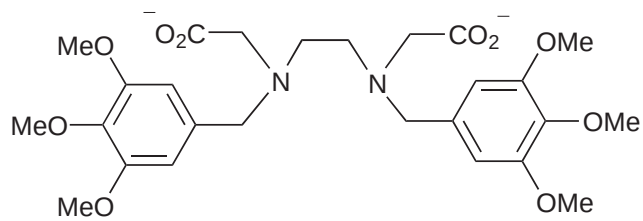


(**171**)

Extensive efforts have been made to establish and rationalize the kinetics of dioxygen oxidation of iron(II) polyaminocarboxylate complexes.[742,952,953] The kinetics of dioxygen oxidation of iron(II) complexes of 1,2- and of 1,3-propylenetetraacetate show the influence of steric factors on these electron transfer reactions.[954]

NMR and UV–visible techniques have been used in the characterization of intermediates in the $[Fe^{III}(edta)]^{n-}$-promoted decomposition of hydrogen peroxide.[955] Fe^{II} complexes of edta, nta, and dtpa react with HSO_5^- by an inner-sphere one-electron transfer mechanism with transient production of $SO_4^{\bullet -}$, in contrast to Cu^I, which reacts by an outer-sphere mechanism to give SO_4^{2-} and hydroxy radicals.[956,957] Fe^{II}–edta redox properties are relevant to $Fe^{II}/Cu^{II}/H_2O_2$ systems.[958]

Fe^{2+} complexes of edta, hedta, and nta react with $Br_2^{\bullet -}$, $(NCS)_2^{\bullet -}$, $CO_2^{\bullet -}$, and $Me^{\bullet}$ with rate constants between $10^7\,dm^3\,mol^{-1}\,s^{-1}$ and $10^8\,dm^3\,mol^{-1}\,s^{-1}$ at 293 K. Activation volumes of $-0.3\,cm^3\,mol^{-1}$ to $-4.2\,cm^3\,mol^{-1}$ suggest interchange mechanisms with small and variable associative character.[959] The Fe^{2+} complex of the edda derivative (**172**) reacts with H_2O_2 to give a stable phenolate complex. [Fe(**172**)$(H_2O)_2$] might thus provide protection against oxidation in biosystems.[960] Several iron(III) polyaminocarboxylate complexes have been claimed to have superoxide dismutase activity.[470] The mechanism of iron uptake from complexes with low molecular weight ligands such as nitriloacetate in cells has been discussed.[167]

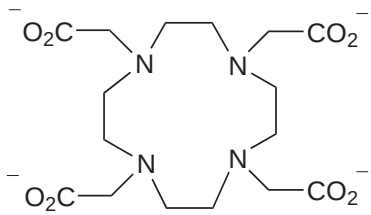


(**172**)

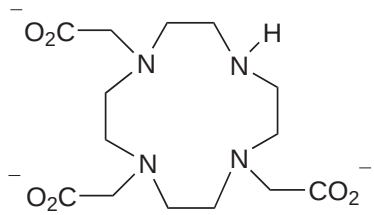
5.4.4.1.4 Polyazamacrocycles with pendant carboxylates

Iron(III) complexes of dota (**173**) and of dotria (**174**), tetrazamacrocycles with four and three $CH_2CO_2^-$ pendant arms, have been synthesized and characterized. These complexes are potential MRI contrast agents (cf. Section 5.4.1.11.3), with [Fe(dotria)] having the advantage for pharmacological applications of being uncharged. Crystal structure determinations of $[Fe(dotria)]\cdot 3H_2O$ and of Na[Fe(dota)] show the iron to be seven-coordinated (N_4O_3-donor set) in both cases—the fourth $CH_2CO_2^-$ pendant arm dangles in the latter compound.[961] The stability constant (log K at 298 K) for the Fe^{3+} complex of dota is 29.4.[962]

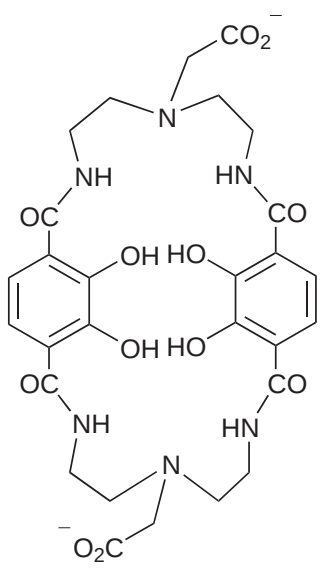
Incorporation of two catechol moieties into appropriate hexaazacrowns gives the ligands (**175**) and (**176**), stability constants of whose Fe^{3+} complexes are $\log_{10}K_1 = 37.6$ and 36.0, respectively.[963]



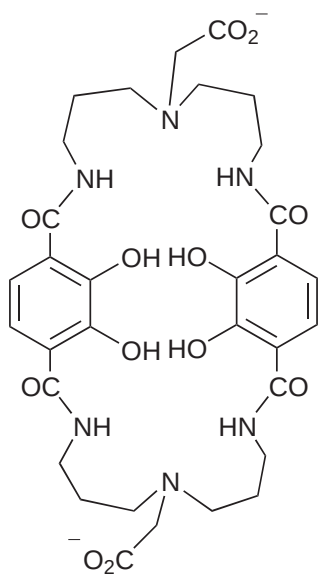
(**173**)



(**174**)



(**175**)



(**176**)

5.4.4.1.5 Other N,O donors

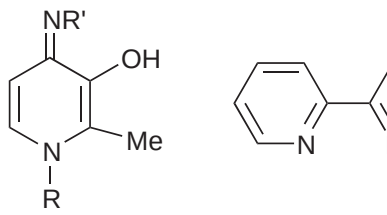
Several bis-amino acid complexes of iron(II) have been prepared and characterized. Their magnetic and spectroscopic properties indicate high-spin octahedral Fe^{2+} and the presence of extensive carboxylate bridging.[964] Stability constants have been determined for complexation of Fe^{3+}aq and of $FeOH^{2+}$aq by glycine,[965] and by L-serine and L-glutamate.[966] There are a very few values for iron complexes in a critical compilation of stability constants of aliphatic amino acids.[967]

Treatment of Fe^{3+}aq with glycine and 3-acetylpyridine gave not the expected Schiff base complex but a binuclear complex containing both coordinated glycine and coordinated 3-acetylpyridine.[968]

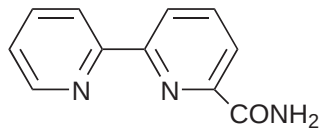
Hydroxypyridonimine analogues (**177**) of the much-studied 3-hydroxy-4-pyridinones (cf. Section 5.4.5.5.2), are prepared from maltose or lactose.[969] They form stable iron(III) complexes.

Several picolinate-containing complexes have been invoked in mechanisms of Gif-type oxidations of hydrocarbons by hydrogen peroxide.[458]

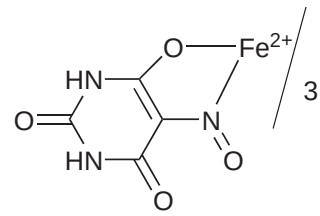
Carboxamides are good donors for iron(III), giving a range of water-stable high-spin and low-spin complexes with Fe—N bond distances between 1.8 Å and 2.2 Å.[970] The mono-ligand iron(II) complex of the carboxamide derivative of bipy, Fe(**178**)$Cl_2 \cdot H_2O$, is high-spin.[489] Dihydrogenvio-lurate, $violH_2^-$, gives a low-spin tris-ligand complex of iron(II), $[Fe(violH_2)_3]^-$ (**179**), and (at least in DMSO) the same sequence of stability constants, viz $K_1 > K_2 \ll K_3$, as the well-known Fe^{2+}/bipy and Fe^{2+}/phen sequences.[971] However $[Fe(violH_2)_3]^-$ is very labile, in contrast to $[Fe(bipy)_3]^{2+}$ and $[Fe(phen)_3]^{2+}$. This surprising feature is attributed to ready protonation and thus labilization of coordinated H_2viol^-. IR and Mössbauer evidence for the existence of $[Fe(violH_2)_2(violH_3)]$ in the solid state provides support for this hypothesis.[972] The ferroverdin chromophore is very similar to $[Fe(violH_2)_3]^-$; four synthetic ferroverdins, (**180**) with R = Me, Bu^t, Cl, Br, have been synthesized, and have been oxidized (by Fe^{3+}aq or by $[Fe(bipy)_3]^{3+}$) to the corresponding ferriverdins.[973]



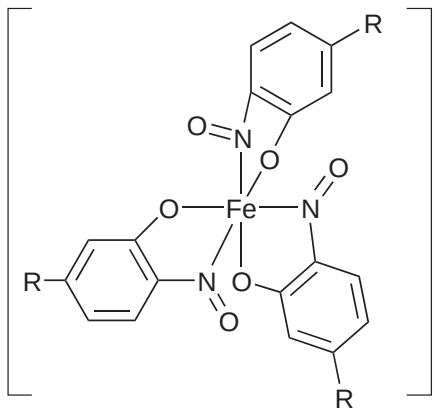
(**177**)



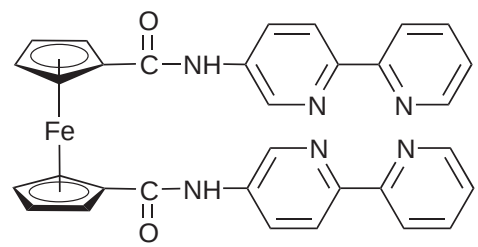
(**178**)



(**179**)



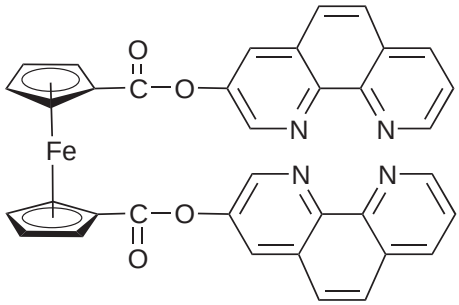
(**180**)



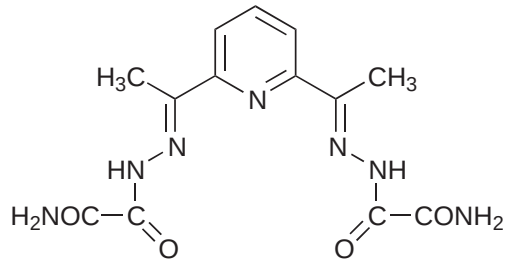
(**181**)

The ferrocene-linked bis-bipy and bis-phen ligands (**181**) and (**182**) form very stable iron(II) complexes in which the ligands are bonded to the metal through two carbonyl oxygens in addition to the two diimine groups.[492]

Benzoylacetone-S-*n*-propylisothiosemicarbazonatodichloroiron(III) contains five-coordinated iron(III), even in its mono-ethanol solvate.[974] The bis-aqua-iron(III) complex of 2,6-diacetylpyridine-bis(semioxamazidate), $[Fe(dapsox)(H_2O)_2]^+$ ($dapsoxH_2$ = (**183**)), contains seven-coordinate Fe^{3+} (the thirteen other then-known seven-coordinate Fe^{3+} complexes are referenced)—the ligand is *O*,*N*,*N*,*N*,*O*-pentadentate. The strongly electron-withdrawing properties of the $dapsox^{2-}$ ligand are reflected in the unusually short Fe—OH_2 bond distances, which average 2.028(3) Å. Despite the high coordination number of the iron, kinetic parameters for replacement of the first water molecule by thiocyanate suggest associative substitution (I_a).[975] The pentadentate N_4O-donor ligand 1,5-bis[(2-pyridylmethyl)amino]pentan-3-ol provides the key to the preparation of linear and cubane-like tetranuclear, as well as two binuclear, iron(II) complexes.[976]

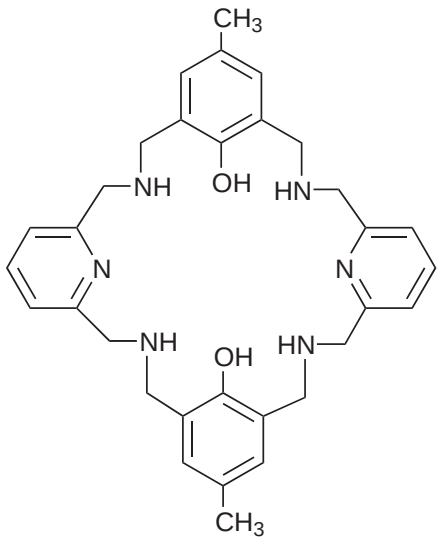


(**182**)

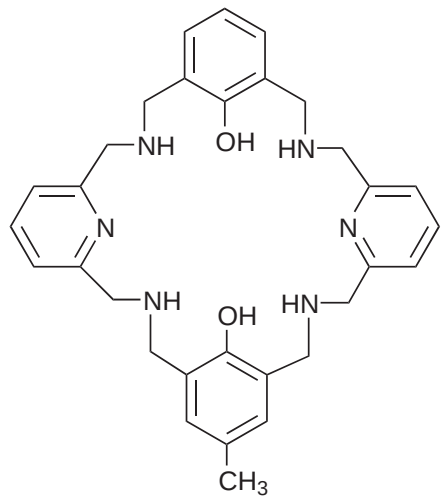


(**183**)

A review of the stabilities and catalytic properties of binuclear metal complexes of large-ring *N*,*O* macrocycles concentrates on the iron(II) and iron(III) complexes of (**184**) and (**185**).[977]



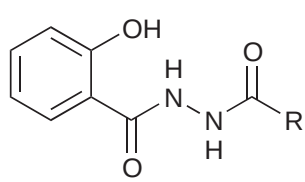
(**184**)



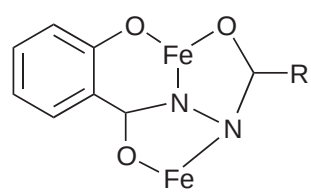
(**185**)

The tetranuclear cluster $Fe^{III}[Fe^{III}(salicylhydroximato)(MeOH)(OAc)]_3$ is in effect an Fe^{3+} complex of a tris-metallo-9-crown-3 ether ligand.[978,979] Salicylhydrazidate ligands, (**186**), can form polynuclear metallacrown complexes with iron(III), including a hexa-iron compound from *N*-acetylsalicylhydrazidate, (**186**) with R = Me,[980] and a deca-iron compound from *N*-benzoylsalicylhydrazidate, (**186**) with R = Ph.[981] The Fe^{3+} cations are in binding sites of the type shown in (**187**).

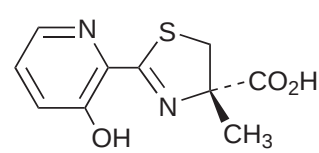
(*S*)-Desferriferrithiocin, (**188**), is a naturally occurring siderophore of unusual structure, mediating iron uptake by *Streptomyces antibioticus*. It coordinates Fe^{3+} through carboxylate and phenoxide oxygens plus the thiazole nitrogen. Its substitution-inert chromium(III) and cobalt(III) complexes have been investigated in order to glean information relevant to likely properties of its labile iron(III) complexes.[982]



(**186**)



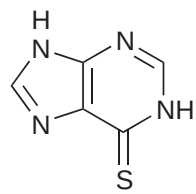
(**187**)



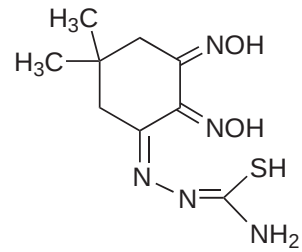
(**188**)

5.4.4.2 Nitrogen and Sulfur Donors

The Fe^{3+} coordination shell comprises three *fac*-*S* and three *fac*-*N*-donor atoms in $[Fe(6mp)_3][FeCl_4]Cl$, where 6mp = 6-thiopurine, (**189**).[983] Both iron(II) and iron(III) complexes are included in a review of transition metal complexes of thiosemicarbazones.[984] 5,5′-Dimethyl-1,2,3-cyclohexanetrione-1,2-dioxime-3-thiosemi-carbazone, dcdt (**190**), acts as an *N*,*N*′,*S*-donor to Fe^{3+}, giving a bis-ligand complex (contrast $[Fe(N,N'\text{-dcdt})_3]$ with Fe^{2+}).[135] The Schiff bases from pyridine 2-carboxaldehyde and thiosemicarbazide or 4-phenyl thiosemicarbazide also act as *N*,*N*′,*S*-donors, both to Fe^{3+} and to Fe^{2+}. The antibacterial activity of these complexes was assessed, *in vitro*.[985]

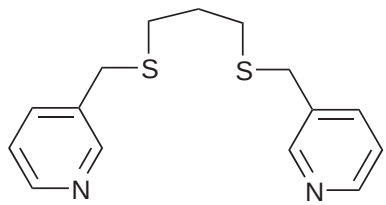


(**189**)

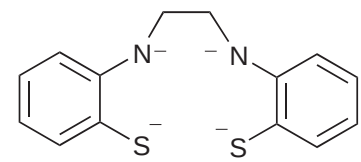


(**190**)

The tetradentate tripodal ligand $N(CH_2CH_2S)_3^{3-}$ (teta) forms mononuclear complexes $[Fe(teta)(CNR)]^-$ with alkyl isocyanides and trinuclear complexes $[M\{Fe(teta)(CNR)\}_2]$, M = Fe, Co, or Ni, in which two trigonal bipyramidal Fe-containing units are linked through tetrahedral MS_4 (edge-sharing).[986] Trigonal bipyramidal $[Fe^{III}(teta)Cl]^-$ is reduced by sodium in the presence of carbon monoxide to give the $[Fe^{II}(teta)(CO)]^-$ anion.[987] The kinetics of transfer of the tetradentate *N*,*S*,*S*,*N*-donor bis-(2-picolyl)-1,3-dithiopropane, bpdtp (**191**), from Fe^{2+} in $[Fe(bpdtp)Cl_2]$ to Cu^{2+} indicate a complex mechanism.[988] The *S*,*N*,*N*,*S*-donor (**192**) stabilizes iron(IV) in complexes [Fe(**192**)(PR_3)][29] and even iron(V) in [Fe(**192**)I].[30]

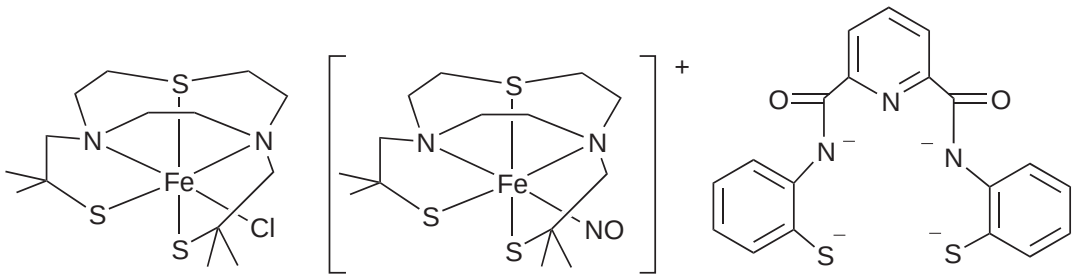


(**191**)



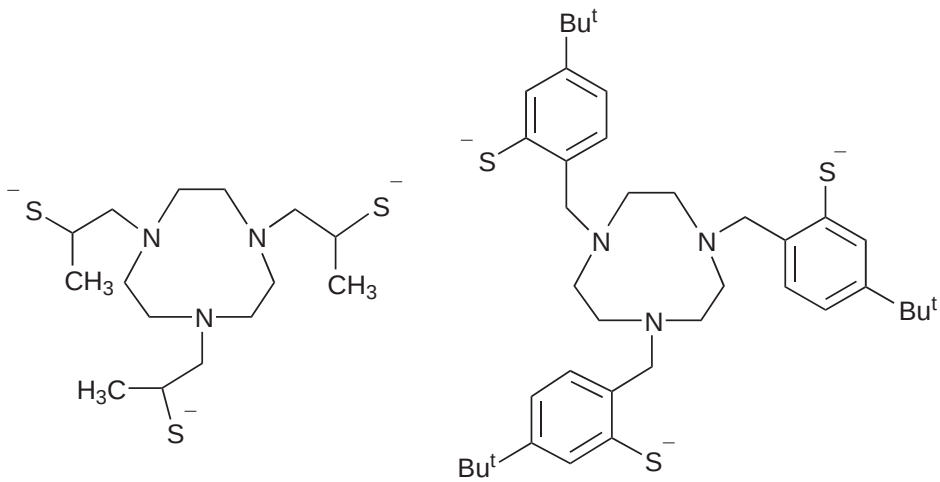
(**192**)

Blue (**193**) reacts with nitric oxide to give brownish violet (**194**), isolated as its BPh_4^- salt.[989] This low-spin iron(III) nitrosyl is a model for nitrile hydratase, which catalyzes the hydration of nitriles to give amides. One form of nitrile hydratase is a mononuclear low-spin iron(III) complex in which the metal is coordinated by three cysteine-sulfurs, two amide-nitrogens, and either water or hydroxide.[990–992] Nitrile hydratase is photochemically activated by nitric oxide, an unusual case of photoregulation of enzyme activity. The bonding of NO to the iron center has been probed by resonance Raman spectroscopy.[993] The spectroscopic (ESR; IR; electronic) and kinetic characteristics of this system have been monitored.[994] The N_3S_2-donor ligand (**195**) also forms a five-coordinate (trigonal bipyramidal) complex with iron(III) which can add a Lewis base such as methanol, pyridine, *n*-methyl imidazole, or an aryl thiolate (but not a nitrile) to give a low-spin octahedral species whose ESR spectrum closely resembles that of the nitrile hydratase which it models.[995] The NS_3-donor ligand $N(CH_2CH_2SH)_3$ again gives five-coordinate trigonal bipyramidal complexes $[Fe\{N(CH_2CH_2S)_3\}X]^-$ with X = Cl or N_3; these can react with CO to give paramagnetic $[Fe\{N(CH_2CH_2S)_3\}(CO)]$.[996] Another five-coordinate N_4S-donor complex, $[Fe(H_2NCH_2CH_2NHCH_2CH_2N{=}CMeCMe_2S)]^+$ (S apical; Fe—S and Fe—N distances normal for Fe^{II}), is a superoxide reductase model; its Fe^{III} analogue is octahedral, with MeCN from the solvent in which it is prepared completing the coordination shell ($Fe—N_{MeCN} = 1.95$ Å). Both the brown iron(II) and the deep blue iron(III) complexes are prepared by condensation of coordinated 3-methyl-3-thiobutanone with tris(aminoethyl)amine (tren).[997]



(**193**) (**194**) (**195**)

The Fe^{3+} complex of the linear hexadentate *N*,*N*,*S*,*S*,*N*,*N*-coordinating ligand derived from 1,8-diamino-3,6-dithiaoctane and pyrrole-2-aldehyde has been synthesized and characterized, especially by Mössbauer spectroscopy.[513] The hexadentate tripodal N_3S_3-donor triazamacrocyclic ligands (**196**) and (**197**) give brown–violet and green black Fe^{3+} complexes, respectively; the former is predominantly high-spin, the latter predominantly low-spin. In the complex of (**197**) the Fe—N bond distances are between 2.06 Å and 2.08 Å, Fe—S between 2.269(3) Å and 2.288(3) Å.[998]



(**196**) (**197**)

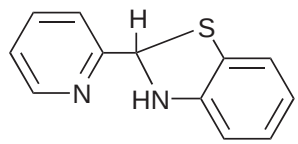
Reactions of carbonyl compounds such as pyridine 2-carboxaldehyde, glyoxal, biacetyl, or benzil with 2-aminothiophenol on an Fe^{2+} template give benzothiazolinate (**198**) complexes.[999] The complex from pyridine 2-carboxaldehyde, for example, was formulated, on the basis of ^1H NMR and Mössbauer spectroscopy and of analysis (C, H, N, and Fe) as the bis-(*N*,*S*)-ligand-bis-aqua complexes of (**199**), an isomeric form in equilibrium with (**198**). However as they are diamagnetic it seems more likely that they are [Fe(**199**)$_2$]·2H_2O, containing terdentate (*N*,*N*,*S*) (**199**), than the proposed [Fe(**199**)$_2$(H_2O)$_2$].

Reaction of iron(II) chloride with the carbothioamide derivative of bipy, bcta (**200**), gave three compounds, [Fe(bcta)$_2$]Cl_2·H_2O, [Fe(bcta)$_2$][$FeCl_4$], and [Fe(bcta)$_2$]$_2$[$Cl_3FeOFeCl_3$]Cl_2·3H_2O. This last compound contains low-spin Fe^{II} and high-spin Fe^{III}; its Mössbauer spectrum exhibits an unusual temperature dependence.[489]

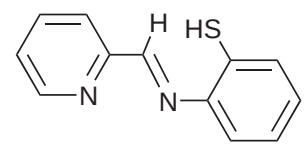
The dianion of 6,6′-bis(2,2′-diphenyl-2-sulfanylethyl)-2,2′-bipyridine (**201**) gives a chloro-iron(III) complex in which the metal is pentacoordinated (distorted square pyramid with the tetradentate ligand equatorial, chloride axial) and in the $S = 3/2$ state.[529]

5.4.4.3 Nitrogen, Oxygen, and Sulfur Donors

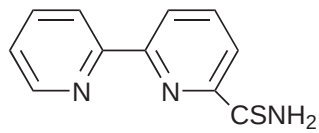
The preparation, characterization and Mössbauer spectroscopy of the Fe^{3+} complex of the linear hexadentate *O*,*N*,*S*,*S*,*N*,*O*-coordinating ligand derived from 1,8-diamino-3,6-dithiaoctane and



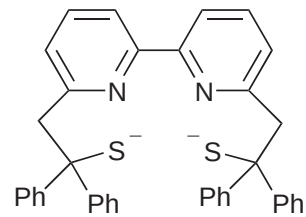
(**198**)



(**199**)

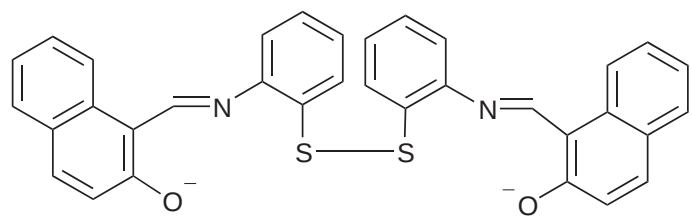


(**200**)



(**201**)

3-methoxysalicaldehyde have been reported.[513] The Schiff base (**202**) acts as a pentadentate (*O*,*N*,*S*,*N*,*O*) ligand to Fe^{3+}; octahedral geometry at the metal is attained by coordination of a chloride.[1000]



(**202**)

5.4.5 GROUP 16 DONORS

5.4.5.1 Simple *O*-donor Ligands

5.4.5.1.1 Introduction

This section covers water, hydroxide and oxide, with a little material on alkoxides and phenoxides, and on dioxygen species. Water is of paramount importance as a ligand—all the way from simple Fe^{2+}aq and Fe^{3+}aq through a range of ternary aqua-ligand complexes to its presence in, e.g., metalloproteins, as for example the single axial water ligand bonded to the metal in catalase isolated from *Micrococcus lysodeikticus*.[798] Water is important not only in the primary coordination sphere but also in the secondary coordination sphere, where it can have, usually through hydrogen-bonding to coordinated ligands, significant effects on structure and properties, not only for classic inorganic complexes (e.g., in determining structures of hydrated salts) but also in bioinorganic systems (as for example in peroxidase and catalase mechanisms[1001]).

Hydroxide and oxide[1002] are especially important as ligands for iron(III), both in simple mono- and polynuclear species in hydrolyzed iron(III) solutions and in more complicated environments, as in biomineralization[1003] and other natural processes.[1004] The extreme slowness of attainment of equilibrium in certain alkaline iron(III) systems needs to be borne in mind, for this may take days, sometimes even years, depending on the pH and the nature and concentrations of other species present.[1005,1006] Oxide and hydroxide are important as bridging ligands in bi- and polynuclear complexes, as also, to a lesser extent, are alkoxides and phenoxide. There are many bi- and polynuclear iron(III) complexes where bridging oxide, hydroxide, or alkoxide groups are supported by bridging carboxylates (see Section 5.4.5.4.3 below).[1007] Oxide as a ligand is important in

stabilizing high oxidation state ferrates (see Section 44.1.3) and as ligand in polyoxometallates (see Section 5.4.5.2).

5.4.5.1.2 The aqua-ions—general

The aqua cations Fe^{2+}aq and Fe^{3+}aq are included in several general reviews[1008–1011] of aqueous solutions, in a comprehensive book[1012] and review[1013] on aqua-cations, and in a review of ionic radii in aqueous solution.[1014]

A primary hydration number of 6 for Fe^{2+} in aqueous (or D_2O) solution has been indicated by neutron diffraction with isotopic substitution (NDIS),[1015] XRD,[1016,1017] and EXAFS,[1018] and for Fe^{3+} by NDIS[1019] and EXAFS.[1018] Fe—O bond distances in aqueous solution have been determined, since 1984, for $Fe(H_2O)_6^{2+}$ by EXAFS[1020] and neutron diffraction,[1015] for ternary Fe^{2+}-aqua-anion species by XRD (in sulfate and in chloride media,[1017] and in bromide media[1022]), for $Fe(H_2O)_6^{3+}$ by neutron diffraction,[1019] and for ternary Fe^{3+}-aqua-anion species. The NDIS studies hint at the second solvation shell in D_2O solution; high energy-resolution incoherent quasi-elastic neutron scattering (IQENS) can give some idea of the half-lives of water-protons in the secondary hydration shell of ions such as Fe^{3+}aq. This is believed to be less than 5×10^{-9}s, whereas $\tau \geq 5 \times 10^{-9}$s for the binding time of protons in the primary hydration shell.[1023,1024] X-Ray absorption spectroscopy (XAS—EXAFS[1025] and XANES) has been used to probe the structure and speciation of chloride-containing iron(II) and iron(III) solutions over a range of pHs, ionic strengths and Fe:Cl ratios.[1020] XAS has also been used to probe the environment, especially the short-range order, of Fe^{3+} during the precipitation of gels, in both chloride and nitrate media.[1026]

In the solid state $Fe(D_2O)_6^{2+}$ has been examined in Mohr's salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6D_2O$, by low temperature neutron diffraction. At 4.3 K there is a small but significant deviation of the FeO_6 core from octahedral symmetry.[1027] Polarized neutron diffraction, at 1.5 K, indicated a large magnetic anisotropy at the iron sites.[1028] A charge density study indicated that there was a drift of charge from the S to O in the sulfate anions, from sulfate to coordinated water, and thence to the Fe^{2+}. The orbital populations of the iron were calculated as $d_{xy}^{1.40}$-$d_{yz}^{1.43}d_{zx}^{1.30}d_{x^2-y^2}^{1.22}d_{z^2}^{0.98}$.[1029] Spin and charge density calculations are consistent with the experimentally established magnetic moment of 5.4 BM (at around room temperature) for $Fe(H_2O)_6^{2+}$.[1030]

Neutron diffraction examination of $CsFe^{III}(SO_4)_2 \cdot 12H_2O$ and $CsFe^{III}(SeO_4)_2 \cdot 12H_2O$ at 15 K showed a small but significant difference between Fe—O bond distances, 1.994(1) Å in the sulfate, 2.002(1) Å in the selenate. This difference is attributed to the different tilt angles of the coordinated water, 0.6° and 18.6°, respectively.[1031] A XRD structure determination on $CsFe^{III}(SO_4)_2 \cdot 12H_2O$ gave Fe—O = 1.989(4) Å (at room temperature). This selenate has the α-alum structure, whereas the corresponding sulfate has the β-alum structure.[1032] These results have been placed in the context of X-ray and neutron diffraction studies of structures of hydrated cations in aqueous solution.[1033]

From Fe—O distances in Fe^{2+}aq and Fe^{3+}aq ionic radii for the bare ions have been calculated (0.72 Å and 0.64 Å, respectively) and compared with established crystal radii.[1014] Theoretical calculations on the aqua-cations have estimated the effects of the *d*-electrons through optimization of geometry and energy minimization.[1034] SCF calculations for $[Fe(H_2O)_x]^{n+}$, for $x = 5$, 6, and 7, and $n = 2$ and 3, have been coupled with measured activation volumes, $\Delta V^{\ddagger}$, for water exchange to give insight into the mechanisms involved.[1035] Such considerations, complemented by consideration of measured $\Delta G^{\ddagger}$ and $\Delta H^{\ddagger}$, are claimed to indicate a *D* mechanism for Fe^{2+}aq, *A* or I_a for Fe^{3+}aq.[1036] *Ab initio* quantum chemical calculations on the exchange of water molecules between the primary hydration shell of Fe^{2+} and bulk solvent, using a model in which the secondary hydration shell and bulk water form a dielectric continuum, are also claimed to be consistent with dissociative activation.[1037] There is some measure of disagreement between these theoretical approaches and the usual interpretations of those who determine activation volumes, for the theoretical ruling out of I_d exchange in these systems is rather at variance with the view that the mechanism of water exchange at Fe^{2+}aq ($\Delta V^{\ddagger} = -4\,cm^3\ mol^{-1}$) is close to the I_a/I_d borderline, at $FeOH^{2+}$aq I_d. I_a water exchange at Fe^{3+}aq seems generally acceptable. Kinetic parameters (k, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, $\Delta V^{\ddagger}$) for water exchange at Fe^{3+}aq and at $FeOH^{2+}$aq have been compared with those for other metal(III) centers (Ga, Ti, Cr, Ru, Rh, Ir).[1038]

Activation volumes for the Fe^{2+}aq/Fe^{3+}aq and Fe^{2+}aq/$FeOH^{2+}$aq self-exchange reactions are $-11.1\,cm^3\ mol^{-1}$ and $+0.8\,cm^3\ mol^{-1}$, respectively.[1039] The Marcus cross-relation has been modified to allow for significant nonadiabaticity in the Fe^{2+}aq/Fe^{3+}aq couple,[1040] and theoretical calculations carried out on the H/D isotope effect on Fe^{2+}aq/Fe^{3+}aq self-exchange.[1041]

5.4.5.1.3 Aqua- and hydroxo-iron(II)

(i) Oxidation of Fe^{2+}aq

Oxidation of Fe^{2+}aq in solution by ozone, at pH 0–2, showed evidence for an oxygen atom transfer mechanism with $Fe^{IV}O^{2+}$ as a transient intermediate en route to Fe^{3+}. The rate constant at 298 K is $8 \times 10^5\,dm^3\,mol^{-1}\,s^{-1}$.[19] The activation energy for O—O bond breaking in the primary Fenton reaction intermediate, viz $[Fe^{II}(H_2O)_5(H_2O_2)]^{2+}$ has been estimated; subsequent intermediates include $[Fe^{IV}(H_2O)_4(OH)_2]^{2+}$ and $[Fe^{IV}(H_2O)_5O]^{2+}$.[1042] Reaction of Fe^{2+}aq with t-butyl hydroperoxide is a modified Fenton system.[1043] Reaction of Fe^{2+}aq with alkyl hydroperoxides and carbon monoxide produces acyl radicals $RC^{\bullet}O$; $MeC^{\bullet}O$ reduces Fe^{3+}aq much more quickly than does $^{\bullet}Me$.[1044] Oxidation of Fe^{2+}aq by $Br_2^{\bullet-}$ has $k = 4 \times 10^6\,dm^3\,mol^{-1}\,s^{-1}$ at 293 K and $\Delta V^{\ddagger} = +2.6\,cm^3\,mol^{-1}$ (and is therefore I_a in character). Similar reactions of aqua-polyaminocarboxylate and aqua-phosphate species have activation volumes ranging down to $-4.2\,cm^3\,mol^{-1}$, suggesting a modest range of interchange mechanisms from slightly dissociative to slightly associative. The correlation observed between k and $\Delta V^{\ddagger}$ for these reactions shows that varying the nature of the ligand effects on reactivity and mechanism are coupled.[959] Added salt effects, up to 4.0 mol dm^{-3} KCl, 6.0 mol dm^{-3} $NaClO_4$, have been examined for Fe^{2+}aq reduction of tris-oxalatocobaltate(III).[583]

(ii) Solution properties

In contrast to Fe^{3+}aq, there is very little hydrolysis or polymerization of Fe^{2+}aq in aqueous media, though there has been a claim for the existence of $[Fe^{II}(OH)_4]^{2-}$ in strong NaOH solution.[18] The partial molal volume of Fe^{2+}aq has been derived over the temperature range 288.2–318.2 K. The value at 298.2 K, $-22.7\,cm^3\,mol^{-1}$, differs slightly from values published earlier.[1045] Gibbs energies of transfer, $\Delta G_{tr}(Fe^{2+})$, have been calculated for transfer to methanol–water[1046–1048] and to acetonitrile–water mixtures.[1049] The methanol–water values provoked disagreement, entailing as they must rather indirect methods of estimation; the acetonitrile–water values are in the context of ΔG_{tr} values for numerous other M^{n+} ions. Enthalpies of transfer, $\Delta H_{tr}(Fe^{2+})$, to ethanol–water mixtures, again in the context of other $\Delta H_{tr}(M^{n+})$, should be regarded with caution (see Table 8 footnote *b*; $\Delta H_{tr}(Fe^{2+})$ could also be estimated from, e.g., $\Delta H_{tr}(Ni^{2+})$ or $\Delta H_{tr}(Cu^{2+})$ in binary aqueous solvent mixtures for several other cosolvents).[1050]

(iii) Complex formation

The marked dependence of k_f on the charge of the incoming group, but small dependence on its nature (for a given charge) supports a dissociative interchange (I_d) mechanism.[1051] The activation volume of $+6.1\,cm^3\,mol^{-1}$ for formation of $FeNO^{2+}$aq also indicates an I_d mechanism, though the very small negative value for the activation entropy ($\Delta S^{\ddagger}_f = -3\,J\,K^{-1}\,mol^{-1}$) suggests that the interchange must be, as expected, very close to the dissociative/associative boundary.[871,872]

The stability constant ($\log \beta_2 = 5.4$) for complex formation between Fe^{2+}aq and $[Cr(en)_2(OH)]_2^{+}$ indicates effective hydroxide bridging between the Fe^{II} and Cr^{III} centers.[1052] $[Cr(tren)(OH)(H_2O)]^{2+}$ may be used as a substitution-inert model for labile Fe^{2+}aq, as in a study of iron uptake by ferritin.[1053]

5.4.5.1.4 Aqua- and hydroxoaqua-iron(III)

(i) General

A review of iron(III) in aqueous solution covers hydrolysis and polymerization, the formation and dissociation of binuclear species, and kinetics and mechanisms of water exchange and complex formation.[1054] Kinetic and equilibrium data for hydrolytic reactions of iron(III) have been conveniently assembled.[1055] Reviews of hydrolysis of Fe^{3+}aq, and subsequent precipitation of hydrated oxide-hydroxide species,[1056–1058] cover a very wide range of media, from geochemistry to biology to human metabolism.[169,170,1059] Added anions or pH variation can affect which form

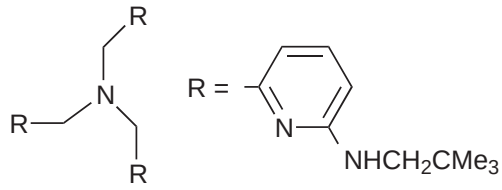
of iron(III)—Fe_2O_3, α-, β-, or γ-FeO(OH), or polynuclear anion-containing species—precipitates.[1060] This has been investigated for chloride, nitrate, and sulfate,[1061–1063] complementing earlier studies on anion effects on products and time-scales for their precipitation.[1005,1064]

The pK_a of Fe^{3+}aq is affected by the presence of anions due to their interactions with the aquacation; formation quotients have been estimated.[1065] Fe^{3+}aq is hydrolyzed to a much smaller extent in 80% (w/w) DMSO + water than in water.[928] Molecular dynamics simulation of iron(III) and its hydrolysis products successfully matched the known pK_1 value, but was unsuccessful in reproducing pK_2.[1066]

The reaction volume (ΔV°) for $Fe^{3+}aq \rightarrow FeOH^{2+}aq + H^+aq$ is $+4.8\,cm^3mol^{-1}$ (extrapolated to zero ionic strength; ΔV° decreases significantly with increasing ionic strength, to reach a value of $+1.6\,cm^3mol^{-1}$ at $I = 2.0\,mol\,dm^{-3}$.[1067] Laser flash photolysis kinetics indicate the formation of hydroxyl radicals in the primary photoprocess of $FeOH^{2+}$aq photolysis.[1068]

Layered double hydroxides are materials of current interest; iron-containing versions include Fe^{3+}/Ni^{2+} and Fe^{3+}/Mg^{2+} with carbonate as intercalated counterion and Fe^{3+}/Ni^{2+} with sulfate.[1069] It is also possible to intercalate $[Fe(CN)_6]^{4-}$ (see Section 5.4.2.1.1), though apparently tris-oxalatoferrate(III) is reluctant to intercalate, at least into Al^{3+}/Mg^{2+} layered double hydroxide.[1070]

Hydroxide is rarely found coordinated to Fe^{3+} in a mononuclear octahedral complex, but has been demonstrated in the purple salt $[Fe(tnpa)(OH)(OOCPh)]ClO_4$, where tnpa is the tetradentate tripodal ligand tris(6-neopentylamino-2-pyridylmethyl)amine, (**203**); the hydroxide is *cis* to the benzoate ligand.[465]



(**203**)

(ii) Complex formation

Kinetics and mechanisms of complex formation have been reviewed,[1054] with particular attention to the inherent $Fe^{3+}aq + L^-$ vs. $FeOH^{2+}aq + HL$ proton ambiguity.[1071] Table 11 contains a selection of rate constants and activation volumes for complex formation reactions from Fe^{3+}aq and from $FeOH^{2+}$aq, illustrating the mechanistic difference between I_a for the former and I_d for the latter. Further kinetic details and discussion may be obtained from earlier publications[265,1072] and from those on reaction with azide,[1073] with cysteine,[1074] with octane- and nonane-2,4-diones,[1075] with 2-acetylcyclopentanone,[1076] with fulvic acid,[265–267] and with acethydroxamate and with desferrioxamine. For the last two systems the various component forward and reverse reactions were studied, with values given for k and K;[1077] $\Delta H^\ddagger$ and $\Delta S^\ddagger$; ΔH° and ΔS°;[1078] $\Delta V^\ddagger$ and ΔV°.[1079] Activation volumes are reported and consequences of the proton ambiguity discussed in relation to the reaction with azide. For the reactions of $FeOH^{2+}$aq with the salicylate[1080] and oxalate[1081] complexes *cis*-$[Co(en)_2(NH_3)(sal)]^{2+}$, $[Co(tetraen)(sal)]^{2+}$(tetraen = tetraethylenepentamine), and $[Co(NH_3)_5(C_2O_4H)]^{2+}$ both formation and dissociation are retarded in anionic micelles.

The reaction volume, ΔV°, for formation of the monoacethydroxamate (ahdx) complex from Fe^{3+}aq is $+9.3\,cm^3mol^{-1}$ (for $Fe^{3+}aq + ahdxH \rightarrow [Fe(ahdx)(H_2O)_4]^{2+} + H^+$); ΔV° values for formation of $Fe(NCS)^{2+}$aq and of $Fe(OH)(NCS)^+$aq from Fe^{3+}aq[1082] and from $FeOH^{2+}$aq[1083] are $+10.0\,cm^3mol^{-1}$ and $+17.1\,cm^3mol^{-1}$, respectively.

The kinetics of reaction of Fe^{3+}aq, of $FeOH^{2+}$aq, and of $Fe_2(OH)_2^{4+}$aq with variously protonated forms of phosphate, phosphite, hypophosphite, sulfate, and selenite have been investigated, mainly at 283 K. The formation mechanism from the dimer is somewhat complicated, e.g., by formation of mononuclear complexes, probably via μ-hydroxo-μ-oxoanion di-iron intermediates, after the initial I_d complexation step.[1055]

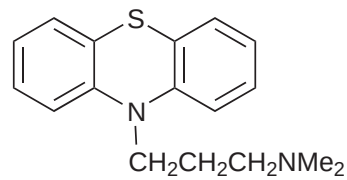
Table 11 Rate constants and activation volumes for complex formation from the hexa-aqua- and hydroxo-aqua forms of iron(III), in aqueous solution at 298.2 K.

	k_f ($dm^3\,mol^{-1}\,s^{-1}$)		$\Delta V^{\ddagger}$ ($cm^3\,mol^{-1}$)	
Ligand	$Fe^{3+}aq$	$Fe(OH)^{2+}aq$	$Fe^{3+}aq$	$Fe(OH)^{2+}aq$
Desferrioxamine ($dfoH_4^+$)	3.8	3,000	−5	+ 4
Acethydroxamic acid	4.8	5,700	−6	+ 5
Cysteine		11,400		
HN_3	4,000	6,800		
Cl^-	4.8	5,500	−5	+ 8
NCS^-	122	23,200	−6	+ 9
$Cl_3CCO_2^-$	63	7,800		
$Cl_2HCCO_2^-$	118	1,900		
$ClH_2CCO_2^-$	1,500	4,100		
SO_4^{2-}	2,300	11,000		
$FeOH^{2+}$	6.8	670		
$Fe(dfoH_2)^{2+}$	1.3	1,600		
$[Co(NH_3)_5(salH)]^{2+}$	5.6	770		
$[Co(en)_2(NH_3)(salH)]^{2+}$	5.1	766		
$[Co(NH_3)_5(C_2O_4H)]^{2+}$		4,600		

References to the rate constants and activation volumes in this table are cited in the text.

(iii) Oxidation by $Fe^{3+}aq$

Fe^{3+}aq reacts with chloranilic acid to give iron(II) chloranilate.[1084] Fe^{3+}aq reacts with promazine, (**204**), to give the promazine radical cation complex of Fe^{2+}. The volume profile for this combined substitution and electron transfer reaction has been established.[1085] The activation volumes for the forward and reverse reactions are $-6.2\,cm^3\,mol^{-1}$ and $-12.5\,cm^3\,mol^{-1}$; the respective activation entropies[1086] are $-67\,J\,K^{-1}\,mol^{-1}$ and $-125\,J\,K^{-1}\,mol^{-1}$. Both pairs of values indicate a major contribution from electrostriction effects, especially in the back reaction. Kinetic studies of Fe^{3+}aq oxidations have included those of ascorbic acid,[1087] of hydroxylamine,[1088] and of $[Co(sep)]^{2+}$.[1089] Kinetic parameters (k, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) have been determined for Fe^{3+} oxidation of [VO(salen)], [VO(salenOR)] with R = H, $O(CH_2)_nMe$ with $n = 2$, 5, 9, or 11, and binuclear complexes in which two [VO(salen)] units are bridged by —$O(CH_2)_nO$— where $n = 3$, 6, 10, or 12. The mononuclear complexes react by outer-sphere electron transfer; oxidation of the binuclear complexes proceeds through an intermediate adduct with the Fe^{3+}.[1090] For anaerobic Fe^{3+}aq oxidation of cysteine the kinetics of formation of a transient blue species, presumed to be Fe^{III}(cyst), and of onward reaction to Fe^{II} and cystine, have been established.[1074,1091] Fe^{3+}aq catalyzes S—O bond cleavage in phenyl phosphatosulfate, $[C_6H_5OPO_2—O—SO_3]^{2-}$, in contrast to M^{2+}aq cations, which catalyze P—O bond cleavage.[1091] Fe^{3+}aq also catalyzes autooxidation of sulfur(IV).[1093] The effects of various alkyl substituents on Fe^{3+}aq oxidation of a range of ferrocenes in cationic and nonionic micellar systems suggest that the ferrocenes are located within the micelles.[1094]



(**204**)

(iv) μ-Oxo- and μ-hydroxo-aquairon(III) species

In relation to the long-standing argument over $[Fe^{III}(\mu\text{-}O)Fe^{III}]^{4+}$ vs. $[Fe^{III}(\mu\text{-}OH)_2Fe^{III}]^{4+}$ in hydrolyzed iron(III) solutions, EXAFS provided evidence in favor of $[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(OH_2)_4]$[1095] but Mössbauer spectroscopy suggested the μ-oxo-dimer form.[1096] Fe^{3+}

on a Nafion membrane seems to be predominantly $[Fe^{III}(\mu\text{-}O)Fe^{III}]^{4+}$, but there is evidence for significant amounts of $[Fe^{III}(\mu\text{-}O_2H_3)Fe^{III}]^{5+}$.[1097] IQENS has proved of value for examining polynuclear hydroxospecies of Al^{III} and Zr^{IV}, so could perhaps usefully be applied to Fe^{III}.[1098]

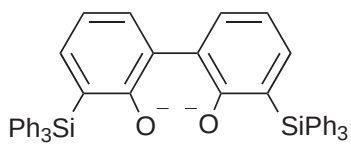
The half-life of $Fe_2(OH)_2^{4+}$ at room temperature is a few seconds. An improved model for the kinetics of dissociation of this dinuclear cation recognizes significant participation by $Fe_2(OH)_3^{3+}$ at higher pHs, thus clearing up earlier slight anomalies in this area.[1099] Phosphate ester hydrolysis at the di-iron center of uteroferrin has now been shown to involve nucleophilic attack by bridging hydroxide (as proposed but not conclusively demonstrated for several M—OH—M-containing catalytic species) rather than by hydroxide bonded to just one Fe.[1100]

Tetranuclear species are believed to play a key role in the growth of species of higher nuclearity, both for iron(III)[1101] and for mixed iron(II)/iron(III) systems.[1102] Assessment of the physical and chemical properties of aqueous solutions of Fe^{3+}, Al^{3+}, and Ga^{3+} suggested that the tridecamer $[FeO_4\{Fe(OH)_2(H_2O)\}_{12}]^{7+}$— cf. the now well-established Al_{13} species of this formula — may be a component under certain conditions.[1103]

5.4.5.1.5 *Alkoxides; phenoxide*

The sterically encumbered alkoxide ligand $PhMe_2CO^-$ forms a binuclear complex $[Fe_2(OCMe_2Ph)_6]$ containing two tetrahedral Fe^{3+} linked by two alkoxide bridges.[1104] A pair of ethoxides bridge the Fe^{3+} ions in the 2-propanenitronate, pn, complex $[(pn)_2Fe(\mu\text{-}OEt)_2Fe(pn)_2]$.[1105]

The sterically hindered dianionic bidentate phenoxide ligand (**205**) gives several tetrahedral iron(II) complexes, e.g., $[Fe^{II}(\mathbf{205})(THF)_2]$, $[Fe^{II}(\mathbf{205})(py)_2]$, $[Fe^{II}(\mathbf{205})(bipy)]$, and $[Fe^{II}(\mathbf{205})(2,6\text{-xylylNC})_2]$. The first of these is prepared from $FeCl_2$ and $(\mathbf{205})H_2$ in tetrahydrofuran; the others are prepared from the dimer $[Fe_2(\mathbf{205})_2]$. The 2,6-xylylNC complex is low-spin, the others high-spin. There is also a five-coordinate iron(III) complex, red-black $[Fe(\mathbf{205})(bipy)Cl]$, whose structure is intermediate between trigonal bipyramidal and square pyramidal.[437]



(**205**)

5.4.5.1.6 *Dioxygen, peroxide, and superoxide*

Interaction of dioxygen species with Fe^{2+}aq and with Fe^{3+}aq has been very briefly reviewed.[1106] In relation to oxo-, peroxo-, and superoxo-complexes as models for intermediates in oxygenase activity, a brief report on a 2000 symposium on activation of oxygen summarizes the then-current situation in the search for a mechanism common to mono- and dinuclear iron sites, mono- and dinuclear copper sites, and copper–iron sites.[1107] The outline proposals comprise:

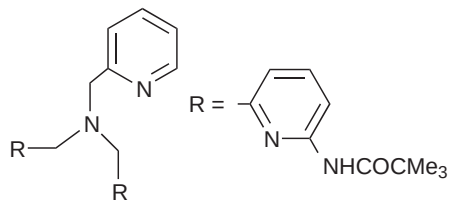
$$M^{n+} \text{ via } M^{(n+1)+} - OOH \text{ then } M^{(n+3)+}{=}O \tag{3}$$

$$M^{n+} \cdots M^{n+} \text{via } M^{(n+1)+} - O_2 - M^{(n+1)+} \text{ then } M^{(n+2)+} \begin{array}{c} O \\ \diagup\diagdown \\ O \end{array} M^{(n+2)+} \tag{3}$$

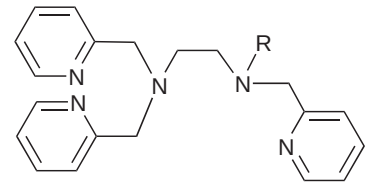
The preparation of a novel mononuclear iron(III)–*t*-butylperoxo-complex, end-on coordinated, with bis(6-pivalamido-2-pyridylmethyl)(2-pyridylmethyl)amine, bppa = (**206**), to Fe^{III},[466] was followed by the isolation of a similar complex containing hydroperoxide. The latter reacts by O—O bond cleavage and a $[(bppaH_2)Fe^{III}—O^{\cdot}]$ intermediate.[467]

In contrast to the numerous I_d mechanisms mentioned elsewhere in this chapter for substitution at hydroxoiron(III) species, substitution by H_2O_2 at $[Fe(Rtpen)(OMe)]^{2+}$ (Rtpen = (**207**); R = alkyl, phenyl, or benzyl), to form the relatively stable $[Fe(Rtpen)(\eta^1\text{-}OOH)]^{2+}$, is, like complex formation from $Fe^{3+}aq$, I_a in character. $[Fe(Rtpen)(\eta^1\text{-}OOH)]^{2+}$ complexes can also be generated from iron(II) in solution.[125] The purple iron(III) hydroperoxo complexes are converted into blue iron(III)-η^2-peroxo species on addition of base.[1109]

The electronic spectrum of Fe—O_2 in a hemerythrin derivative has been reported.[1110] Further references to reactions of iron porphyrins with dioxygen species appear in Section 5.4.3.7.2.



(**206**)



(**207**)

5.4.5.2 Inorganic Oxoanions

There are two closely related aspects here, concerning species where an oxoanion such as sulfate or chromate forms a recognizably classical coordination complex and polyoxometallates where one, two, or many iron centers are incorporated in a multi-oxide-bridged polynuclear complex.

5.4.5.2.1 Oxoanion complexes of Fe^{2+} and Fe^{3+}

$(pyH)[Fe(HPO_4)_2(H_2O)_2]$ and $(imH_2)[Fe(HPO_4)_2(H_2O)_2]$ have layered structures with alternating FeO_6 octahedra and PO_4 tetrahedra.[1111] $AlP_2O_8^{3-}$ chains can be assembled into 3D structures through the use of transition metal cations such as Fe^{2+}, which bind parallel chains into layers by complexing with phosphate groups.[1112] The Fe—O bond distance to coordinated nitrate in $[Fe^{III}(oep)(NO_3)]$ is 2.016(3) Å.[767]

Equilibrium constants for formation of iron(III) complexes of several oxoanions, of phosphorus, arsenic, sulfur, and selenium, have been reported.[1055] The kinetics and mechanism of complex formation in the iron(III)-phosphate system in the presence of a large excess of iron(III) involve the formation of a tetranuclear complex, proposed to be $[Fe_4(PO_4)(OH)_2(H_2O)_{16}]^{7+}$.[1113] The high stability of iron(III)-phosphate complexes has prompted suggestions that iron-containing mixed hydroxide or hydroxy-carbonate formulations be tested for treatment of hyperphosphatemia.[1114]

The weakly ferromagnetic ($T_N = 25$ K) $Fe(MePO_3)\cdot H_2O$ has a structure consisting of alternate organic and inorganic layers. The former consists of the methyl groups of the anion, the latter of six-coordinated Fe^{2+} cations, with their attendant five phosphonate-oxygens and one water.[1115] $[Fe_2\{O_3P(CH_2)_3PO_3\}_2]\cdot 2H_2O$, believed to have a pillared structure, is also weakly ferromagnetic.[1116]

Information on the formation and decomposition of iron(III)–sulfur(IV) complexes, in the presence and absence of dioxygen, is vital to the understanding of iron-catalyzed autooxidation of sulfur(IV).[1093,1117] The kinetics and mechanism of formation of mono-, bis-, and tris-sulfito-iron(III) from $Fe^{3+}aq/FeOH^{2+}aq$, have been established, together with estimates of their stability constants[1118] and with kinetic data on their two-stage redox decomposition.[1119,1120] Stability constants for the Fe^{3+}/sulfate system in water have been measured, with a speciation diagram presented.[1121] Extraction of iron(III) from aqueous sulfate-containing solutions by Primene 81R (a mixture of primary aliphatic amines $R^1R^2R^3CNH_2$; 12 to 14 carbon atoms) may involve transfer of a binuclear sulfato-complex $[Fe(OH)(SO_4)]_2$.[1122]

Coordinated perchlorate occurs in the binuclear complexes $[(H_2O)(tpa)Fe(\mu\text{-}O)Fe(tpa)(ClO_4)](ClO_4)_3$ (tpa = tris(2-pyridylmethyl)amine)[1123] and $[(ClO_4)(quaterpy)Fe—O—Fe(quaterpy)(ClO_4)]\cdot 8.5H_2O$.[632] It is bidentate in the latter, bonded to seven-coordinate Fe^{2+}.

Iron(III)-pyrophosphate looks promising as an alternative to iron(III)-carbohydrate preparations for parenteral administration for treatment of anemia.[1124] Kinetics of removal of iron from transferrin (tf) by pyrophosphate (pp) were found to be biphasic under certain conditions, with the rapid first phase attributed to the formation of a pp—Fe—tf—CO_3^{2-} intermediate.[1125] A later study of the kinetics of removal of iron from transferrin employed pyrophosphate and tripodal phosphonates such as nitrilotris(methylenephosphonic acid), $N(CH_2PO_3H_2)_3$. For the tripodal ligands there are parallel first-order and saturation pathways, with the latter dominant (contrast the exclusively first-order reaction of ferritin with nitrilotriacetate); for pyrophosphate the paths are roughly equal in importance. The saturation kinetics suggest that tf-Fe-phosphonate intermediates play an important role in the kinetics.[1126]

Fe^{2+} complexes of trimetaphosphate and of atp react with $Br_2^{\bullet-}$ with rate constants of $3 \times 10^6\,dm^3\,mol^{-1}\,s^{-1}$ and $\sim 5 \times 10^6\,dm^3\,mol^{-1}\,s^{-1}$ at 293 K; activation volumes are $+0.3\,cm^3\,mol^{-1}$ and $+0.7\,cm^3\,mol^{-1}$, respectively.[959]

Novel species developed for molecular switching have magnetic Fe_3O_4 particles linked to the control moiety by derivatized silicate linkages. Two of the control units themselves contain iron, in a ferrocene derivative and in a heme derivative.[1127]

5.4.5.2.2 Polyoxometallates

A review of polyoxometallates, covering magnetism, new materials, and high nuclearity mixed valence clusters, contains a few brief mentions of iron.[1128] "Keplerates," very large polyoxometallates, link molecular characteristics to bulk properties, for example the water-soluble $Fe_{30}Mo_{72}$ cluster containing 30 high-spin iron(III) centers is transitional between a molecular and a bulk magnet.[1111] Smaller clusters, such as Fe^{III}_8, Fe^{III}_{10} (so-called "ferric wheels," see Section 5.4.5.4.3), Fe^{III}_{17}, Fe^{III}_{19} species, with their variety of magnetic behaviors, form the transition towards mononuclear species.[1130]

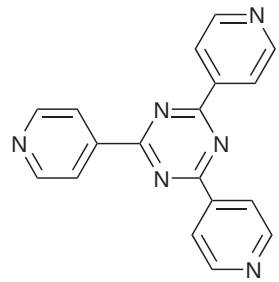
A few iron atoms may be incorporated into large polyoxoanions, generally those with high tungsten content and often with a few group 15 atoms, e.g., P, occasionally As, Sb, or Bi, or group 16 (Se, Te). The isomers (α_1 and α_2) of $[P_2W_{17}O_{61}]^{10-}$, so-called lacunary anions, can act as ligands for a wide variety of metal centers, ranging from Ca^{2+} to Mo^{VI} and including Fe^{3+}.[1131] The spectroelectrochemistry of these Fe^{3+} complexes has been compared with that of Fe^{3+} complexes of related molybdenum-containing polyoxoanions such as α_2-$[P_2W_{15}Mo_2O_{61}]^{7-}$.[1132] These species often contain water coordinated to Fe^{3+}, with one H_2O per iron in the complex anions just mentioned. This coordinated water may under certain conditions be deprotonated to give species such as $[Fe(OH)P_2W_{17}O_{61}]^{8-}$.[1133] Cyclic voltammetry was carried out on all these species.

The tetranuclear $[Fe^{III}_4(H_2O)_2(PW_9O_{34})_2]^{6-}$ anion contains planar Fe_4 units, with each Fe octahedral—half the Fe^{3+} ions have one coordinated water. This anion can be partially reduced to a mixed valence Fe^{II}/Fe^{III} form; there is no evidence for $Fe^{II} \rightarrow W^{VI}$ IVCT in the electronic spectrum of the reduced form.[1134] The sodium salt of $[Fe^{III}_4(H_2O)_2(P_2W_{15}O_{56})_2]^{12-}$ crystallizes from $2\,mol\,dm^{-3}$ NaCl at pH ~3 in a form containing discrete, well separated, anions, but crystallization from $1\,mol\,dm^{-3}$ NaCl at pH ~1 gives a form in which hydrated Na^+ ions associate strongly with the anions to give a 1D polymeric structure.[1135] These two anions are reported to be effective catalysts for oxidation of hydrocarbons by hydrogen peroxide.

Similar antimony- and bismuth-containing polyoxoanions often have three waters coordinated to each incorporated Fe^{3+}. Thus in the $[Fe^{III}_2(H_2O)_6(Sb_2W_{20}O_{70}]^{8-}$ anion[1136] and in its bismuth analogue[1137] the $(M_2W_{20}O_{70})^{14-}$ units may be considered as *fac*-tridentate ligands completing the octahedral coordination shell of the *fac*-$[Fe(H_2O)_3]$. $[Fe^{III}_4(H_2O)_{10}(\beta\text{-}MW_9O_{33})_2]^{n-}$, M = As or Sb with $n = 6$ or M = Se or Te with $n = 4$, consist of a pair of (β-MW_9O_{33}) units joined by a central pair and a peripheral pair of Fe^{3+} ions. All the Fe^{3+} ions are octahedral, the peripheral pair each with three water ligands, the central pair each with two. Reduction of the iron centers, monitored by cyclic voltammetry and controlled potential coulometry, occurred in four discrete steps.[1138]

$[Fe(\mathbf{208})_2]Mo_4O_{13}$ contains a 2D bimetallic oxide network, consisting of chains of tetrahedra and octahedra. These inorganic layers are linked by the bidentate tris-pyridyltriazine ligands (**208**), though due to geometrical constraints each linking unit is limited to three metal atoms, viz Mo—tpytrz—Fe—tpytrz—Mo. Each Fe is octahedral, with an O_4N_2-donor set.[476]

The environment and oxidation state of iron in borosilicate glasses has been probed by IR, Raman, and Mössbauer spectroscopies,[1139] in lead vanadate ($Pb_2V_2O_7$) glasses by XRD and IR and Raman spectroscopies.[1140]



(**208**)

5.4.5.3 Organic Oxoanions

Thermal decomposition of mixtures of iron(II) and iron(III) oxalates, giving γ-Fe_2O_3, has been studied by XRD, Mössbauer and FTIR spectroscopy.[1141] A standard addition kinetic method for the simultaneous determination of Fe^{II} and Fe^{III} is based on the vastly different rates of complex formation of Fe^{II} and Fe^{III} with gallic acid;[144] this study is complemented by kinetics of formation of gallate (3,4,5-trihydroxybenzoate) complex.[1142]

5.4.5.3.1 Iron(II)

Iron(II) trifluoroacetate can be prepared by photolysis of $Fe(CO)_5$ in $CF_3CO_2H/(CF_3CO_2)_2O$. It presumably contains bridging trifluoroacetate ligands like its manganese analogue.[1143] Fe—O distances in *catena*-[Fe(μ-oxalate)(bipy)]$_n$ are 2.092(3)–2.162(4) Å,[500] very similar to those in [Fe(bipy)$_3$][Fe$_2$(oxalate)$_3$], where Fe—O = 2.122(2) Å, 2.128(2) Å.[494]

5.4.5.3.2 Iron(III)

Iron(III) citrate,[1144] or iron(III) ammonium citrate, is the usual vehicle for administering supplementary iron to an iron-deficient patient, for inducing iron-overload in rats or other creatures prior to testing the efficacy of iron chelators, or for introducing the isotope ^{59}Fe for metabolic tracer studies. Stability constants for the aqueous iron(III)–citrate system have been established.[1145] The 2:1 complex is claimed to be the dominant species in iron(III)/citrate/DMF systems.[1146] There has been a very qualitative study of the incorporation of iron into transferrin from iron citrate.[1147] Iron(III) citrate reacts relatively slowly with the aluminum(III)–transferrin complex to give the thermodynamically strongly favored combination of iron(III)–transferrin with aluminum(III) citrate.[1148] The mechanism of iron uptake from citrate complexes in cells has been briefly discussed.[167] An octa-iron citrate complex appears in Section 5.4.5.4.3 below.

Iron–gluconate complexes are sufficiently stable not to cause iron toxicity (in contrast to Fe^{2+}aq, Fe^{3+}aq, and complexes of low stability) and are safe and effective in hemodialysis.[1149] There is information on iron transfer between gluconate and transferrin.[1150] Dithionite releases Fe^{3+} from gluconate.[1151]

Alkali metal salts of tris-maleato-ferrate(III) are high spin; the isomer shifts of their Mössbauer spectra reflect the electronegativity and polarizing power of the cations.[1152]

XRD and EXAFS studies of [Fe^{III}($O_2CCH_2COCH_2CO_2$)(H_2O)$_2$X], X = Cl, Br, show the oxodiacetate to be terdentate and planar, giving a *mer* complex. with the central ether-O *trans* to X^-.[1153]

The quantum yield for formation of iron(II) in the photoreaction of tris-oxalato-ferrate(III) in ethane-1,2-diol–water mixtures increases as the viscosity of the medium decreases. This result is ascribed to the ease of movement of an oxalate anion radical away from the iron.[1154] A study of the synthesis and magnetic properties of the hydrate of the μ-squarate di-iron(III) complex (**209**) and its μ-oxalato and μ-hydranilate (2,5-dihydroxy-1,4-benzoquinonate) analogues has revealed that bridging oxalate is particularly effective in transmitting antiferromagnetic coupling between Fe^{3+} ions as much as 5 Å apart. The intramolecular Fe—Fe distance in (**209**) is 7.8 Å, but the nearest intermolecular Fe $\cdots$ Fe distances are 6.6 Å.[1155] The bis(ethylenedithio)tetrathiafulvalene (bedt-ttf, (**51**)) compound [bedt-ttf][Fe(C_2O_4)$_3$(H_2O)]·PhCN was the first molecular superconductor containing a paramagnetic metal ion. It contains alternate layers of bedt-ttf cations and of

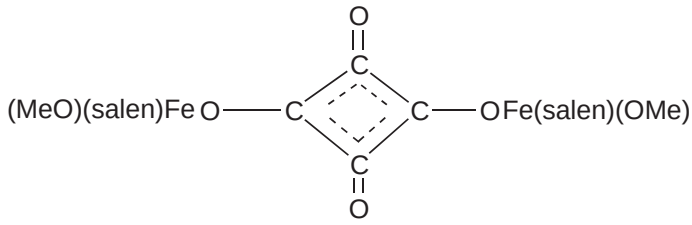
$[Fe(C_2O_4)_3]^{3-}$ anions with associated water and PhCN.[1156] The tetrathiafulvalene derivatives $(ttf)_7[Fe(C_2O_4)_3]_2 \cdot 4H_2O$ and $(ttf)_5[Fe(C_2O_4)_3] \cdot 2C_6H_5Me \cdot 2H_2O$ are semiconductors with stacked structures.[1157]

Humic acid binds Fe^{3+} predominantly or exclusively through carboxylate groups, though there may be a very small amount of ligation by phenolate. Some qualitative observations on stabilities and complex formation and dissociation reactivities are available for humic acid[1158] and for fulvic acid.[265–267]

Tris-(3,5-di-isopropylsalicylato)iron(III) is a serviceable scavenger for *t*-butylperoxyl radicals, though it is not as effective as bis-(3,5-di-isopropylsalicylato)manganese(II).[1159] An electrochemical study of salicylate and of 2,3- and 3,4-dihydroxybenzoates focused on DMF as solvent.[1160]

By use of appropriate sterically demanding carboxylates it is possible to generate four-, five-, and six-coordinated mononuclear iron(III) complexes. Ligand flexibility and electronic properties provide fine-tuning. These complexes are subunits of the models for di-iron(II) sites in metalloproteins mentioned in the following section.[1161]

Most bi- and polynuclear complexes of organic oxoanions contain bridging oxide or hydroxide in addition to bridging carboxylate, and are dealt with at appropriate points in the following section.



(**209**)

5.4.5.4 Binuclear and Polynuclear Complexes

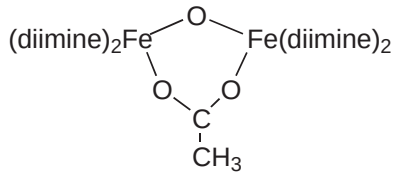
5.4.5.4.1 Di-iron complexes

(i) μ-*Oxide*

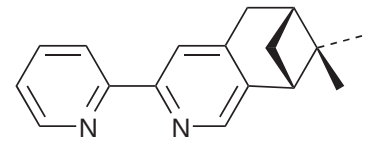
It has long been known that whereas oxidation of $[Fe(phen)_3]^{2+}$ in solution gives blue $[Fe(phen)_3]^{3+}$, reaction of an iron(III) solution with 1,10-phenanthroline gives a brown solution. In 1936 this was, on the basis of analysis and of conductimetric and magnetic measurements, proposed[1162] to be a dihydroxy-bridged species $[(phen)_2Fe(\mu\text{-}OH)_2Fe(phen)_2]^{4+}$. Many years elapsed before XRD studies indicated that this and related cations contained bridging oxide rather than hydroxide, as in $[(phen)_2ClFe(\mu\text{-}O)FeCl(phen)_2]Cl \cdot nH_2O$,[1163] $[(H_2O)(phen)_2Fe(\mu\text{-}O)Fe(phen)_2(H_2O)](NO_3)_4 \cdot 5H_2O$,[1164] and $[(H_2O)_3(phen)Fe(\mu\text{-}O)Fe(phen)(H_2O)_3](NO_3)_4 \cdot H_2O$.[1165]

The di-iron(III) complex $[Fe_2(\mu\text{-}O)(bpia)_2Cl_2]Cl_2 \cdot 7MeOH$, where bpia is (1-methylimidazol-2-ylmethyl)bis(2-pyridylmethyl)amine, has a linear Fe—O—Fe bridge.[1166] Simple μ-oxo-di-iron complexes,[1167] of which the bis-iron(III) complexes $[Fe_2(\mu\text{-}O)(diimine)_4(H_2O)_2]^{4+}$ provide examples, can act as models for the structure and catalytic activity of di-iron sites in proteins (e.g., in methane monooxygenase) and also as catalysts for oxygen transfer to hydrocarbons or sulfur. $[Fe_2(\mu\text{-}O)(phen)_4(H_2O)_2]^{4+}$ was obtained as a result of an electrochemical study of $[Fe(phen)_3]^{2+/3+}$ in aqueous solution.[1168] Subsequently the other members of the group $[Fe_2(\mu\text{-}O)(diimine)_4L_2]^{n+}$, where diimine = phen, bipy, or 4,4′-Me_2bipy and L = H_2O, Cl^-, or $CF_3CO_2^-$, and the slightly different acetate complex $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CMe)(diimine)_4L_2]^{n+}$ (**210**), were synthesized, characterized, and assessed as alkane oxidation catalysts.[1169] The use of the hindered ligand (−)-4,5-pinene-2,2′-bipyridine (**211**) in place of bipy in $[Fe_2(\mu\text{-}O)(bipy)_4(H_2O)_2]^{4+}$ gives a much improved catalyst for stereoselective oxidation of organic sulfides by H_2O_2.[1170] The electrochemistry of $[Fe_2(\mu\text{-}O)(bipy)_4(solv)_2]^{4+}$ (solv = H_2O or MeCN)[1171] has been investigated in acetonitrile. Electrochemical or chemical reduction of $[Fe_2(\mu\text{-}O)(bipy)_4(solv)_2]^{4+}$ in acidic acetonitrile generates $[Fe(bipy)_2(MeCN)_2]^{2+}$.[486]

Complexes with a double oxide bridged core, $[Fe_2(\mu\text{-}O)_2]$, are known.[1172]



(**210**)

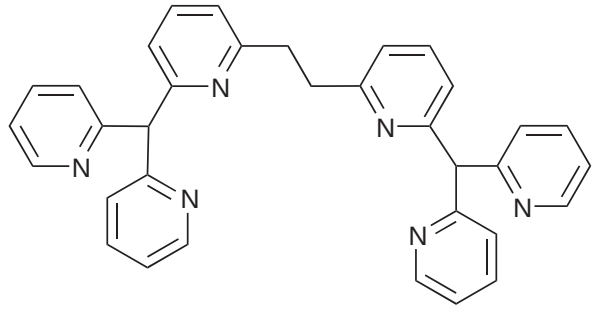


(**211**)

(ii) Supported μ-*oxide—general*

There is a single $Fe^{III}(\mu\text{-O})Fe^{III}$ bridge in the tris(2-pyridylmethyl)amine (tpa) complex $[(H_2O)(tpa)Fe(\mu\text{-O})Fe(tpa)(ClO_4)](ClO_4)_3$. Treatment of this red complex with triethylamine gives a green complex containing $\mu\text{-}O_2H_3$ as well as μ-O; this complex promotes the hydrolysis of acetonitrile, giving, in a matter of hours, an acetamido bridge supporting the oxide bridge, $[(tpa)Fe(\mu\text{-O})(\mu\text{-MeCONH})Fe(tpa)](ClO_4)_3$.[1123] Dichloro, $[Cl(tpa)Fe(\mu\text{-O})Fe(tpa)Cl](ClO_4)_2$, and μ-sulfato, $[(tpa)Fe(\mu\text{-O})(\mu\text{-}SO_4)Fe(tpa)](ClO_4)_2$, derivatives can be prepared from the parent bis-aqua complex. Fe ⋯ Fe distances are 3.565(2) Å in the dichloro complex, 3.389(2) Å in $[(H_2O)(tpa)Fe(\mu\text{-O})Fe(tpa)(OH)](ClO_4)_3$.[1173]

The reaction between $[Fe^{II}{}_2(\mu\text{-OH})_2(tmpma)_2]^{2+}$, tmpma = tris(6-methyl-2-pyridylmethyl)amine, and dioxygen follows a simple second-order rate law. A mixed valence superoxo-containing intermediate is suggested en route to the final oxo-peroxo-bridged product, $[Fe^{III}{}_2(\mu\text{-O})(\mu\text{-}O_2)(tmpma)_2]^{2+}$.[1174] Another oxo-peroxo-bridged species also has an acetate bridge and the hexa-pyridyl ligand (**212**) both providing a fourth bridge and occupying the remaining coordination sites on both iron atoms. This thermally stable complex catalyzes alkane oxidation.[1175]



(**212**)

Specific oxide plus carboxylate and oxide plus alkoxide complexes are detailed below.

(iii) μ-*Alkoxide;* μ-*oxide plus* μ-*alkoxide*

The binuclear complex $[Fe_2(OCMe_2Ph)_6]$ contains two alkoxide bridges,[1104] while in the dimer $[Fe_2(heidi)_2(H_2O_2)_2]$ the metal ions are bridged by alkoxide bridges derived from the $heidi^{2-}$, $N(CH_2CH_2OH)(CH_2CO_2^-)_2$.[1176] Bridging oxide supports bridging alkoxide in $[Fe_5(\mu_5\text{-O})(OEt)_{13}]$[1104] and in $[Fe_9O_3(OEt)_{21}]\cdot EtOH$.[1177]

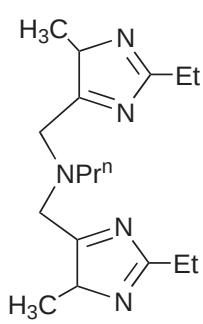
(iv) μ-*Carboxylate*

Di-μ-2,6-di(*p*-tolyl)benzoatedi-iron(II) complexes provide structural and functional models for enzymes such as ribonucleotide reductase and methane monooxygenase hydroxylase.[1178,1179] A valence-delocalized iron(II,III) analogue ($S = 9/2$) has Fe ⋯ Fe = 2.698 Å,[1180] while an iron(III,IV) species has been generated by dioxygen oxidation.[1181] Similar complexes with two bis-mesityl-phenylcarboxylate bridges also model the iron-containing site of nonhem di-iron enzymes.[1182]

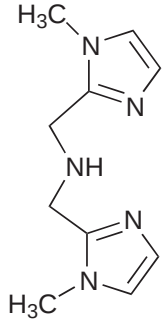
(v) μ-Oxide with μ-carboxylate

There are many bi- and polynuclear iron(III) complexes where bridging oxide is supported by carboxylates.[1007] Combinations of Fe—O—Fe plus carboxylate bridges occur in model compounds for proteins and in biomineralization.[268] Electronic spectra of $[Fe(\mu\text{-}O)(\mu\text{-}O_2CR)_2Fe]$ complexes have been reviewed briefly.[1110] $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2(bipy)_2Cl_2]$ is both an alkane activation catalyst and a bio-model.[1183]

Many $LFe^{III}(\mu\text{-}O)(\mu\text{-}O_2CR)_2Fe^{III}L$ complexes have terdentate, triazamacrocyclic, or triazatripodal ligands L. Examples include species with L = $HB(pz)_3$, R = Me;[1184] with L = tacn, R = Me;[1185] with L = bis(2-benzimidazolylmethyl)amine, R = Me, Ph;[1186] with L = *N*,*N*-bis(2-ethyl-5-methylimidazol-4-ylmethyl)aminopropane (**213**), R = Ph;[1187] with L = *N*-alkyl-*N*,*N*-bis(2-pyridylmethyl)amine, alkyl = Me, Bz, adamantyl for R = Ph, also several other R for alkyl = Me;[1188] and with L = bis((1-methylimidazol-2-yl)methyl)amine (**214**), R = Ph. In this last case hydrogen-bonding between lattice water and μ-oxo in the hydrated form results in a significant decrease in $Fe^{III} \cdots Fe^{III}$ interaction.[1189] Tetrakis(picolyl)propane-1,3-diamine and its butane-1,4-diamine analogue each contain two terdentate chelating units and can thus provide the groups L on both iron atoms, giving further bridging (see also Section 5.4.5.4.3 below).[1190]

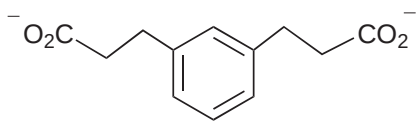


(**213**)

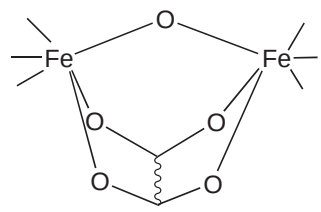


(**214**)

An unusual variant is to have both carboxylates in the same molecule, as in the *m*-phenylenedipropionate (mpdp, (**215**)), which can support an oxide bridge as shown schematically in (**216**). Complexes containing such iron–iron bridging include $[Fe_2(\mu\text{-}O)(\mu\text{-}\mu\text{-mpdp})\{HB(pz)_3\}_2]$ and $[Fe_2(\mu\text{-}O)(\mu\text{-mpdp})(bipy)_2Cl_2]$.[1191]



(**215**)



(**216**)

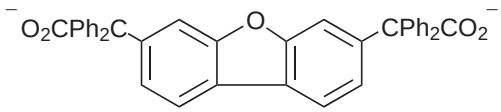
(vi) μ-Hydroxide with μ-carboxylate

Binuclear iron(II) complexes in which a hydroxide bridge is supported by the dinucleating bis-carboxylate ligand dibenzofuran-4,6-bis(diphenylacetate), (**217**), have proved useful models for hemerythrin.[1192] The nature of the binuclear iron center in hemerythrin itself, and in other metalloproteins, has been reviewed,[1193] the binding of O_2, NO, N_3^-, and NCS^- to the iron of hemerythrin discussed,[1194] and the volume profile for hemerythrin reacting with O_2 established.[825,826] Bulky tolyl-substituted carboxylate ligands, both bridging and terminal, and

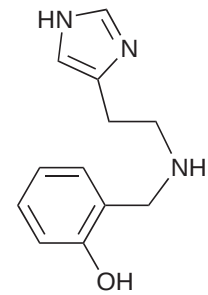
bulky benzyl-substituted ethane-1,2-diamine terminal ligands, stabilize the $[Fe_2(\mu\text{-}OH)_2(\mu\text{-}O_2CR)]$ core and provide a good model for methane mono-oxygenase hydroxylase.[1195] The iron(III,IV) species mentioned in the μ-carboxylate paragraph above has two bridging hydroxides in addition to the two carboxylate bridges. This quadruple bridging results in a short Fe ⋯ Fe distance of 2.84 Å.[1181]

(vii) μ-*Carboxylate with* μ-*alkoxide or* μ-*phenoxide*

A di-iron(III) complex containing two methoxide bridges supporting one acetate bridge has been synthesized as a model for the active site of purple acid phosphatases; the ligand completing the coordination shell of each Fe^{3+} is [(2-hydroxybenzyl)(2-(imidazol-2-yl)ethyl)]amine, (**218**), in *mer* geometry. The iron atoms are weakly antiferromagnetically coupled; Fe ⋯ Fe is 3.105 Å—there is a useful table of 24 Fe ⋯ Fe distances in complexes of this type in this publication).[1196] Bis-mesitylphenylcarboxylate ligands act as terminal ligands and provide a supporting bridge to two isopropoxide bridges in $[Fe_2(2,6\text{-}mes_2C_6H_3CO_2)_3(OCHMe_2)_2]$, which is a mixed valence species crystallizing in two slightly different forms with short Fe ⋯ Fe distances of 2.624 Å and 2.749 Å.[1197]



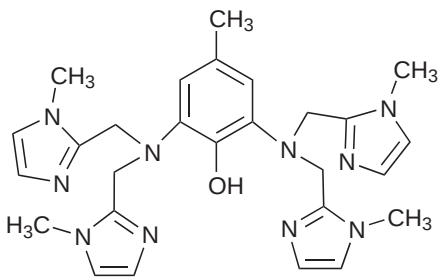
(**217**)



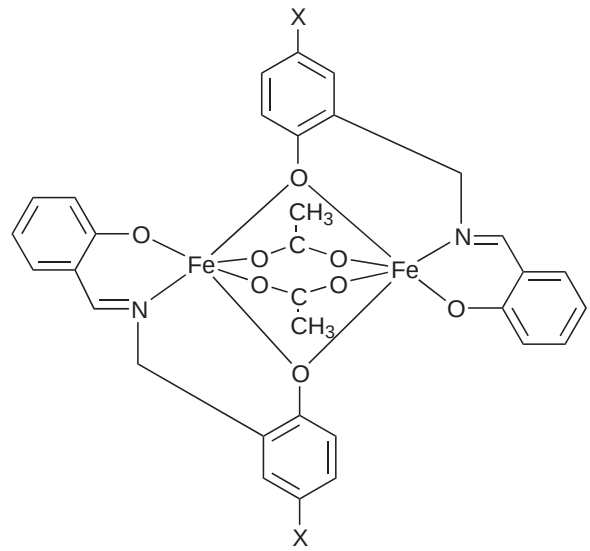
(**218**)

Several complexes contain bridging carboxylates supporting a phenoxide bridge. The phenoxide is generally part of a polyatomic ligand which also contains pyridine or imidazole groups which also bond to the two iron atoms. Examples are provided by the mixed valence species $[Fe_2(bimp)(\mu\text{-}O_2CR)_2]^{2+}$, where bimpH = (**219**) and R = Me, Et, or Ph. An X-ray structural determination of the BPh_4^- salt of the complex with R = Me indicated a trapped-valence (class I) species; the Fe to phenoxide-oxygen distances are 2.13 Å and 1.95 Å for the Fe^{II} and Fe^{III} atoms, respectively. The ESR and Mössbauer properties of this group of compounds are markedly affected by the natures of R, of the anion, and of any solvent of crystallization present.[1198] Spectroscopic and magnetic properties of heterobimetallic species containing cores such as $—Fe^{III}(O_2CMe)_2(bpmp)Zn^{II}—$, where bpmp = 2,6-bis[(bis(2-pyridylmethyl)amino)-methyl]-4-methyl-phenoxide, contribute to the elucidation and understanding of the properties of mixed valence $Fe^{III}Fe^{II}$ analogues.[1199] A terminal phenoxide from each ligand supports two carboxylate bridges in $[Fe^{III}{}_2L_2(O_2CR)_2]$ (**220**), where X = H, Cl, Br for R = Me and a range of R for X = Br. The Fe distance is 2.957(1) Å in the complex with X = Br, R = Me, similar in the others.[1200]

The phenoxide unit can be at the center of ligand molecule which has two terminal terdentate units, as in (**221**).[1201] The main incentive to develop such complexes was that it proved possible to generate mixed valence $Fe^{II}Fe^{III}$ species, which had proved impossible to prepare from simpler $LFe(\mu\text{-}O)(\mu\text{-}O_2CR)_2FeL$ species. Other examples of mixed valence complexes with bis-terdentate-phenoxide bridging ligands include species $[Fe^{II}Fe^{III}(L)(\mu\text{-}O_2CR)_2]$ with L = 2,6-bis[bis(2-pyridyl-methyl)aminomethyl]-4-methyl-phenoxide and O_2CR = benzoate, acetate,[1202] or propionate[1203] and with L = *N*,*N*′-(2-hydroxy-5-methyl-1,3-xylylene)bis[*N*-(carboxymethyl)glycine] with O_2CR = acetate[1204] (the $Fe^{III}{}_2$ form had been characterized earlier [1205]). Mössbauer spectra and near-IR bands which may be assigned to IVCT transitions support a Robin and Day[334,335] class II assignment. More recently Raman spectroscopic evidence has been obtained for the formation of a simpler trapped-mixed-valence complex $[(tmtcn)Fe^{II}(\mu\text{-}O)(\mu\text{-}O_2CPh)_2Fe^{III}(tmtcn)]$ on oxidation of $[(tmtcn)Fe^{II}(\mu\text{-}OH)(\mu\text{-}O_2CPh)_2Fe^{II}(tmtcn)]$ (tmtcn = 1,4,7-trimethyl-1,4,7-triazacyclononane) by dioxygen.[1206]



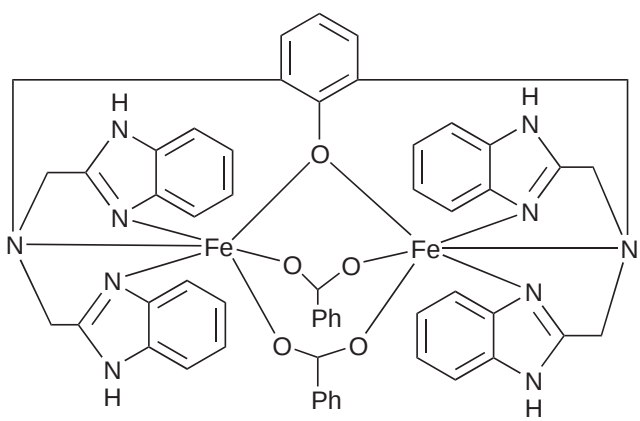
(**219**)



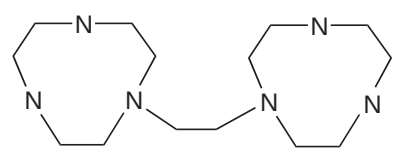
(**220**)

(viii) μ-*Carboxylate with other* μ-*ligands*

The two iron centers may be linked by using a hexadentate ligand containing two tridentate chelating moieties sufficiently separated to permit them to coordinate to both iron atoms. The bis-triazacyclononane ligand (**222**), btacn, can perform this function, forming the complexes $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2(\mu\text{-btacn})]$[736] and $[Fe_4(\mu\text{-}O)_2(\mu\text{-btacn})_2(O_2CMe)_4]^{4+}$.[737] The latter complex may serve as a model for hemerythrin. The di-iron complex $[Fe^{III}{}_2(\mu\text{-bpman})(\mu\text{-pcxc})_2]^{2+}$, where bpman = 2,7-bis[bis(2-pyridylmethyl)aminomethyl]-1,8-naphthyridine, (**223**), and pcxc = 1-phenyl-cyclohexane-carboxylate, is of particular interest in that it exhibits two reversible one-electron waves in its cyclic voltammetry. The Fe···Fe distance in this complex (in its $Fe^{III}{}_2$ form) is 3.74 Å, in its hydroxo analogue $[Fe^{III}{}_2(\mu\text{-bpman})(\mu\text{-pcxc})(\mu\text{-OH})]^{2+}$ 3.22 Å.[1207]



(**221**)



(**222**)

5.4.5.4.2 Oxotri-iron complexes

Trinuclear complexes $[Fe_3O(O_2CR)_6L_3]^{n+}$, with planar triangular $[Fe_3(\mu_3\text{-}O)]$ cores, are of considerable interest in relation to factors determining intramolecular communication between metal centers.[1208] The usual oxidation states are $Fe^{III}{}_3O$ and $Fe^{III}{}_2Fe^{II}O$, giving cationic (1+) and uncharged complexes, respectively. This group of complexes can be tailored in many ways — R may be, e.g., Me or Ph, or a long alkyl chain,[1209] L may be, e.g., H_2O or (substituted) pyridine,

R and L may be isotopically substituted (H vs. D;[1210] ^{16}O vs. ^{18}O[1211]), for the cationic $Fe^{III}{}_3O^+$ complexes the counterion may be varied, and for the uncharged $Fe^{III}{}_2Fe^{II}O$ complexes there is often solvent of crystallization to provide another variable. A further attractive feature of these complexes is that they can be studied by a variety of instrumental techniques, including XRD and X-ray scattering, inelastic neutron scattering (INS),[1212–1216], calorimetry,[1217,1218] magnetic measurements (many exhibit spin cross-over behavior), and NMR, ESR, Mössbauer, and IR-Raman spectroscopy.[1219] Much information may therefore be obtained on structural and dynamic properties, particularly in relation to iron–iron interaction, the extent of delocalization, and rates of intramolecular electron transfer in the mixed valence $Fe^{III}{}_2Fe^{II}O$ complexes. These are affected not only by the nature of R and L, but also by the nature of the counterion (for $Fe^{III}{}_3O^+$ complexes) and solvent of crystallization. Lattice dynamics associated with ligand motion and with movements of the solvate molecules,[1220] and of counterions when present, are sometimes manifested as phase transitions, and usually have effects on rate constants for intramolecular electron transfer.[1221] The importance of solvate molecules is also apparent from the fact that $[Fe_3O(O_2CMe)_6(4Etpy)_3]\cdot 4Etpy$ is a spin cross-over compound, but $[Fe_3O(O_2CMe)_6(4Etpy)_3]$ itself is valence-localized at all temperatures.[1222] Electrochemical reduction of a wide range of complexes of this type has been documented.[1223]

Many references cover several aspects and techniques. Thus a combination of XRD, vibrational spectroscopy, and solution redox chemistry was employed in studying electron delocalization in the mixed valence complexes $[Fe_3O(O_2CMe)_6L_3]$, L = H_2O or py;[1224] different time-scales for different techniques permit qualitative estimates of rates even when precise rate constants may not be obtainable.[1225] ^2H NMR, Mössbauer spectroscopy, and XRD combined to delineate the role of benzene of crystallization in $[Fe_3O(O_2CMe)_6(4Mepy)_3]\cdot C_6H_6$,[1226] further combined with H/D isotope effects in the examination of the role of lattice dynamics in determining intramolecular electron transfer rates in mixed-valence $[Fe_3O(O_2CPh)_6(py)_3].py$.[1210] Determination of the structure of $[Fe_3O(O_2CMe)_6(4Etpy)_3]\cdot 4Etpy$ at 163 K and at 298 K showed that the Fe_3 triangle changed from an isosceles to an equilateral triangle—this and information on Fe—O bond distances showed that the valence-localized representation $Fe^{III}{}_2Fe^{II}O$ applied at the lower temperature, but that the three iron atoms were identical, i.e., the complex was valence-delocalized (class III in the Robin and Day classification[334,335]) at 298 K.[1222] A XRD examination of $[Fe_3O(O_2CPh)_6(py)_3]ClO_4\cdot py$ at 233 K indicated three-fold symmetry, but INS at 1.5 K showed two inequivalent sets of iron centers. This situation is ascribed to "spin frustration," arising from the fact that antiferromagnetic coupling is forbidden for the three half-integral spins located at the corners of an equilateral triangle.[1227,1228] Heat capacities and phase transitions correspond to the onset of intramolecular electron transfer and orientational reorganization of the solvent molecules which are generally present in the lattices of this type of compound and play an important role in their properties. Transition entropies of 28 $J\,K^{-1}\,mol^{-1}$, 31 $J\,K^{-1}\,mol^{-1}$, 14 $J\,K^{-1}\,mol^{-1}$, and 15 $J\,K^{-1}\,mol^{-1}$ have been determined for $[Fe_3O(O_2CMe)_6(py)_3]\cdot CHCl_3$ (for which $\Delta H = 5.1\,kJ\,mol^{-1}$),[1229] $[Fe_3O(O_2CMe)_6(py)_3]\cdot py$,[1217,1218] $[Fe_3O(O_2CMe)_6(3Mepy)_3]\cdot 3Mepy$,[1230] and $[Fe_3O(O_2CMe)_6(3Mepy)_3]\cdot PHMe$,[1229], respectively.

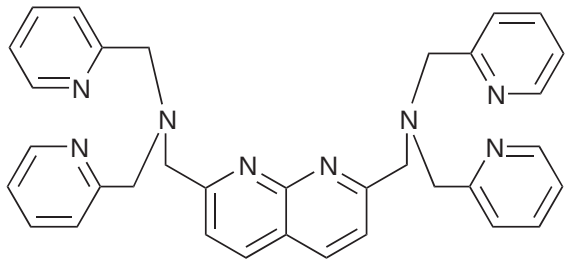
A further variant is the extension from planar triangular homonuclear $[Fe_3(\mu_3\text{-}O)]$ cores to heteronuclear $[Fe_2M(\mu_3\text{-}O)]$ or $[FeM_2(\mu_3\text{-}O)]$ cores,[1211,1212,1231] as in, for example, $[Fe_2CoO(O_2CMe)_6(3Clpy)_3]\cdot 0.25(3Clpy)\cdot 0.25Me_2CO\cdot 0.5H_2O$[1232] or $[FeZn_2O(O_2CMe)_6(py)_3]\cdot py$— though there is a linear arrangement of the three metals in $[Fe^{II}Zn_2(O_2CMe)_6(py)_2]$.[456]

In the cation of triaquahexakis(μ_2-betaine)-μ_3-oxotri-iron(III) bis-tetrachloromanganate trichloride hexahydrate each betaine is in the dipolar zwitterionic form and links pairs of iron atoms.[1233] The perchlorate heptahydrate of this trinuclear cation contains a perfectly coplanar central Fe_3O core.[1234]

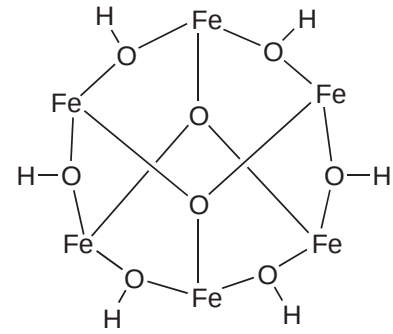
So-called basic iron(III) benzoate reacts with H_2O_2 to give a product $[\{Fe_3O(O_2CPh)_5(H_2O)_2\}(\mu_4\text{-}O_2)(\mu_2\text{-}O_2CPh)_2]$ in which a peroxide anion and two benzoates bridge two Fe_3O cores.[1235] In the presence of iminodiacetate, ida, $NH(CH_2CO_2^-)_2$, one can prepare $M_4[Fe_6(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_6(ida)_6]\cdot nH_2O$ (M = Na, K), again containing only oxide and hydroxide bridges—the core consists of two Fe_3O units joined by six hydroxide bridges, (**224**).[1236] Similarly the oxoiron core of $[Fe_6O_3(O_2CMe)_9(OEt)_2(bipy)_2](ClO_4)$ consists of two Fe_3O units, this time joined by a tetrahedral oxide ligand.[1237]

5.4.5.4.3 Other polynuclear complexes

In contrast to the numerous tri-iron complexes in the preceding section, the bis(2-pyridylmethyl)-glycine complex $[Fe_3(O_2CMe)_3(bpmg)_3]$ has a space at the center of the Fe_3 triangle. This can



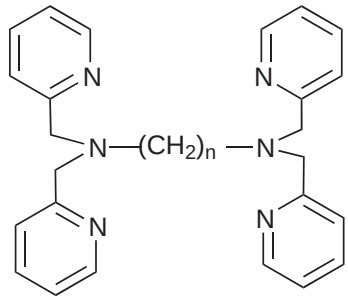
(**223**)



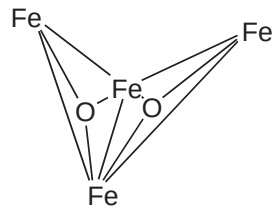
(**224**)

accommodate another iron, to give a tetranuclear species in which the central iron is bonded to three pairs of carboxylate oxygens.[1238] The dipivaloylmethane complex $[Fe_4O(dpm)_6]\cdot 2C_6H_5Me$ has an $[Fe_4(\mu_4\text{-}O)]$ core.[1239] The tetrakis(picolyl)diamine ligands (**225**) give tetranuclear complexes in which two $[Fe_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2(\mathbf{225})_6]^{2+}$ units are linked by the aliphatic chains, the choice of $n = 3$ or 4 in (**225**) permitting tuning of the Fe ··· Fe distance.[1190] *N*,*N*,*N*′-tris(2-pyridyl)-*N*′-(2-hydroxybenzyl)-1,3-diaminopropanol bridges support both oxide and acetate bridges in a tetranuclear complex with features reminiscent of purple acid phosphatase.[1240] The unusual μ_4-OHO entity occurs in the core of the tetranuclear clusters $[Fe(\mu_4\text{-}OHO)(\mu\text{-}OH)_2(O_2CMe)_4(bipy)_4]^{3+}$ and its phen analogue. These complexes have a $S = 0$ ground state, with strong antiferromagnetic interaction between the iron atoms.[1241]

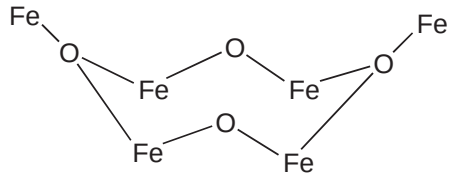
A species with a "butterfly" tetra-iron $[Fe_4(\mu_3\text{-}O)_2]^{8+}$ core (**226**)[1242] is believed to be an intermediate in the reaction of $[Fe_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CPh)_6(H_2O)_3](O_2CPh)$ with pyridine, whose final product is $[Fe_6(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(O_2CPh)_{12}(py)_2]$. This hexanuclear product contains the core shown in (**227**). The Fe_2Zr_2 core in $[Fe_2Zr_2(\mu_3\text{-}O)_2(\mu\text{-}O_2CPh)_6(OBu^t)_4(py)_2]$ is similar to (**226**), with the Zr atoms at the wing tips of the butterfly.[1243]



(**225**)



(**226**)



(**227**)

$[Fe_6O_2(O_2CR)_6(hmp)_6](NO_3)_2$, hmpH = 2-(hydroxymethyl)pyridine and R = Ph or Bu^t, contains an octahedral Fe_6O_2 core in which the two oxides bridge opposite faces (cf. the $[(Fe_3O)_2]$ core of (**224**) above); $[Fe_8O_4(O_2CPh)_{11}(hmp)_5]$ and $[Fe_8O_4(O_2CMe)_{12}(hmp)_4]$ have $[Fe_8(\mu_3\text{-}O)_4]$ cores. All these hmp complexes have $S = 0$ ground states.[1244] Hydrolysis of the 1,4,7-triazacyclononane complex

$[Fe(tacn)Cl_3]$ at pH 9 in the presence of bromide gives $[Fe_8(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_{12}(tacn)_6]Br_8\cdot 9H_2O$.[1245] The essentially flat Fe_8 unit has an $S = 10$ ground state and shows superparamagnetic behavior.[1246] ESR spectra have been obtained for single crystal samples of this molecular magnet.[1247] All the iron atoms in $[Fe_8O_5(O_2CMe)_8(tren)_4]$ are octahedrally coordinated. Each iron of the square Fe_4O core is μ-O, μ-O_2CMe linked to its neighbors, with each of the four peripheral (tren)Fe units bonded to a core μ-O_2CMe and linked to a core Fe through another μ-O_2CMe.[1248]

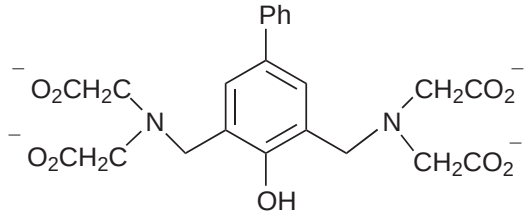
$[Mn_8Fe_4O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$ contains nonplanar rings of alternating Fe^{3+} and Mn^{3+} ions linked by μ_3-O and μ-O_2CMe ligands; $[Mn^{IV}{}_4O_4]^{8+}$ cubane units lie inside these rings. The marked Jahn-Teller distortions of the Mn^{3+} ions permit their distinction from the Fe^{3+} centers. The magnetic and redox properties of this species were examined in detail.[1249]

The synthesis, structure, and magnetic properties of an octairon(III) citrate complex, $[Fe_8(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(citrate)_6(O_2CMe)_2(imidazole)_2]^{8-}$, have been described. This complex consists of two equivalent tetranuclear units linked by two citrates; the Fe ions are antiferromagnetically coupled in a four $S = 5/2$ spin system.[1250] $[Fe_9O(citrate)_8(H_2O)_3]^{7-}$ has a three-layer citrate-bridged structure.[1251]

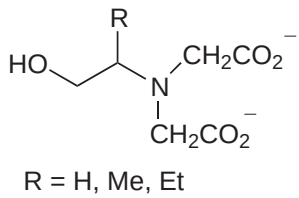
Acetate and chloroacetate bridges, along with methoxide bridges, hold together the cyclic decanuclear "ferric wheel" complexes $[\{Fe(OMe)_2(O_2CR)\}_{10}]$ with R = Me[1252] or CH_2Cl.[1253,1254] The former was obtained on refluxing $[Fe_3O(O_2CMe)_6](H_2O)_3]Cl$ in methanol for several hours, the latter prepared from basic iron chloroacetate plus iron(III) nitrate. The ten iron atoms in each of these species are approximately coplanar, the species having essentially D_{5d} symmetry. $[Fe(OMe)_2(PhCOCHCOPh)]_{12}$ afforded the first example of a dodecanuclear "ferric wheel".[1255] Reaction of $[NEt_4]_2[Fe_2OCl_6]$ with sodium benzoate followed by sodium 6-chloro-2-pyridinonate (clpd), in acetonitrile, gave another decanuclear complex, $[Fe_{10}Na_2(O)_6(OH)_4(O_2CPh)_{10}(clpd)_6(Me_2CO)_2]$, this time with a compact oxo-iron core approximating to two Fe_6O_6 hexagonal prisms sharing a square face. Other polynuclear iron complexes containing such distorted Fe_6O_6 hexagonal prismatic units include the benzoate derivatives $[Fe_{11}O_6(OH)_6(O_2CPh)_{15}]$[1256] (a ferritin model which is soluble in acetonitrile, in acetone, and in DMF[1257]) and $[Fe_{16}MO_{10}(OH)_{10}(O_2CPh)_{20}]$ (M = Mn, Co).[1258] The 6-chloro-2-pyridinonate-containing complex $[Fe_{10}Na_2(O)_6(OH)_4(O_2CPh)_{10}(clpd)_6(Me_2CO)_2]$, with its $S = 11$ ground state, is potentially a single-molecule magnet.[1259] In the decanuclear complex $[Fe_{10}(\mu_3\text{-}O)_3(\mu_4\text{-}O)_3(O_2CNEt_2)_{17}Cl]$ all carbamates are bridging, the chloride is terminal, and the irons are five- or six-coordinated.[1260] $[Fe_{10}Cl_8O_4(OMe)_{14}(MeOH)_6]\cdot 2MeOH$, which includes no polydentate ligands, contains iron in four different coordination environments.[1261]

The mineralized core of ferritin can be modeled by mixed valence species such as $[Fe^{III}{}_4Fe^{II}{}_8O_2(OMe)_{18}(O_2CMe)_6]\cdot 4.67MeCN$, whose 3D close-packed layer structure mimics ferritin. This compound can be prepared by oxidizing a methanolic solution of iron(II) acetate and lithium methoxide with a slow stream of dioxygen; it can be reduced to give $[Fe^{III}{}_2Fe^{II}{}_{10}O_2(OMe)_{18}(O_2CMe)_6]^{2-}$.[1262]

There are both oxide and hydroxide bridges in $[Fe_{17}(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{10}(heidi)_8(H_2O_2)_{12}]^{3+}$ and in $[Fe_{19}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_8(heidi)_{10}(H_2O_2)_{12}]^{+}$, obtained as nitrates from slow crystallization from slightly basic solution containing pyridine and $heidi^{2-}$, $N(CH_2CH_2OH)(CH_2CO_2^-)_2$.[1176,1263] Fe_{19} clusters are also obtained when $N(CHRCH_2OH)(CH_2CO_2^-)_2$ with R = Me or Et is used instead of heidi itself; such clusters can be considered as molecular magnets.[1264] Controlled hydrolysis of iron(III) solutions containing iminodiacetates such as (**228**) has produced disc-shaped Fe_{17} and Fe_{19} aggregates, with an iron-oxide-hydroxide core surrounded by an organic shell; the phenol derivative (**229**) gives the smaller but similar complex $[Fe_4O(OH)_3(\mathbf{229})_2]^{3-}$.[1265]



(**228**)



(**229**)

The magnetic properties of large oxo-iron clusters, with auxiliary hydroxide, methoxide, or carboxylate bridging or terminal ligands, have been reviewed.[1266]

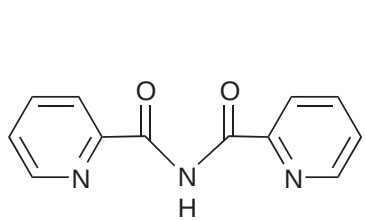
5.4.5.5 Diketones and Hydroxyketones

5.4.5.5.1 β-*Diketones and hydroxyketones—general*

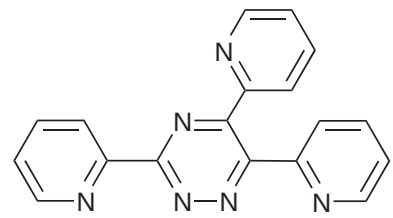
(i) β-*Diketones*

The structure of [Fe(MeCOCOCHCOMe)$_3$] has been determined,[1267] of [Fe(acac)]$_3$ redetermined at 20 K (Fe—O = 1.977 to 2.004 Å).[1268] Iron(III) forms mainly 1:1 and 1:3 complexes with acetylacetone and with benzoylacetone in DMF; their reduction has been monitored electrochemically.[1146] Solubilities, and derived transfer chemical potentials, of [Fe(acac)$_3$] in various binary aqueous solvent mixtures give a measure of preferential solvation.[1269] Rate constants have been determined, at 283 K, for formation of 2,4-octanedione and 2,4-nonanedione complexes of iron(III).[1075]

The complex [Fe^{II}(bpca)$_2$][Fe^{II}(hfac)$_2$]$_2$, where Hbpca = bis(2-pyridylcarbonyl)amine, (**230**), consists of a pair of high-spin tris-β-diketonate units bridged by a low-spin N_6 entity.[462] [Fe^{II}(hfac)$_2$] can bridge through the pyridyltriazine ^{3,5,6}tptz, (**231**), to molybdenum(0), in Mo(CO)$_4$(^{3,5,6}tptz),[478] and rhenium(I) in ReCl(CO)$_3$(^{3,5,6}tptz).[479]



(**230**)



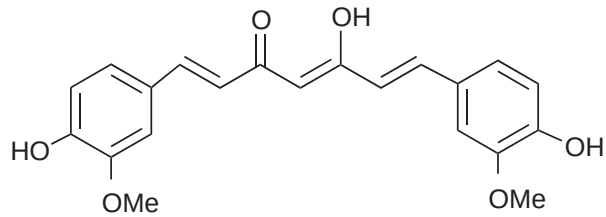
(**231**)

Controlled methanolysis of $FeCl_3$ in the presence of β-diketones and of LiOMe or NaOMe in anhydrous methanol gives cyclic hexanuclear yellowish–red cationic clusters [MFe$_6$(OMe)$_{12}$L$_6$]$^+$ (LH = e.g., PhCH$_2$COCH$_2$COCH$_2$Ph ; M = Li, Na), in which the Fe$_6$(OMe)$_{12}$ unit accommodates the alkali metal cation, both in the solid state and in solution.[1270,1271]

(ii) Hydroxyketones

Iron(II) chloranilate trihydrate contains zigzag chains in which bidentate chloranilate anions bridge octahedral iron centers, each of which has two *cis* water ligands. Iron(III) chloranilate is dinuclear, with one chloranilate bridge.[1084]

Iron(III) complexation by 5-nitrotropolone[1272] follows the usual mechanistic pattern, I_a at Fe^{3+}, I_d at $FeOH^{2+}$aq. Dinuclear $Fe_2(OH)_2^{4+}$aq, like $FeOH^{2+}$aq, reacts by an I_d mechanism. Curcumin (**232**) and its diacetyl derivative form complexes with Fe^{3+} whose stabilities approach that of Fe^{3+}-desferrioxamine, hence their suggested use for treatment of iron overload—a topic which dominates the following section devoted to two specific classes of hydroxyketones, viz hydroxypyranones and hydroxypyridinones.[223]

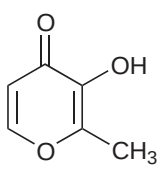


(**232**)

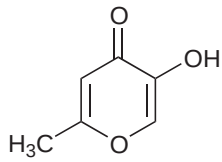
5.4.5.5.2 Hydroxypyranones and hydroxypyridinones

(i) Introduction

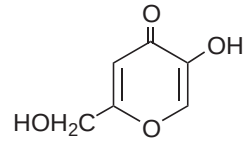
Several hydroxypyranones, such as maltol (**233**), allomaltol (**234**), kojic acid (**235**), meconic acid (**236**), pyromeconic acid (**237**), and comenic acid (**238**) are natural products; maltol is of considerable importance in the food industry. They form stable iron(III) complexes, but are more important as starting materials for the preparation of hydroxypyridinones and their complexes. 1-Hydroxy-2(1*H*)-pyridinone (**239**) (tautomer of 2-hydroxy-pyridine-*N*-oxide), 1,4-dihydroxy-2-pyridinone (tautomer of 2,4-dihydroxy-pyridine-*N*-oxide), 3-hydroxy-2(1*H*)-pyridinone (**240**), 3-hydroxy-4(1*H*)-pyridinone (**241**), and a range of their derivatives, also all form stable iron complexes which are generally of higher thermodynamic stability than the corresponding hydroxypyranonate complexes. The hydroxypyridinones were first developed for analysis, but have subsequently assumed a major role as potential and actual chelators for the introduction or removal of iron in cases of iron deficiency or overload. Their role in the control of iron levels in the body is documented in Section 5.4.1.11.3 above.



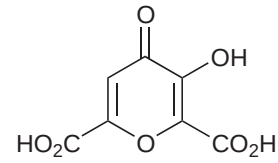
(**233**)



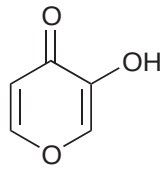
(**234**)



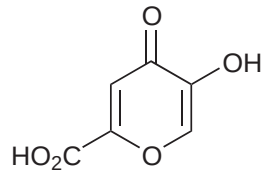
(**235**)



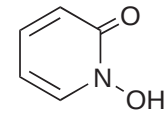
(**236**)



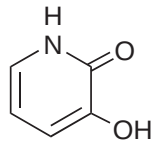
(**237**)



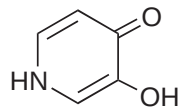
(**238**)



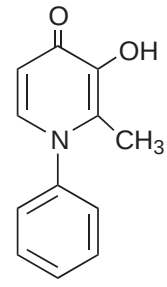
(**239**)



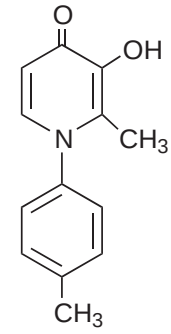
(**240**)



(**241**)



(**242**)



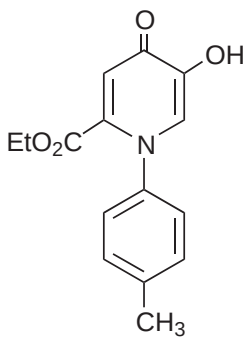
(**243**)

(ii) Preparation of ligands for complexes

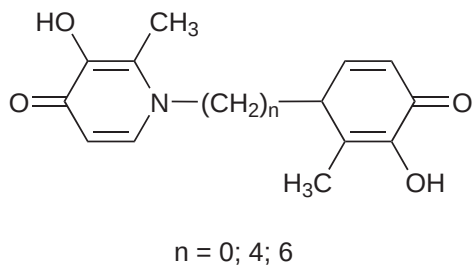
The preparation of metal complexes from hydroxypyridinones is usually simple and straightforward—the more difficult task is generally the synthesis of the required ligand. There may also be difficulties in separating complex from ligand, especially for the more lipophilic complexes; sublimation, used in the case of *N*-*n*-hexyl, may be more successful than recrystallization.[1273] 3-Hydroxy-4-pyridinones are for the most part accessible from hydroxypyranones. Reagents developed for analytical and separation purposes (preparative methods[1274] may be traced back

to 1964[1275]) included (**242**)[1276] and (**243**)[1277] from maltol and (**244**)[1278] from kojic acid. 3-Hydroxy-4-pyridinones for pharmacological investigations have generally been prepared from maltol or, more recently, ethylmaltol, often by a seven-stage method based on benzyl-[1279] or methoxy-[1280,1281] protection of the 3-hydroxy group. *N*-Aryl,[1274,1282] *N*-benzyl,[1283] and *N*-carboxyalkyl[1284] ligands can often be prepared by direct reaction,[210,1285] though many hours of refluxing may be required. The attachment of pharmacologically attractive fluorine-containing groups, such as $—CH_2CF_3$ or $—CH_2CH_2C_6F_{13}$,[1286] to the ring nitrogen is harder, but may be achieved by the use of such solvents as dimethyl sulfoxide or acetonitrile.[1287] However this method may fail through Schiff base formation dominating over the required Michael reaction.[210] Occasionally a one-pot synthesis of a tris-3-hydroxy-4-pyridinonato-iron(III) complex, e.g., from methylamine, maltol, and $FeCl_3$, is successful.[1288] 3-Hydroxy-4-pyridinones can also be prepared from maltose or lactose.[969]

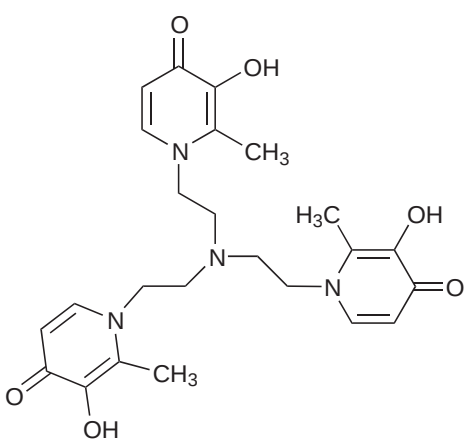
There has been much tailoring of these ligands and their complexes to optimize such properties as structure, stability, inertness, solvation, and targeting.[1289,1290] This may be exemplified by the development of ester prodrugs for targeting the liver,[1291,1292] and the introduction of hydrophilic substituents to promote iron mobilization.[210] Tailoring has generally involved substituents on the ring-nitrogen, though attention has also been paid to varying the substituents on ring carbons. Thus 2-(1′-hydroxyalkyl)- and 2-amido-derivatives of 3-hydroxypyridin-4-one have been found to be more effective at binding Fe^{3+} over the pH range 5–8.[1293–1295] Higher denticity normally increases stability, so potentially tetradentate (**245**)[1296] and hexadentate, (**246**)[1296] and (**247**),[178,1297,1298] hydroxypyridinonate ligands have been synthesized for complexing iron(III). The tetradentate ligands form various complexes of stoichiometry 1:1, 1:2, and 2:3 (see Section 5.4.3.5.7 for similar Fe_2L_3 complexes of tetradentate bis-diimine ligands).



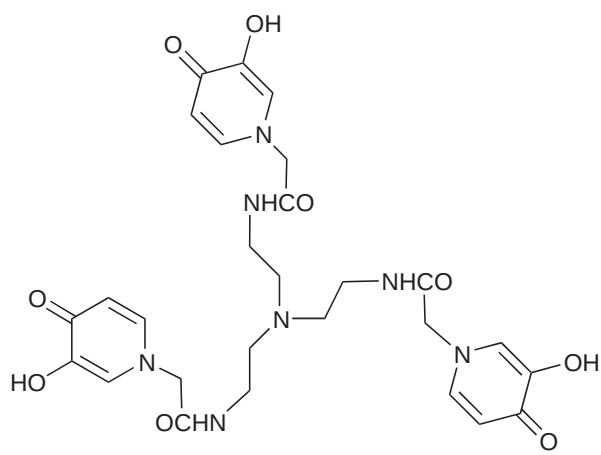
(**244**)



(**245**)



(**246**)



(**247**)

5.4.5.5.3 Preparations, properties, and structures

The crystal structure of *mer*-tris(3-hydroxy-2-methyl-4*H*-pyran-4-onato)iron(III), [Fe(malt)$_3$], has been determined, and variable-temperature Mössbauer data reported for this complex.[195] The report of the preparation and characterization of tris(1-hydroxy-2-pyridinato)iron(III) includes a crystal structure determination. Its 6-CONMe$_2$ derivative is considerably more soluble than the parent complex, but has significantly lower stability.[198] Tris(3-hydroxy-2-pyridinonato)iron (III)[1299] and some *N*-alkyl derivatives[1300] have been prepared; the crystal structure of the iron(III) complex of the *N*-butyl ligand was solved. A full range of properties, including crystal structure (partial[1301] and complete[1302]), mass spectrum, magnetic susceptibility, IR-Raman spectrum, and cyclic voltammetry (in MeCN) has been reported for the key compound [Fe(L1)$_3$], tris(1,2-dimethyl-3-hydroxy-4-pyridinonato)iron(III).[1299] Other reported crystal structures include those of tris(1-ethyl-2-methyl-3-hydroxy-4-pyridinonato)iron(III) trihydrate,[1303] tris(1-CH$_2$CH$_2$OMe-2-methyl-3-hydroxy-4-pyridinonato)iron(III),[1304] tris(1-(4′-methylphenyl)-2-ethyl-3-hydroxy-4-pyridinonato)iron(III),[1305] and the iron(III) complex of the hexadentate ligand (**247**).[1306]

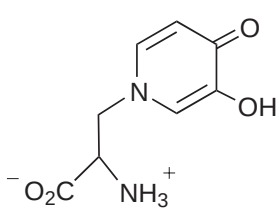
EXAFS studies on tris-maltolatoiron(III) in the solid state and in solution, and on [Fe(L1)$_3$] hydrate, pave the way for detailed investigation of the hydration of complexes of this type in aqueous media.[1307] Solubilities and transfer chemical potentials have been determined for tris-maltolatoiron(III) in methanol–water,[1308] and for tris-ethylmaltolatoiron(III) in alcohol–water mixtures[1309] and in isobutanol, 1-hexanol, and 1-octanol.[660] Solubility maxima in mixed solvents, indicating synergic solvation, is relevant to trans-membrane transport of complexes of this type. Solubilities of tris-ethylmaltolatoiron(III) and of [Fe(L1)$_3$] have been determined in aqueous salt solutions (alkali halides; NH_4^+ and NR_4^+ bromides).[1310]

Job plots have established the stoichiometry of several iron(III)-3-hydroxy-2-methyl-4(1*H*)-pyridinone systems in aqueous solution.[1311] Stability constants have been determined for 1,2-dimethyl-,[1312,1313] 1,2-diethyl-,[1314] and several other 3-hydroxy-4-pyridinonato-iron(III) complexes.[1304,1315,1316] These data supplement and update the long-standing set of log β_3 values for this type of complex.[1317] Tris(1,4-dihydroxy-2-pyridinonato)iron(III) and tris(1-hydroxy-4-methoxy-2-pyridinonato)iron(III) have stability constants (log β_3) similar to that for tris-maltolatoiron(III).[1318] Stability constants have also been measured for complexes of hydroxypyridinonate ligands from allomaltol (**234**) and pyromeconic acid (**237**).[1293] Stability constants for the iron(III) complexes of 1-hydroxy-2-pyridinonate (**239**), 3-hydroxy-2-pyridinonate (**240**), and 3-hydroxy-4-pyridinonate (**241**), are given by log $\beta_3 = 26.9$, 29.6, and 35.1, strongly favoring the 3,4-isomer. These values are of a similar order of magnitude to that for complexation of Fe^{3+} by the natural product mimosine ((**248**); log $\beta_3 = 34.8$[1319,1320]). They suggest that the effectiveness of hydroxypyridinones for sequestering iron(III) should lie between monohydroxamates and dicatecholates. However their relatively high acidities makes them relatively more effective than hydroxamates or catecholates at pHs in the vicinity of 7.[198] The stabilities of hexadentate complexes containing three 3-hydroxy-2-pyridinonate units (log $K_1 = 28.8$)[1321] are, surprisingly, lower than for their bidentate analogues (log $\beta_3 \sim 32$). Presumably there is a steric or conformational problem associated with binding all six donor atoms of the hexadentate ligand to the metal. A recent iron/aluminum comparison of stability constants[1322] collated log β_n ($n = 1$, 2, 3) values for the iron complexes of several 3-hydroxy-4-pyridinone ligands. The iron(III)-3-hydroxy-2-methyl-4-pyridinonate system has been used to demonstrate an improved approach to the calculation of stability constants and establishment of speciation diagrams using nonlinear regression analysis.[1323]

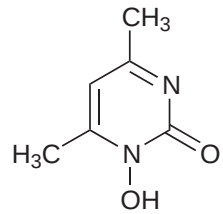
N-Hydroxypyrimidinones, e.g., (**249**), and *N*-hydroxypyrazinones, e.g., (**250**), form stable tris-ligand iron(III) complexes, but these are of much lower stability than iron(III) complexes of hydroxypyridinones. Stability can, as one would expect, be increased greatly by going to analogous hexadentate ligands containing three *N*-hydroxypyrimidinone or *N*-hydroxypyrazinone units.[1324]

Partition coefficients have been measured for tris-maltolatoiron(III) and tris-ligand complexes derived from a range of *N*-substituted 3-hydroxy-4-pyridinones,[1317] particularly (**251**) with R^1 and R^2 variously Me, Et, Pr,[1325,1326] and for a range of complexes with alkyl (up to *N*-butyl) or oxygen-containing (e.g., CH$_2$CH$_2$OH, CH$_2$CH$_2$OMe, CH$_2$CH$_2$CO$_2$Et) substituents on the ligand ring nitrogen.[1327] Partition coefficients vary over a very wide range, whereas stability constants are almost the same for practically all tris(3-hydroxy-4-pyridinonato)iron(III) complexes. Partition coefficients and stability constants for iron(III) complexes of bidentate *N*-alkyl and *N*-CH$_2$CONHR and two hexadentate derivatives of 3-hydroxy-2-pyridinones also show that solvation may be varied greatly with very small variation of stability.[1321] Partition coefficients of iron(III) complexes correlate well with values for the respective ligands, over a million-fold

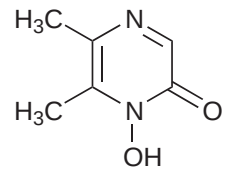
range for the complexes (all log β_3 values are between 36.8 and 37.2!),[1328] and with values for gallium(III) and indium(III) analogues.[1329]



(**248**)



(**249**)



(**250**)

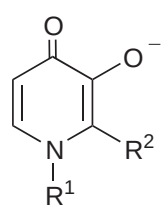
The effects of iron(III) complexation on electrochemical oxidation of 3-hydroxy-4-pyridinones has proved useful in elucidating oxidation mechanisms in these systems.[1330]

(i) Iron transfer and removal

The kinetics of removal of iron(III) from its complexes with the aminocarboxylate-anthraquinone analytical reagent calcein and with the antitumor anthracycline doxorubicin by 1,2-dimethyl-3-hydroxy-4-pyridinone (L1, (**251**) with $R^1 = R^2 = Me$) have been monitored. Rate constants for metal removal are almost independent of the concentration of the replacing ligand, indicating dissociative mechanisms; they are approximately 1×10^{-2} s^{-1} for displacement from doxorubin and between 12×10^{-2} s^{-1} and 2×10^{-2} s^{-1} from calcein.[1331]

1,2-Dimethyl-3-hydroxy-4-pyridinone,[1332] 1-methyl-3-hydroxy-2-pyridinone, and maltol (**233**) remove iron from transferrin at rather similar rates for both steps in these biphasic reactions, but the extent of iron removal is much greater for L1 than for the others.[1333] Iron is removed preferentially from the C-terminal site.[1334] This is consistent with the general pattern in the uptake of iron by and from transferrin,[1335] where there is a small but significant, and environment-affected, difference between the affinities for Fe^{3+} of the C- and N-terminal sites.[1336,1337] Although 1-hydroxy-2-pyridinones remove iron from transferrin (rate constants for these biphasic reactions were measured) neither 2-hydroxy-pyridine-*N*-oxide nor 2,4-dihydroxy-pyridine-*N*-oxide are as effective as the 3-hydroxy-4-pyridinones in competing with transferrin for iron(III).[1338,1339] Aminoalkyl phosphonic acid derivatives also remove iron from transferrin in biphasic processes.[1340]

An order of effectiveness has been established and a mechanism proposed for the removal of iron from ferritin by several 3-hydroxy-4-pyridinone chelators.[1341] The removal of iron from ferritin[1333] is, as one would expect, considerably slower than from calcein or doxorubicin (cf. above) or from transferrin. Rate constants are between 1.5×10^{-5} s^{-1} and 7.5×10^{-5} s^{-1} for removal of iron from ferritin by a series of hexadentate ligands each consisting of three substituted *N*-hydroxypyrimidinone or *N*-hydroxypyrazinone units, the rate decreasing with increasing substituent bulk. The slowest rate approximates to that for removal of iron from ferritin by desferrioxamine. The influence of chirality on the kinetic barrier provides insight into the detailed mechanism of removal in these systems.[1324] Slow removal of iron from ferritin by chelators should be contrasted with rapid reductive removal.[1342]



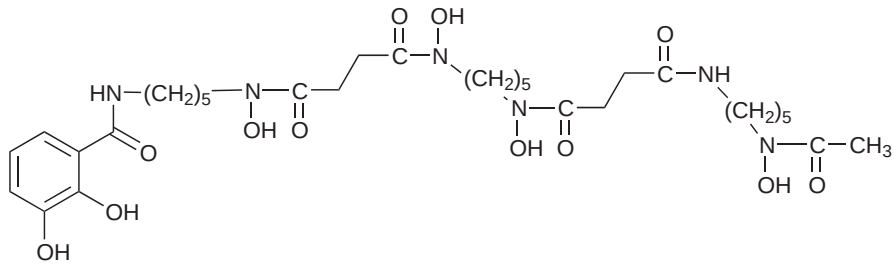
(**251**)

(ii) Analytical applications

An early application of 3-hydroxy-4-pyridinones was to the spectrophotometric determination of iron, either directly or by solvent extraction. More recently several compounds of this type have developed for the determination of, e.g., niobium[1343] and germanium,[1344] and for solvent extraction of, e.g., tungsten[1345] and tantalum,[1346,1347] but the ligands involved are all potentially useful for Fe^{3+}. The large number of other references to spectrophotometric determination, solvent extraction and separation using these ligands may be traced through the references cited in the preceding sentence.

5.4.5.6 Siderophores and Models

Siderophores[130] are iron transport agents, generally hexadentate chelate ligands of low molecular weight, produced by microorganisms to facilitate iron uptake. Their coordination chemistry, and kinetics and thermodynamics of iron chelation and release, have been reviewed.[174] Their ligating functions are hydroxamates and catechols — sometimes two, often three, units of one or the other, but occasionally both are present in one ligand. Thus catechol-derivatized desferrioxamines such as (**252**) offer Fe^{3+} a choice of binding sites. In practice they bind Fe^{3+} through all three hydroxamate units at low pH, but at higher pHs through two hydroxamates and a catechol.[1348] Occasionally carboxylate[1349] or hydroxycarboxylate[259] is present in addition to catechol units, while an amine–amide–hydroxamate combination reportedly has strong complexing ability.[1350] A review on the chirality of metal centers has a number of examples from iron(III)–catechol and iron(III)–hydroxamate systems.[1351] A host–guest supramolecular assembly of ferrioxamine with lariat ether carboxylic acids can be regarded as a model for siderophore–receptor interaction and recognition at a membrane site.[1352]

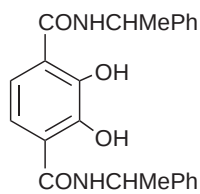


(**252**)

5.4.5.6.1 Catechols

(i) Monocatecholates

Diastereomeric distributions (Δ:Λ) in several tris-ligand Fe^{3+} complexes of chiral catecholamide and terephthalamide ligands have been established in solution by CD and ^1H NMR spectroscopies. The complex of (**253**), whose structure in the solid state was determined, exists wholly in the Λ conformation in aqueous solution. Weak polar interactions determine conformational preferences here.[1353]



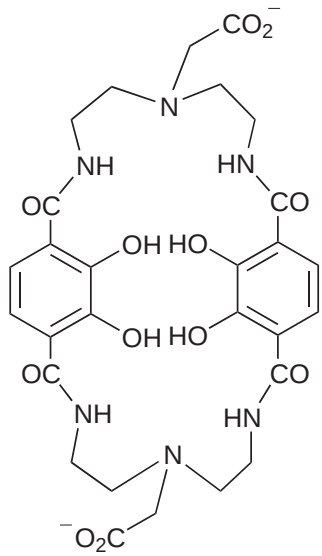
(**253**)

Alterobactin A is a cyclic mono-catechol-bis-hydroxycarboxylate bacterial siderophore with an extremely high affinity for iron(III) (see Table 12). On hydrolysis (in the absence of iron) it gives an acyclic derivative which forms a bis-ligand iron(III) complex.[259]

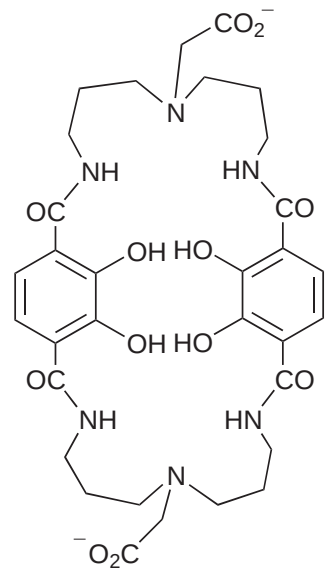
(ii) Biscatecholates

Stability constants for the Fe^{3+} complexes of the bis-catecholate ligands (**254**) and (**255**) are $\log_{10}K_1 = 37.6$ and 36.0, respectively.[963] Rate constants for complex formation between Fe^{3+}aq and two synthetic chelators of the dicatecholspermidine family are, at $450\,M^{-1}s^{-1}$ and $500\,M^{-1}s^{-1}$,[1354] similar to that for desferrioxamine.

When four Fe^{3+} ions are assembled with the aid of six bis-catecholate ligands into a tetrahedral assembly then the rigidity of the resultant species is such that it is very reluctant to racemize. Extrapolation from data on the Ga^{3+} analogue suggests a half-life of months.[1355]



(**254**)

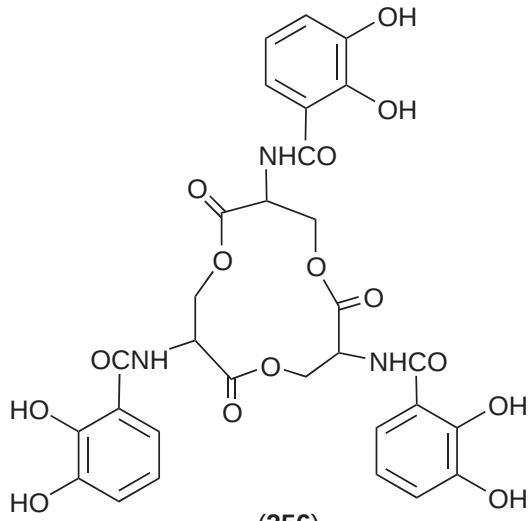


(**255**)

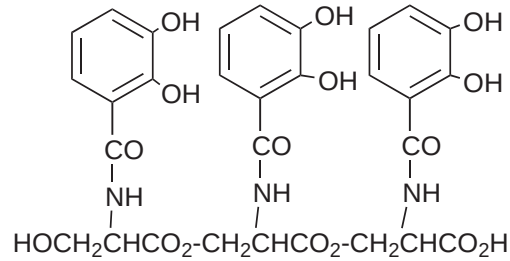
(iii) Triscatecholates

It is often difficult to measure stability constants directly for Fe^{3+} complexes of natural and model siderophores, since their very high stabilities mean there is extremely little free Fe^{3+} in equilibrium with the complex. It is therefore common to use the link between redox potentials and stability constants in the two oxidation states involved in estimating values for $\log K_{Fe^{III}L}$. The correlation of $\log K_{Fe^{III}L}$ with redox potential, established over a range of 10^{19} in $K_{Fe^{III}L}$,[1356] can thus prove useful in estimating such stability constants. Enterobactin (**256**), the key natural siderophore of maximum complexing power for Fe^{3+}, has presented considerable difficulties in respect of determining $K_{Fe^{III}L}$. An improved estimate of K_1 of 10^{49} (for formation of $[Fe(ent)]^{3-}$) was made in 1991.[1357] Stability constants for Fe^{3+} complexes of the enterobactin hydrolysis products the linear *N*-(dihydroxybenzoyl)serine linear trimer (**257**) and its dimer analogue are 10^{43} and 10^{36}, respectively. Enthalpies of formation for the Fe^{3+} complexes of the trimer and of enterobactin are reported.[1358] Linear hexapeptides and decapeptides bearing catechol units derived from dopa (dihydroxyphenylalanine) form stable complexes with Fe^{3+}, with stability constants in the range 10^{38}–10^{40}.[1356]

The tripodal tris-catechol ligand trencam, (**258**), is an enterobactin analogue and is very specific for Fe^{3+} compared with Fe^{2+}, as is reflected in the reduction potential of −1.04V (vs. NHE; for Fe/enterobactin −0.99V). The stability constant for [Fe(trencam)] is $10^{43.6}$.[1359] The macrobicyclic tris-catechol encapsulating ligand (**259**) can be prepared by high dilution techniques; its analogue (**260**) can be prepared much more easily on an Fe^{3+} template.[1360] The Fe^{3+} is, very unusually for this cation, in a trigonal prismatic environment.[1361] Surprisingly, the stability constant for the

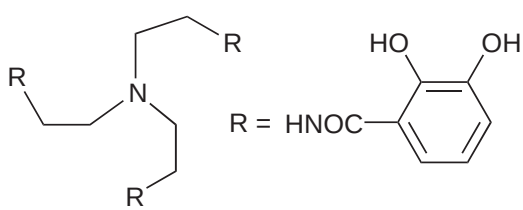


(**256**)

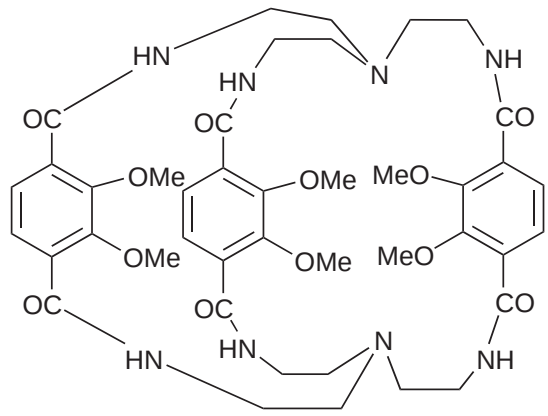


(**257**)

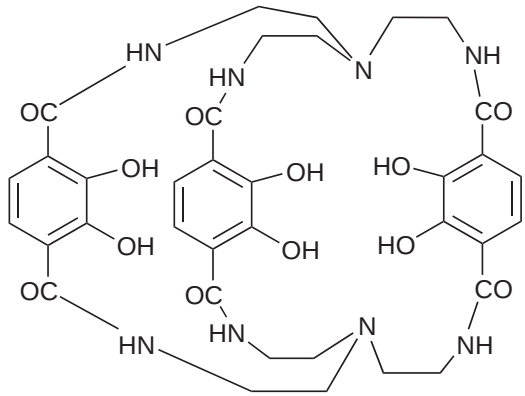
Fe^{3+} complex of bicapped trencam, (**260**), is no higher ($K = 10^{43.1}$) than that for [Fe(trencam)].[1362] The trianionic tris-catecholate tripodal ligands from (**261**)[1363] and (**262**)[1364] are also enterobactin analogues, though their Fe^{3+} complexes do not have quite as high stability constants as Fe^{3+}-enterobactin. The complex of (**262**) is chiral, with the same configuration, Δ-*cis*, as natural Fe^{3+}-enterobactin. The absolute configuration of the Fe^{3+} complex of (**263**) is controlled by the chirality of the alanine residues therein — L-ala gives Λ, D-ala Δ. The stability constant of the complexes of (**263**) and (**264**) are $>10^{41}$ and 10^{38}, respectively.[1365] Variation of the groups R^1 and R^2 in (**265**) has a large effect on their hydrophilic/lipophilic properties and those of their deep red Fe^{3+} complexes. For $R^1 = R^2 = H$ the Fe^{3+} complex partitions effectively completely into water, for $R^1 =$ *n*-decyl into an organic layer. For $R^1 = R^2 = H$ the complex is achiral, but the other three complexes are chiral. The steric effects which induce chirality also reduce stability—the complex with $R^1 = R^2 = H$ is two orders of magnitude less stable than those with $R^1 = H$ or *n*-decyl, $R^2 = Ph$.[1366] The geometry of the cavity of the tris-catechol cage (**266**) is appropriate for the encapsulation of Fe^{3+},[1367] indeed the stability constant for formation of the iron(III) complex is exceptionally high, being approximately 10^{59}.[130] Increasing the size of the cavity, for example by replacing the (**267**) caps of (**266**) by (**268**) or (**269**), reduces the stability dramatically, though the complexes are still very substitution-inert.[1368] The properties of the Fe^{3+}-(**266**) complex have been compared with those of its nonencapsulated analogue Fe^{3+}-(**270**).[1369] Reaction of the tris-catecholatoiron(III) complex of (**271**) with poly(ethylene imine) gives a bicapped cage complex with log $K > 31$ at pH 7.[1370]



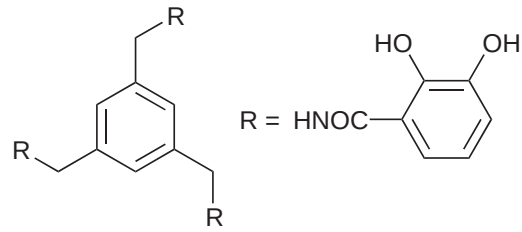
(**258**)



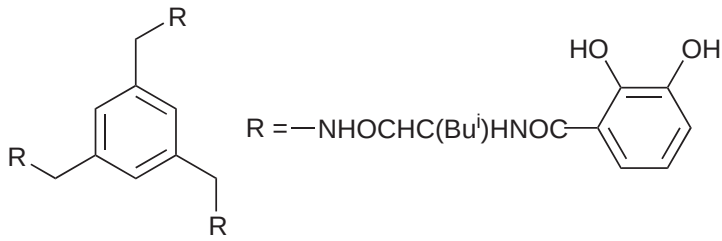
(**259**)



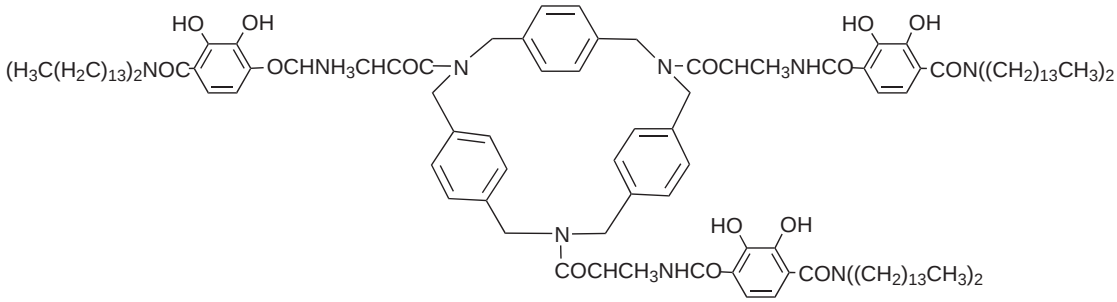
(**260**)



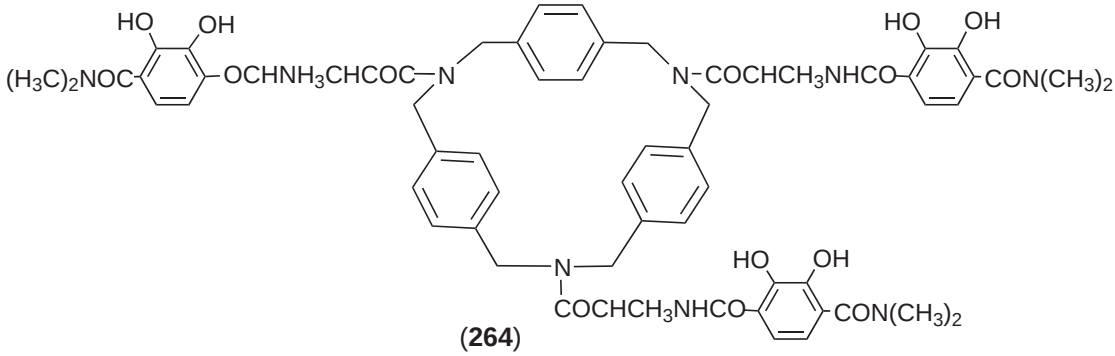
(**261**)



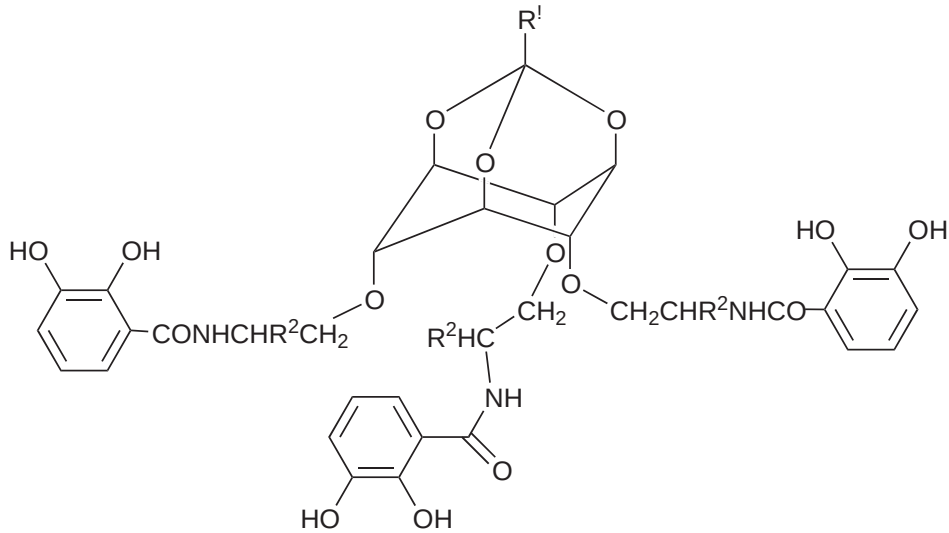
(**262**)



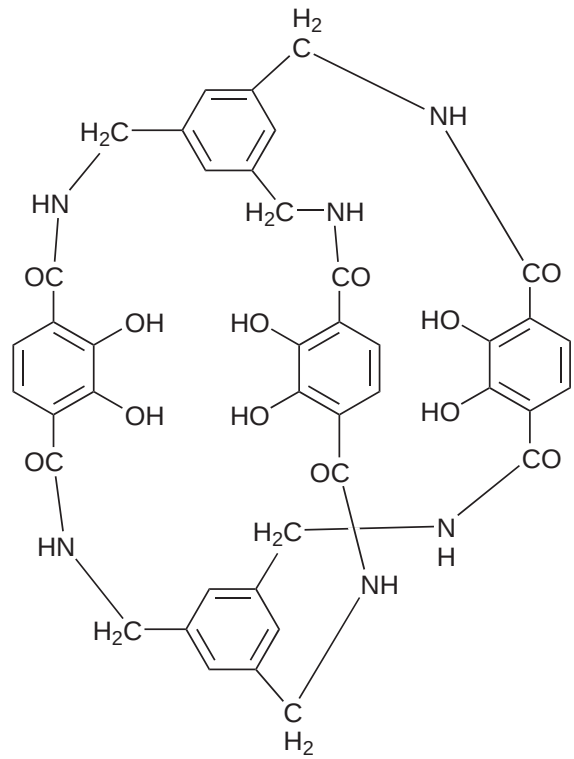
(**263**)



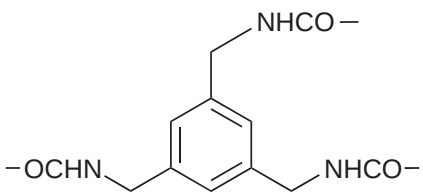
(**264**)


R1
O
O
O
O
HO
OH
CONHCHR2CH2
O
R2HC
CH2
O
CH2CHR2NHCO
HO
OH
NH
O
HO
OH

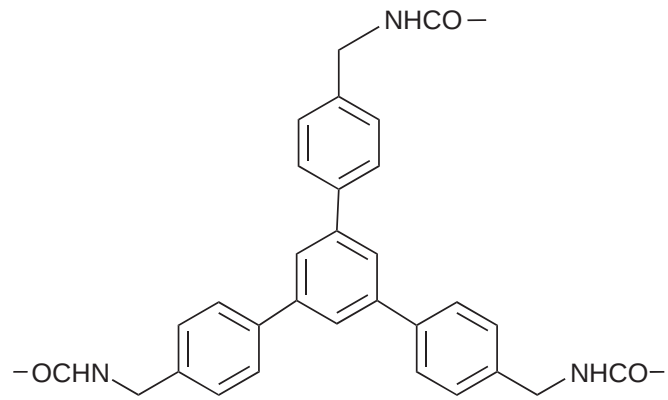
(**265**)


H2C
NH
H2C
HN
H2C
NH
OC
CO
CO
OH
HO
HO
OH
HO
HO
OC
CO
OC
H2C
N
H
HN
NH
H2C
C
H2

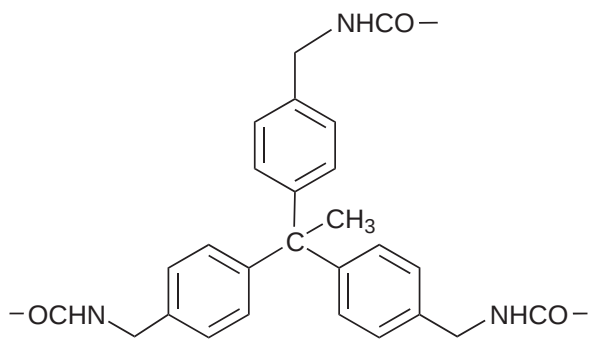
(**266**)



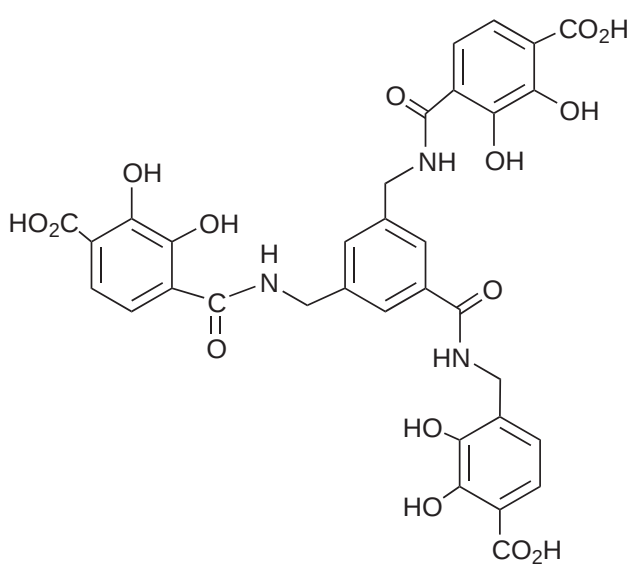
(**267**)



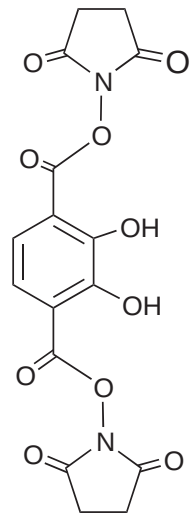
(**268**)



(**269**)



(**270**)

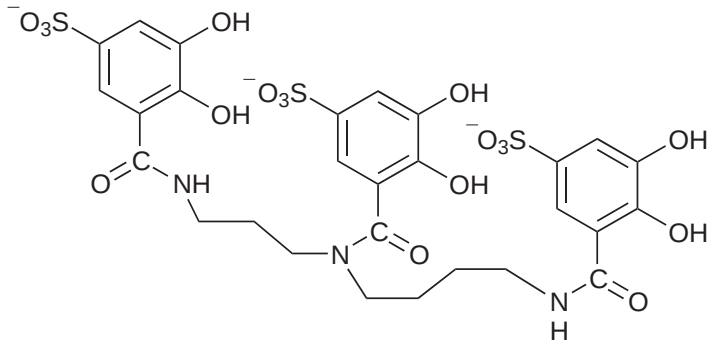


(**271**)

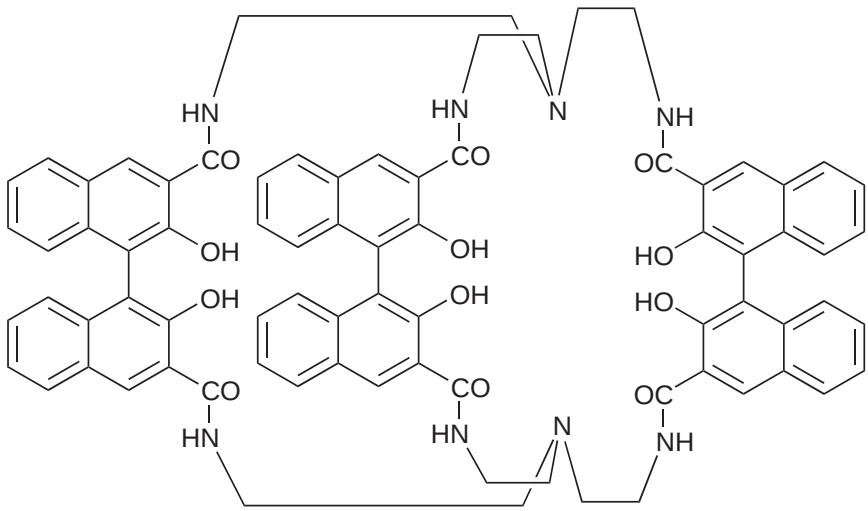
Biphasic kinetics were observed for the removal of iron from ferritin by licams, *N*,*N*′,*N*″-tris (5-sulfo-2,3-dihydroxybenzoyl)-1,5,10-triazadecane (**272**) – Fe^{3+} is removed from the N-terminal site about twice as fast as from the C-terminal site ($E_a \sim 80\,kJ\,mol^{-1}$ for the latter process). It is

thought that the N-terminal site may have to undergo a conformational change before releasing its Fe^{3+}.[1371] A catechol derivative of desferrioxamine has been found to remove iron from transferrin about 100 times faster than desferrioxamine itself; it forms a significantly more stable product with Fe^{3+} (at pH 7.4).[1348] The effects of desferrioxamine and of iron(III) ammonium citrate on the two mechanisms of iron uptake from transferrin have been described.[1372]

The bicapped tris-binaphthol (**273**), and its earlier-synthesized tris-biphenol analogue,[1373] are closely related to tris-catechol cages. The Fe^{3+} complex of (**273**) exists in Δ and Λ forms, derived from the two enantiomers—the six hydroxy groups impose helical chirality.[1374]



(**272**)



(**273**)

(iv) Polycatecholates

Several macrocyclic polycatechols, with up to six catechol units incorporated into the ring, have been designed for possible treatment for iron overload and were prepared using high dilution techniques. They form stable iron(III) complexes; the complex with the three-catechol ring as ligand has log $K = 38.7$.[1375]

5.4.5.6.2 Hydroxamates

Biomimetic iron(III) tris-hydroxamates (diferric helices) have been reviewed briefly.[1376]

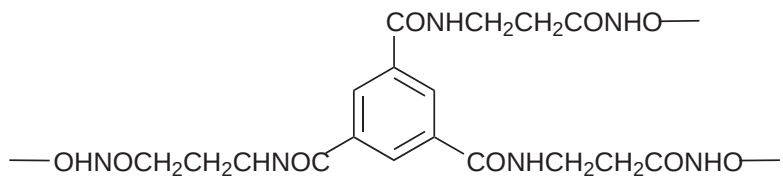
Crystals of the iron(III)–acethydroxamate complex $[Fe(ahdx)_3]\cdot 1.5H_2O$ contain one molecule of the *fac* isomer and one of the *mer* per unit cell,[1377] whereas the benzhydroxamate $[Fe(bhdx)_3]\cdot 3H_2O$ crystallizes simply as the *fac* isomer.[1378]

Iron(III) complexes of aminomonohydroxamates $H_2NCH(R)CONHO^-$ (R = H, Me) and $XC_6H_4CONHO^-$ (X = *o*-NH_2, *p*-NH_2) and dihydroxamates $(CH_2)_n\{CON(R)O^-\}$ (n = 2, 3, 4, 6, 8; R = H, Ph, *o*-tolyl, *p*-tolyl) have been synthesized. The monohydroxamates give mononuclear complexes $[FeL_3]$ or binuclear complexes $[Fe_2(OH)_4L_2(H_2O_2)]$, the dihydroxamates three types of binuclear complex, $[Fe_2(LH)_2L_2]$, $[Fe_2OL_2]$, and $[Fe_2L_3]$.[1379]

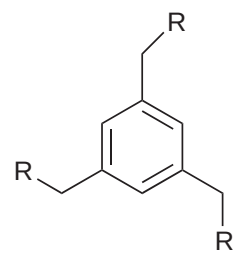
Stability constants of acethydroxamates of Fe^{3+} are available.[198,1312] Three iron(III)–acethydroxamate complexes have been identified in DMF solution.[1146] Solvation of several tris-hydroxamatoiron(III) complexes has been monitored in aqueous methanol and in aqueous *t*-butyl alcohol. The transfer chemical potential trends strongly reflect the overall HLB of the complexes.[1380]

Kinetic and equilibrium data are available for complex formation between iron(III) and 4-$MeOC_6H_4C(O)N(O^-)H$. The formation mechanism is believed to be I_a (associative interchange) both from Fe^{3+}aq and from $FeOH^{2+}$aq. The unusual situation of associative substitution at $FeOH^{2+}$aq here is explained by favorable hydrogen-bonding interactions.[1381] Formation of L-lysinehydroxamato–iron(III) complexes also occurs by an interchange mechanism; formation and dissociation (acid-catalyzed) are significantly affected by charge repulsion (the ligand is $H_3N^+(CH_2)_4CH(NH_3^+)CON(O^-)H$).[1382]

Trihydroxamate analogues of ferrichrome have been synthesized by attaching three succinylhydroxamate moities to a triamine apex. The stability constants of the Fe^{3+} complexes of $N\{CH_2CH_2NHCOCH_2CH_2CON(O^-)C_6H_4\text{-}4\text{-}Me\}_3$,[1383] of $N\{CH_2CH_2NHCOCH_2N(O^-)COMe\}_3$[1384] and of $N\{CH_2CH_2CH_2NHCOCH_2N(O^-)COMe\}_3$[1385] are given by log K = 32.9, 28.7, and 30.6, respectively. Thus these complexes are much more stable than that of (**274**),[1386] for which log K = 26.3—this lower stability is ascribed to the rigid benzene ring of (**274**) making it more difficult for this ligand to interact strongly with the Fe^{3+} at all six donor sites. The similar, but more flexible, tripodal ligand (**275**) forms an Fe^{3+} complex with log $K \sim 28$.[564] Rate constants for incorporation of Fe^{III} into tripodal hydroxamates containing [Ala–Ala–β-(HO)Ala] and [Ala–Ala-β-(HO)Ala]$_2$ units, and of Fe^{III} displacement of Al^{III}, Ga^{III}, or In^{III} from their respective complexes with these tripodal ligands, have been determined. The M^{III}-by-Fe^{III} displacement processes are controlled by the ease of dissociation of Al^{III}, Ga^{III}, or In^{III}; Fe^{III} may in turn be displaced by from these complexes by edta (removal from the two nonequivalent sites gives rise to an appropriate kinetic pattern).[1387] Chloride and, to lesser extents, bromide and nitrate, catalyze dissociation of model siderophore–hydroxamate iron(III) complexes through transient coordination of the added anion to the iron.[1388] The stability constants for the iron(III) and iron(II) complexes of a recently synthesized saccharate-based trihydroxamate analogue of ferrichrome are 31.9 and 12.1, respectively. The pFe value (see Section 5.4.5.6.3 below) for the iron(III) complex indicates that this trihydroxamate should be able to remove iron from ferritin.[1389]



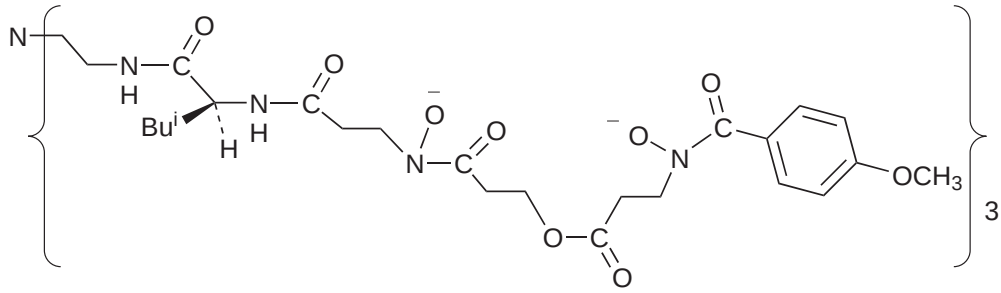
(**274**)



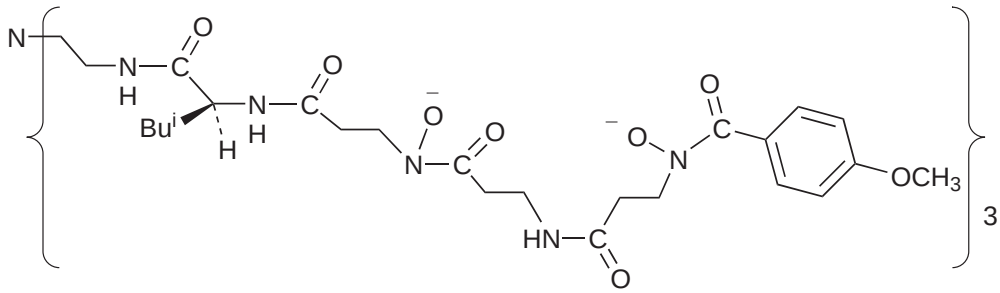
R = $NHCOCH_2CH_2N(O^-)COPh$

(**275**)

Asperchromes are, like ferrichromes, iron chelators with a cyclic hexapeptide backbone—the iron(III) coordination geometry in asperchrome chelates is the same as in ferrichrome chelates.[1390] The tripodal hybrid tris-hydroxamate/peptide ligands (**276**) and (**277**) react with Fe^{3+} to form binuclear triple helical complexes. These helices are stabilized by intra-strand hydrogen-bonding, as established in a comparison with hydroxamate-OH replaced by -OBz. The modest difference between (**276**) and (**277**) is sufficient for the former to give a Λ-*cis* left-handed helix, the latter a right-handed helix and in the Δ-*cis* configuration.[1391] The tris-hydroxamate tripodal ligand $EtC\{CH_2OCH_2CH_2$-$CONHCH(^iBu)CON(O^-)Me\}_3$ is a chiral ferrichrome analogue; its Fe^{3+} complex has the Λ-*cis* configuration, as does the natural complex (contrast natural Fe^{3+}-enterobactin, which is Δ-*cis*).[1392]



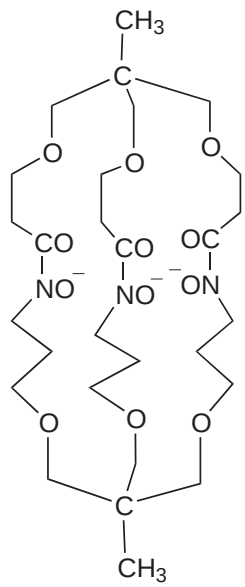
(**276**)



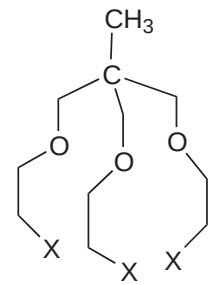
(**277**)

Relative reduction rates of ferrioxamine, hexacyanoferrate(III) and iron(III) complexes of edta and citrate by ferri-reductase have been established.[1393]

The tris-hydroxamate encapsulating ligand (**278**) can be assembled by high dilution acylation of (**279**) with X = NHOBz by (**279**) with X = COCl, followed by removal of the benzyl protecting



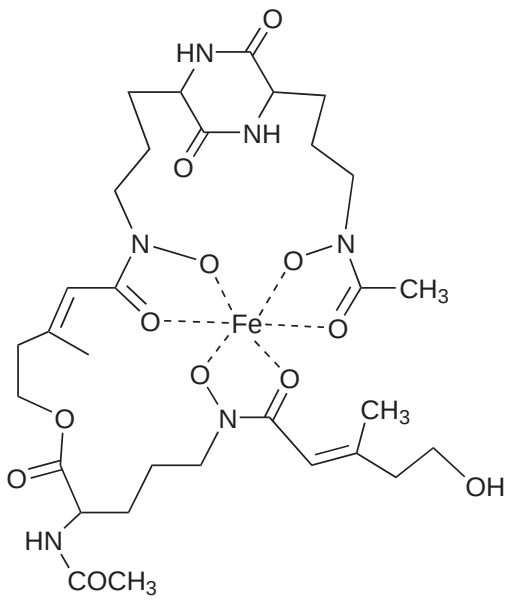
(**278**)



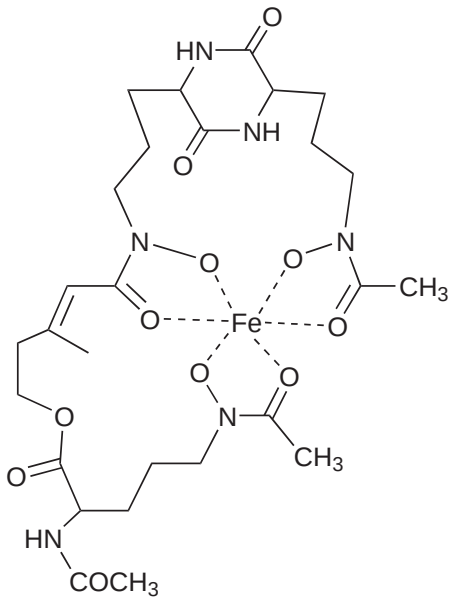
(**279**)

group.[1394] The hydroxamate units of (**278**) are endocyclic and its cavity is sufficiently large that it can act as a cryptand siderophore and form a stable Fe^{3+} complex. This has visible absorption characteristics very similar to those of the Fe^{3+} complex of desferrioxamine ($\varepsilon_{423} = 4{,}700$ for Fe^{III}(**278**), $\varepsilon_{440} = 2{,}640$ for Fe^{III}(dfo)[1395]).

The first of the coprogens (fungal "sideramines") was reported in 1973.[1396] Neocoprogen I (**280**) and neocoprogen II (**281**) are linear tris-hydroxamate siderophores whose chelating groups are derived from *N*-hydroxy-*N*-acylated ornithines. Neocoprogen I is the first structurally established example of a *trans* tris-hydroxamate siderophore.[1397] Subsequent studies have dealt with dimethylcoprogens,[1398] with hydroxycoprogens,[1399] and with connections between coprogens, fusarinines, and dimerumic acid (see next paragraph).[1400]

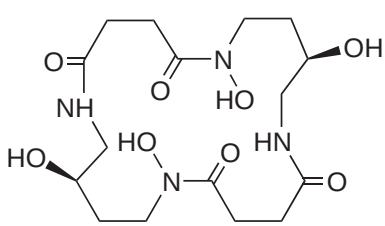


(**280**)

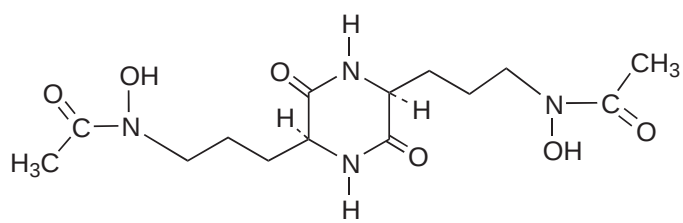


(**281**)

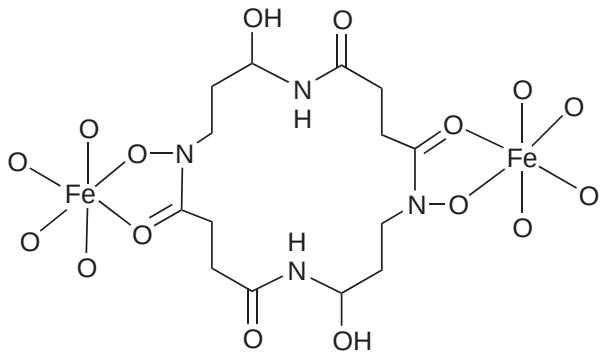
Iron(III) complexes of synthetic dihydroxamates of 1:1 stoichiometry may be monomers or dimers depending on the length of the spacer between the two chelating entities.[1401] Alcaligin, $alcH_2 =$ (**282**),[1402] is a dihydroxamate siderophore which readily forms binuclear complexes $[Fe_2(alc)_3]$ at pHs in the region of 7; mononuclear $[Fe(alc)]^+$ is formed at pH 2—behavior analogous to that of rhodotorulic acid (**283**). The binuclear complex has one ligand bridging the two Fe^{3+} ions, the others binding just one Fe^{3+} each (**284**).[1403] Kinetic patterns for the proton-driven dissociation of iron(III) from mononuclear and binuclear complexes of the tetradentate dihydroxamate siderophores alcaligin (cyclic) and rhodotorulate (linear) have been compared with each other and with the analogous process for the iron complex of desferrioxamine. The high degree of organization of alcaligin (alc) has a marked effect on the dissociation kinetics of $[Fe_2(alc)_3]$, and causes dissociation of mononuclear $[Fe(alc)(H_2O)_2]^+$ to be very slow ($\tau_{1/2}$ is a matter of hours).[1404] Dimerumate, the diketopiperazine–dihydroxamate ligand (**285**), also forms a binuclear iron(III) complex $[Fe_2(\mathbf{285})_3]$, which exists predominantly in the Δ form; for analogous *cis*- and *trans*-fusarinine complexes the Λ form is slightly favored.[1405] Fungal uptake of iron by these siderophores has been monitored by the use of ^{55}Fe.[1406]



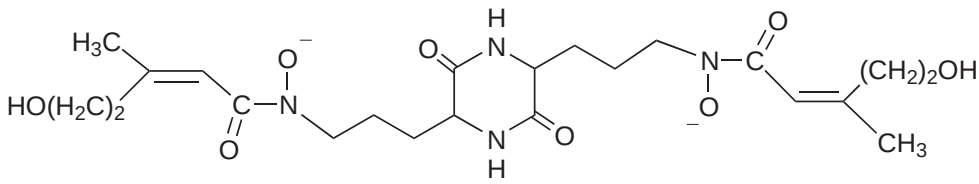
(**282**)



(**283**)



(**284**)

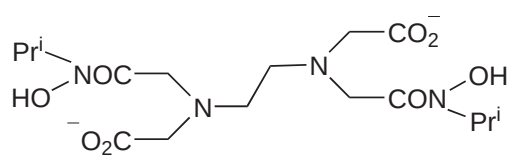


(**285**)

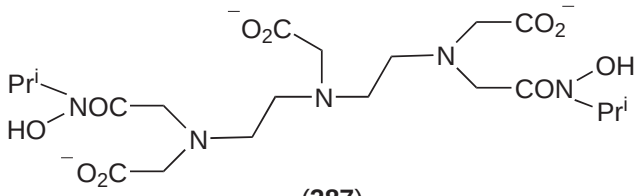
The stability constants for Fe^{3+} complexes of the dihydroxamate derivatives of edta (**286**) and of dtpa (**287**), $\log K_1 = 30.2$ and 29.7, respectively, are considerably higher than usual for Fe^{3+}-dihydroxamate complexes.[951] Stability constants for the binuclear complexes of amide-linked dipodal dihydroxamates such as $H_3CCH\{CONHCH_2CH_2NHCOCH_2CH_2N(O^-)COMe\}_2$ are large ($\log \beta_{230} \sim 59$, equivalent to $\log K_1 \sim 20$; $pFe \sim 21$) somewhat less than that for the Fe^{3+} complexes from rhodotorulic acid (**283**) and of four ligands $RN(O^-)CO(CH_2)_nCON(O^-)R$ (all five have $\log \beta_{230} \sim 62$), which in turn are slightly less than that for the Fe^{3+} complex of the natural cyclic dihydroxamate siderophore alcaligin ($\log \beta_{230} = 64.7$).[1407]

A multiple-path mechanism has been elaborated for dissociation of the mono- and binuclear tris(hydroxamato)–iron(III) complexes with dihydroxamate ligands in aqueous solution.[1408] Iron removal by edta from mono-, bi-, and trinuclear complexes with model desferrioxamine-related siderophores containing one, two, or three tris-hydroxamate units generally follows first-order kinetics though biphasic kinetics were reported for iron removal from one of the binuclear complexes. The kinetic results were interpreted in terms of discrete intrastrand ferrioxamine-type structures for the di-iron and tri-iron complexes of (**288**).[1409] Reactivities for dissociation, by dissociative activation mechanisms, of a selection of bidentate and hexadentate hydroxamates have been compared with those of oxinates and salicylates.[921]

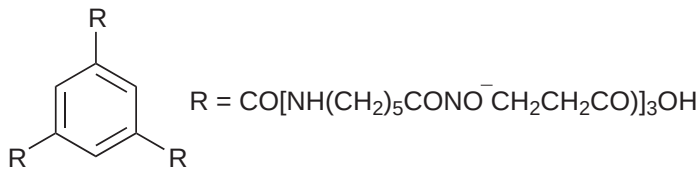
The marine siderophore aquachelin has two hydroxamate and one $—CH(O^-)CO_2^-$ chelating units. Photolysis of its iron(III) complex results in dechelation of the hydroxycarboxylate moiety and reduction to iron(II).[260]



(**286**)



(**287**)

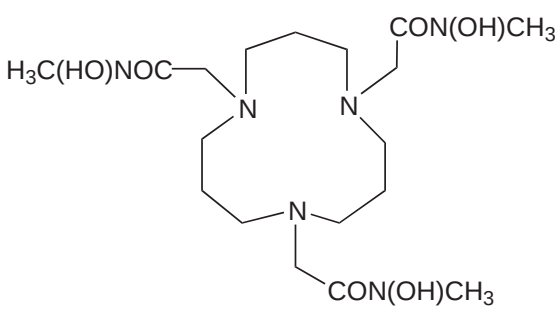


(**288**)

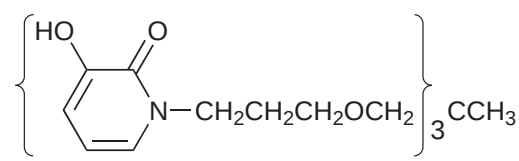
5.4.5.6.3 Comparisons

Stability constants for iron(III) complexes of a selection of natural and model siderophores and iron(III) chelators[1312] are collected in Table 12, together with values for a few simpler ligands for comparison. This table also gives pFe values for some systems — pFe is the negative decadic logarithm of the concentration of free iron(III) present in a system containing total iron(III) and total ligand concentrations of 10^{-6} and 10^{-5} mol dm^{-3}, respectively, at pH 7.4. pFe values provide a more relevant guide than stability constants to the effectiveness of chelators under physiological conditions, and a better means of comparison of bidentate and hexadentate ligands. The extensive comparison of different types of iron(III) chelators mentioned in Section 5.4.1.11.3 details pFe values rather than stability constants.[186]

Table 12 provides comparisons between some of the various catecholate, hydroxamate, hydroxypyranone and hydroxypyridinone chelators mentioned in Sections 5.4.1.11.3, 5.4.5.5.2, and 5.4.5.5.3 (where formulas and references may be found). It also includes data for the tris-hydroxamate-triazacyclododecane tripod dotrmaha (**289**), the tris-hydroxamate tripod trispyr[1410] (**290**) and tris-catechol tripod caccam[1349] (**291**) whose flexible arms permit strong chelation, two hydroxyquinoline chelators, trensox,[1411] (**292**) and trenpypols[1412] (**293**), the tetra-hydroxamate tripod cdtmaha (**294**), designed for chelating eight-coordinate actinides but effective also for Fe^{3+},[1413] and hopobactin,[1414] which is a hydroxamate analogue of enterobactin. The much lower values for iron(II) complexes of some of these ligands have been determined.[1411,1415]



(**289**)

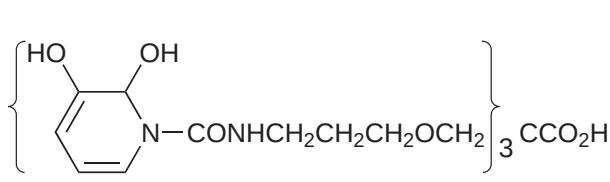


(**290**)

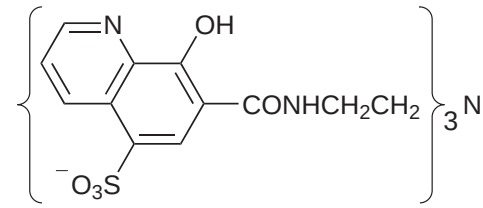
Table 12 Stability constants for iron(III) complexes of natural and model siderophores.

	Ligand type	*log* K_1/β_3	*pFe*
Natural siderophores			
Enterobactin (**256**)	cat_3tripod	49–52	36
Alterobactin	cat_3tripod	49–53	
Ferrichrome A	hdx_3tripod	29–32	25
Desferrioxamine B (**22**)	hdx_3tripod	31	27
Transferrin		34[a]	24
Synthetic catechols			
tris-catechol cage (**266**)	Cage	59	
bicapped trencam (**260**)	Cage	43	
trencam (**258**)	Tripod	43–44	28
caccam (**291**)	Tripod	43	28
licams (**272**)	Tripod	41	29
bis-catechols (**255**), (**254**)	Macrocycles	36, 38	
dimer, trimer (**257**)	Linear	36, 43	
Synthetic hydroxamates			
Cdtmaha	Tripod	48.2	
Trispyr	Tripod	37.6	
tripods (**275**), (**274**)	Tripods	26, 28	
Dotrmaha	Tripod	24.2	
dihydroxamates of edta, dtpa (**286**), (**287**)	Linear	30, 30	
Hydroxypyranones and hydroxypyridinones			
Ethylmaltolate		28	
3-Hydroxy-2-pyridinonates			
Bidentates		29–32	
Hexadentates	Tripod	28–29	25
3-Hydroxy-4-pyridinonates		35–37	19–22
Other synthetic siderophores			
trensox		31	30
Trenpypols		30	24
Glucopyranoside ferrichrome		32	27
Simple ligands			
Catechol		44.9	15.1
hbedda[b]		39.7	
dtpa		28.0	24.6
Acethydroxamate		28.3	12.5
edta		12.2	

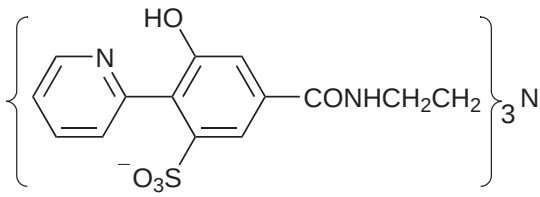
[a] For binuclear $[Fe_2(tf)]$. [b] hbedda = *N*,*N*′-di(hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetate.
Sources, most ligand abbreviations, and formula as indicated will be found in the text, in Sections 5.4.5.5.2 and 5.4.5.6.



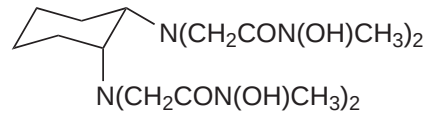
(**291**)



(**292**)



(293)



(294)

5.4.5.7 Other *O*-donor Ligands

Tris-carbamato–iron(III) complexes $[Fe(O_2CNR_2)_3]$ have been prepared for R = ethyl, isopropyl, cyclohexyl (cx), and benzyl, and binuclear μ-oxo derivatives (for R = Et, cx) and various μ_3-oxo, μ_4-oxo, and μ-carbamato polynuclear complexes also obtained.[1260] Iron(III) chloride reacts with potassium 2-propanenitronate, K(pn), to give $[Fe(Me_2C{=}NO_2)_3]$ (mean Fe—O = 2.019 Å, mean bite angle 66.0 Å), which in ethanol gives binuclear $[(pn)_2Fe(\mu\text{-}OEt)_2Fe(pn)_2]$.[1105]

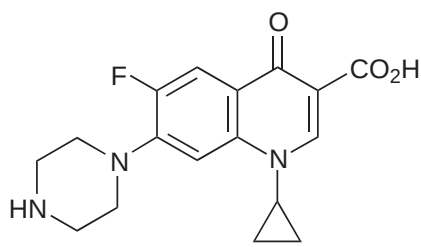
Reaction of $K[FeZr_6Cl_{15}]$[1416] with thiocyanate in the presence of 18-crown-6 gave, most unexpectedly, $[K_4(FeCl_4)(18\text{-crown-}6)_4][Fe_4S_4Cl_4]$. Stabilization by the crown ether is the key to the supramolecular cation.[1417]

In the presence of Fe^{3+} it is possible to deprotonate polyphenols at physiological pHs, to give phenolates which are good ligands for hard 3+ cations such as Fe^{3+}. Speciation in iron(III) — polyphenolate systems has been discussed in relation to possible use of these ligands as iron chelating agents.[1418]

The first reported low-spin iron(III) semiquinonate complex contained the 3,5-di-*t*-butyl-1,2-benzoquinonate radical anion and a tetraazamacrocycle (tazm). It reacts reversibly with acetonitrile to give $[Fe^{II}(tazm)(MeCN)_2]^{2+}$ plus 3,5-di-*t*-butyl-1,2-benzoquinone.[1419] The related 1,2-iminobenzosemiquinonate (ibsq) complexes $[Fe(ibsq)_2X]$ have $S = 5/2$ for X = Cl and $S = 3/2$ for X = I; the complex with X = Br is a mixed spin ($S = 5/2$, 3/2) species.[1420]

Varying the nature of the substituents in calixarenes determines the stabilization of iron(II) vs. iron(III). The calixarene with one —OH and three $—OCH_2CONEt_2$ groups acts as a heptadentate ligand towards Fe^{3+}. The metal is seven-coordinate, with Fe—O distances ranging from 1.792 Å for the phenoxide oxygen to 2.495 Å.[129]

The fluorinated 4-quinoline antibiotic ciprofloxacin (**295**) is known to interact with iron-containing drugs and mineral supplements. Stability constants have been determined for complex formation of iron(III) with ciprofloxacin, presumably acting as a bidentate *O*,*O*-donor, in aqueous[1421] and in micellar media.[1422]



(295)

5.4.5.8 *O*,*S*-donor Ligands

Dithioxalate acts as a bridging ligand in the mixed valence salt $Pr^n{}_4N[Fe^{II}Fe^{III}(dto)_3]$,[60] whose spin properties[61] are most unusual (see Section 5.4.1.4).

Kinetic and equilibrium data are available for complex formation between iron(III) and $4\text{-}MeOC_6H_4C(S)N(O^-)H$, a system studied in relation to the possibility that some natural siderophores may bind iron through a thiohydroxamate moiety. The Fe^{3+} complex of this

thiohydroxamate ligand is more stable, at physiological pH, than that of its parent hydroxamate, 4-$MeOC_6H_4C(O)N(O^-)H$.[1381]

5.4.5.9 Sulfur Donors

5.4.5.9.1 Mononuclear species

$Ba[Fe(SCH_2CH_2OH)_4]$ has been prepared and its crystal structure established, and ESR and Mössbauer spectra of the $[Fe(SCH_2CH_2OH)_4]^{2-}$ anion obtained in solution.[1423]

Solubility products have been obtained for iron(III) xanthates.[1424–1426]

Iron(II)-*S*,*S*-dithiophosphate complexes tend to be unstable with respect to oxidation to iron (III), but 1,10-phenanthroline stabilizes iron(II) in the di-isopropyldithiophosphate complex $[Fe\{S_2P(OPr^i)_2\}_2(phen)]$.[1427]

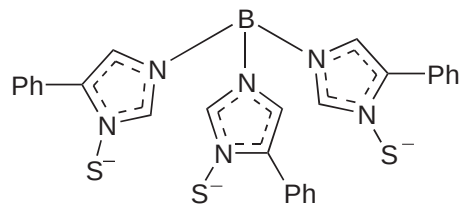
Tris(*N*-alkylcyclohexyldithiocarbamato)iron(III) complexes have been synthesized and characterized.[1428] Tris(di-*N*-alkyldithiocarbamato)iron(III) complexes, $[Fe(S_2CNR^1R^2)_3]$, and their piperidyl and pyrrolidyl analogues, have various modes of thermal decomposition, depending on the nature of the groups on the nitrogen.[1429] Both tris(*N*,*N*-dialkyldithiocarbamato)iron (III)[1430] and tris-(*N*-alkyl,*N*-hydroxyethyl-dithiocarbamato)iron(III) complexes, $[Fe\{S_2CN(R)CH_2CH_2OH\}_3]$,[1431] are spin cross-over species, with high- and low-spin forms both present in equilibrium at room temperature. On heating they decompose, in two stages, to give Fe_2O_3 as final product. $[Fe\{S_2CN(CH_2CH_2OH)_2\}_3]$ and its trihydrate, whose ESR and Mössbauer spectra have been described,[1432] provide the first examples of dithiocarbamato–iron(III) complexes where the spin interconversion rate is similar to the reciprocal of the Mössbauer timescale (all previously studied iron tris-dithiocarbamates have interconverted at rates that are fast on the Mössbauer timescale)—for the trihydrate the upper limit for the rate constant is $10^7\ s^{-1}$.[1433] In solution bis(2-hydroxyethyl)dithiocarbamate forms stable 1:1 and 2:1 complexes with Fe^{3+} ($\log K_1 = 5.7$, $\log K_2 = 4.8$), but interference with formation of the 3:1 complex ($\log K_3 \sim 5.8$) arises from facile reduction of the metal in the 2:1 complex, which has a half-life of about 5 minutes.[1434] Molecular modeling predictions of activation energies for the Bailar and Rây-Dutt twists for racemization of $[Fe\{SCN(CH_2)_4\}_3]$ indicate that the former mechanism should operate,[580] as deduced many years ago from comparisons of racemization rates with rates for *fac* ⇌ *mer* isomerization for tris-dithiocarbamate complexes.

Magnetic moments, derived from NMR measurements, have been tabulated for a series of trisdithiocarbamatoiron(III) complexes $[Fe(S_2CNR_2)_3]$, to show the gradual changeover from predominantly low spin ($S = 1/2$; $^2T_2$) for R = e.g., cyclohexyl through intermediate states (R = e.g., methyl, benzyl) to predominantly high spin ($S = 5/2$; $^6A_1$) for R_2 = pyrrolidyl.[1435] Tris-ligand iron(III) complexes of dithiocarbamates derivatized with substituted piperazines or piperidines are spin cross-over complexes.[1436]

Bis(*N*-methyl-D-glucaminedithiocarbamate)iron(II) and bis(2,3-dithiopropane-1-sulfonate)-iron(II) react with *S*-nitrosothiols with transfer of NO to iron.[1437]

Diethylthiocarbamate ligands are also found in the $[Fe_4S_4(S_2CNEt_2)_4]^{2-}$ cluster anion.[1438]

In the iron(II) complex of tris(thiophenylimidazolyl)borate, $Fe^{II}(tmcptimid)_2$ where $tmcptimid^- =$ (**296**), the Fe may be considered tetrahedrally coordinated by the two $tmcptimid^-$ ligands each bonding through two sulfurs, though there appear to be significant Fe ⋯ H interactions with nearby imidazolylborate-hydrogens. In $[Fe^{III}(tmcptimid)_2]^+$ the ligands are coordinated through all three sulfurs (in contrast to their *S*,*S*,*N*-coordination to the harder Co^{III}), giving octahedral Fe^{3+}. Fe^{II}—S bond distances are 2.381–2.409 Å in the Fe^{II} complex (slightly longer than most Fe^{II}—S bond distances), 2.456–2.473 Å in the Fe^{III} complex.[1439]



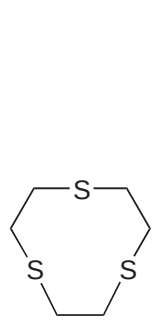
(**296**)

The stabilization of Fe^{2+} by 1,4,7-triathiacyclononane, ([9]-ane-S_3, ttcn = (**297**)}, has permitted the preparation of the first authentic example of a Turnbull's Blue, i.e., an iron(II)–hexacyanoferrate(III) combination, in the form of $[Fe(ttcn)_2][Fe(CN)_6]\cdot 2H_2O$. This so-called "Ukrainian Red," named in honor of the country of origin of several of the authors, is a valence-trapped (Robin and Day class I[334,335]) compound.[336] The redox potential for the $[Fe(ttcn)_2]^{2+/3+}$ couple is +0.98V, in acetonitrile with respect to the ferrocene/ferrocinium couple.[1440] Peroxodisulfate oxidation of $[Fe(ttcn)_2]^{2+}$ does not give the Fe^{3+} complex; the major product is [Fe(ttcn)(ttcn-1-oxide)]$^{2+}$. Oxidation by lead dioxide does however yield $[Fe(ttcn)_2]^{3+}$.[1441] The Fe—S bond distances in high spin $[Fe(ttcn)Cl_3]$ are between 2.538(3) Å and 2.585(3) Å,[1442] whereas in low spin [Fe(tpmbtacn)] (where tpmbtacn is the trianionic tripodal N_3S_3 hexadentate ligand 1,4,7-tris (4-*t*-butyl-2-thiobenzyl)-1,4,7-triazacyclononane, (**197**)) they are between 2.269(3) Å and 2.288(3) Å.[998]

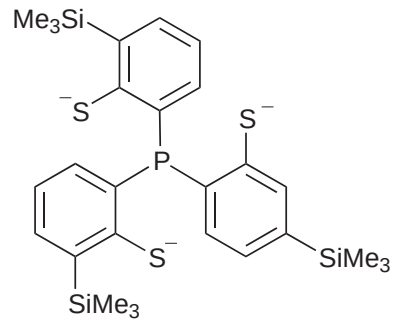
The structures of $(PPh_4)_2[Fe(mnt)_3]$ and $(PPh_4)_2[\{Fe(mnt)_2\}_2]$ have been determined; the latter contains parallel stacks of nearly planar anions.[1443] The structure of $(NBu_4)_2[Fe(mnt)_2(NO)]$ has also been determined, along with the ESR spectrum of a ^{57}Fe-enriched sample.[1444] The redox potential of $[Fe(mnt)_3]^{2-/3-}$, in dichloromethane, has been placed in context with those for other transition metal $[M(mnt)_x]^{n-/(n+1)-}$ couples.[1445]

Tetrathiotungstate complexes of iron(III)–tetraphenylporphyrin can be prepared from iron(III)–tpp–triflate; they undergo slow spontaneous reduction to iron(II).[834]

The ligand (**298**), coordinating through phosphorus and all three sulfurs, stabilizes iron(IV) in [Fe(**298**)Cl], which is the first stable trigonal bipyramidal iron(IV) complex to be prepared.[22]



(**297**)

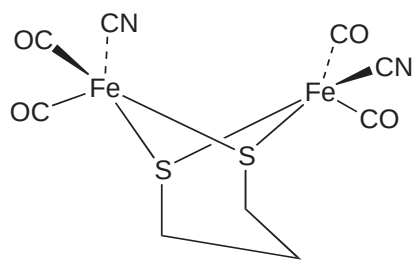


(**298**)

5.4.5.9.2 *Bi- and polynuclear complexes and clusters*

Nonbiological iron–sulfur clusters have been reviewed.[1446]

Determination of the structure of an iron–sulfur–carbonyl–cyanide hydrogenase[427,428] has been complemented by the synthesis and structural characterization of model compounds $(Et_4N)_2[Fe(SPh)_2(CN)_2(CO)_2]$,[420] (**299**),[430,432,1447] and related species in which the sulfur-bridging is provided by the tripodal thioether $MeSCH_2C(Me)(CH_2S)_2$.[435]



(**299**)

Reactions of dithioxamides with $Fe_2(CO)_9$ give a number of μ-S di-iron products, providing a bridge to organometallic chemistry.[1448]

Flash photolysis of Roussin's Red Salt, $Na_2[Fe_2S_2(NO)_4]$, and of Roussin's Black Salt, $NH_4[Fe_4S_3(NO)_7]$, has been described.[1449] Photolysis of $[Fe_2S_2(NO)_4]^{2-}$ has been reviewed, in

particular the initial photoinitiated loss of NO[1450] and the reverse recombination reaction, en route to the eventual product, the anion of Roussin's Black Salt, $[Fe_4S_3(NO)_7]^-$.[1451] $[Fe_2S_2(NO)_4]^{2-}$, $[Fe_4S_4(NO)_4]$, and $[Fe_4S_3(NO)_7]^-$ feature in a review of the synthesis, structure, NMR spectroscopy, reactivity, and bio-relevance of Fe—S—NO complexes.[1452] $[Fe_2S_2(NO)_4]^{2-}$ and $[Fe_4S_3(NO)_7]^-$ have been evaluated as sensitizers for radiotherapy.[242] $[Fe_5S_4(NO)_8]^-$ and $[Fe_7S_6(NO)_{10}]^-$ have been prepared.[1453]

An $Fe_4S_4Cl_4$ anion was one of the unexpected products of the reaction of $K[FeZr_6Cl_{15}]$ with thiocyanate.[1417] A straightforward preparation of $[Fe_4S_4Br_4]^{2-}$ uses Na_2S and DMF as solvent.[1454] Diethylthiocarbamates provide the terminal ligands in the $[Fe_4S_4(S_2CNEt_2)_4]^{2-}$ cluster anion.[1438] Two Fe_4S_4 cores can be bridged by a variety of dithio-ligands, such as *p*-$^-SC_6H_4S^-$, *m*- or *p*-$^-SCH_2C_6H_4CH_2S^-$, or $^-SCH_2CH_2S^-$. Communication between the two cubane units, as judged by comproportionation constants, is minimal for the first three (Fe···Fe between 8.8 Å and 10.4 Å; $K_c \sim 5.4$), very small for the fourth (Fe···Fe = 7.8 Å; $K_c = 15$), and only significant ($K_c = 5.4 \times 10^3$) when there is a direct Fe—S—Fe bridge (Fe···Fe = 4.20 Å).[1455] Direct Fe—S—Fe sulfide bridging has also been established in $(Bu^n_4N)_2(Ph_4P)_2[(Fe_4S_4Cl_3)_2S]$.[1456] A report of the preparation of $Fe_6S_6(PEt_3)_4X_2$, X = halide or PhS^-, with a prismane core is accompanied by a summary of topological relations between various Fe_xS_y cores and conversions experimentally achieved to date.[1457]

A 4-$RC_6H_4S^-$ group (R = H, Me, OMe, Cl, or CF_3) replaces one of the chloride ligands in $[Fe_4S_4Cl_4]^{2-}$ via a five-coordinate intermediate, with the detailed sequence of steps acid-dependent.[1458] Loss of chloride is pH-dependent, with the rate depending on the electron-withdrawing properties of the substituent R.[1459] Reactions of $[Fe_4S_4Cl_4]^{2-}$ and of $[Fe_4S_4(SPh)_4]^{2-}$ with diethyldithiocarbamate are dissociatively activated.[1460] mechanisms of reaction of $[Fe_4S_4Cl_4]^{2-}$ with Bu^tNC depend on the p*K* of the protonated organic base present. For the weakest acid, azacyclopentaneH^+, Bu^tNC binds before proton transfer ($k = 2.1 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$), but in the presence of protonated triethylamine or lutidine Bu^tNC or Br^- attack after addition of the first proton ($k \sim 10^6\ dm^3\ mol^{-1}\ s^{-1}$) but before addition of the second (SH) proton ($k \sim 10^3\ dm^3\ mol^{-1}\ s^{-1}$) to the cluster. The p$K_a$ of $[Fe_4S_3(SH)Cl_4]^{2-}$ is 18.8,[1461] of $[Fe_4S_2(SH)_2Cl_4]$ 16.6,[1462] of $[Fe_4S_3(SH)(SCHCH(OH)Me)_4]$ 8.5.[1463] $[Fe_4S_4(SMe)_4]^{n-}$ and $[Fe_4S_4(SPh)_4]^{n-}$, $n = 2$ or 3, react with sulfonium cations $[PhMeSCH_2R]^+$.[1464] Reaction of $[Fe_4(SPh)_{10}]^{2-}$ with PhS^- takes place by initial associative attack at one of the tetrahedral Fe atoms, to give $[Fe_4(SPh)_{11}]^{3-}$, followed by a sequence of rapid reactions to give the final product $[Fe(SPh)_4]^{2-}$. In contrast the first step in reaction of $[Fe_4(SPh)_{10}]^{2-}$ cluster anions with $[MoS_4]^{2-}$ is, at least at low $[MoS_4]^{2-}$ concentrations, dissociative in character.[1465] A review of the chemistry of $[Mo_3S_4(H_2O)_9]^{4+}$ and related clusters contains some information on substitution in mixed metal derivatives such as $[Mo_3FeS_4(H_2O)_{10}]^{4+}$.[1466] $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ can be generated in solution by reducing $[Mo_3S_4(H_2O)_9]^{4+}$ with Fe^{2+}aq and BH_4^- or with iron wire,[1467] or electrochemically in the presence of Fe^{2+}aq.[1468] Replacement of the Fe^{2+} in $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ by Cu^{2+} takes about a second; the very slow reaction of this cluster cation with Ni^{2+} gives not $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ but rather $[Mo_3S_4(H_2O)_9]^{4+}$.[1469]

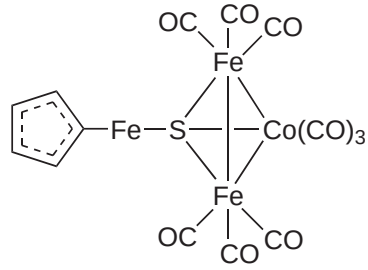
Fe_4S_4 clusters with bulky 2,4,6-tri-isopropylbenzylthiolate (tipbt) ligands are HiPiP models. However they, unlike HiPiP, are not stable in solution in the $[Fe_4S_4]^{3+}$, i.e., $[Fe_4S_4(tipbt)_4]^{3-}$, state.[1470] Other synthetic HiPiP models include the 2,6-bis(acylamino)benzenethiolate (babt) derivatives $[Fe_4S_4(babt)_4]^{2-}$ and $[Fe_2S_2(babt)_4]^{2-}$, modeling bacterial (Fe_4S_4) and plant (Fe_2S_2) ferredoxins. In these models protection of the Fe—S bonds by NH ··· S hydrogen-bonding both prevents ligand exchange and has a significant effect on redox potentials.[1471] HiPiP electron transfer proteins have particularly hydrophobic peripheries. This can be modeled by wrapping a cyclic $\{N(CH_2)_8\}_4$ sheath around an Fe_4S_4 core; the resultant complex undergoes three of the four possible one-electron transfers in DMSO solution, with redox potentials of 0.36 V, 0.85 V, and 1.64 V for the −/2−, 2−/3−, and 3−/4− couples, respectively.[1472]

The geometric and electronic structures of seventeen iron-containing derivatives of pentlandite, Co_9S_8, ranging from Co_8FeS_8 through to such species as $CoFe_4Ni_4S_8$ and $Fe_4Ni_4AgS_8$, have been discussed, with particular reference to stabilities of octahedral and tetrahedral coordination.[1473]

Magnetic studies and theoretical calculations on $(Et_4N)_3[S_2Mo(\mu\text{-}S)_2Fe(\mu\text{-}S)_2MoS_2]$ suggest that the anion is best regarded as a bis-$[MoS_4^{2-}]$ complex of iron(I).[13] A group of mixed metal clusters based on MFe_3S_4 cores has been developing over several decades. This group includes the $ReFe_3S_4^{3+}$ core in the black crystalline solid $(EtN)[ReFe_3S_4(SEt)(dpme)]_4$[1474] and earlier examples of compounds with $MoFe_3S_4$, WFe_3S_4,[1475] VFe_3S_4(single[1476] and double cubane clusters[1477]) and $NiFe_3S_4$[1478] cores. These and related species may be regarded as complexes of the various metal ions M^{n+} with ligands $Fe_3S_4L_4$. The relative reactivities of the Fe and Co sites of $CoFe_3S_4$ have been established.[1479]

There are many clusters of high nuclearity (i.e., 5 or more metal ions), e.g., $[Fe_6S_6(PEt_3)_4L_2]$, $[Fe_6S_6(PEt_3)_6]^-$, $[Fe_7S_6(PEt_3)_4Cl_3]$,[1457,1480] $[Fe_6S_6L_6]^{3-}$ (L = Br or 4-MeCHO),[1481] $[Fe_8S_8(PR_3)_n]$ and $[Fe_{12}S_{12}(PR_3)_n]$ species derived from $[Fe_4S_4(PR_3)_n]$ precursors.[1482] There are also several analogues with heteronuclear cores, e.g., $[Fe_4MS_6(PEt_3)_4Cl]$ with M = V or Mo,[1483] $[Fe_3Mo_2S_5(PEt_3)_5(ccat)_2]$ and $[Fe_6Mo_2S_8(PR_3)_6(ccat)_2]$ (ccat = tetrachlorocatecholate)[1486,1487] and $[Fe_{18}Na_2S_{30}]^{8-}$.[1488] In this type of system the nature of the nonbridging ligands, of the counterion for charged species, and of the solvent can be of great importance in determining the nature and geometry of the $Fe_nM_mS_x$ core. There are usually several possible geometries of very similar energies, often with small kinetic barriers to interconversion. Product control by the nature of the phosphine ligands in the $Fe_4S_4 \rightarrow Fe_8S_8 \rightarrow Fe_{12}S_{12}$ series mentioned above provides a good example.

A tetranuclear Fe_3Co cluster with a central μ^4-S ligand appears in $[Fe_3Co(\mu^4\text{-}S)(\eta^5\text{-}C_5H_5)(CO)_{11}]$, (**300**).[1489]



(**300**)

5.4.5.10 Selenium and Tellurium Donors

A straightforward preparation of $[Fe_4Se_4Br_4]^{2-}$ uses Na_2Se, with DMF as solvent.[1454] Selenium can replace sulfur in a few high-nuclearity iron–sulfur clusters, e.g., $[Fe_6Se_6(PEt_3)_4Cl_2]$[1480] and $[Fe_{20}Na_9Se_{38}]^{9-}$.[1488] The synthesis, spectroscopic and magnetic properties, and structure of an Fe_4Te_4 cluster, specifically $[Fe_4Te_4(SPh)_4]^{3-}$ in the form of its Et_4N^+ salt, have been reported.[1490]

5.4.6 GROUP 17 DONORS

The dependence of Fe—X bond length on the nature of the halide X and on the oxidation state and coordination number of the iron in about 300 species containing FeX_n units has been documented.[1491]

5.4.6.1 Fluoride Complexes

The kinetics of FeF_2^+ formation have been monitored over the pH range 1.9–4.0; the kinetic pattern is not simple.[1492] The volume of the $[FeF_6]^{3-}$ anion is referenced in Section 5.4.1.1 above.

The F^- ligand in a series of complexes *trans*-[Fe(R-salen)(MeOH)F] stabilizes the Fe^{3+} with respect to photoredox processes in comparison with Cl^-, Br^-, or I^- analogues; quantum yields are lower for the F^- complexes.[931]

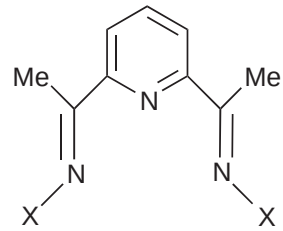
The octaethylporphyrin complex $[Fe(oep)(OClO_3)]$ reacts with $[Cu_2F_2(bnpy)_2]^{2+}$ (bnpy = *N*,*N*-bis(2-(2-pyridylethyl))benzylamine) to give $[(oep)FeFCu(bnpy)_2(OClO_3)]^+$ in acetone, $[(oep)FeFCu(bnpy)_2(MeCN)]^{2+}$ in acetonitrile. Crystal structures have been determined for these two fluoride-bridged species and for $[Fe(oep)F]\cdot CHCl_3$. This last was prepared by refluxing $[Fe(oep)]_2O$ with HF in CH_2Cl_2, though the crystal used for the structure determination was grown from $CHCl_3$/pentane.[1493]

5.4.6.2 Chloride Complexes

Both $FeCl_2$ and $FeCl_3$ form ionic liquids on mixing with 1-butyl-3-methylimidazolium chloride, with $FeCl_2$ forming $[FeCl_4]^{2-}$, $FeCl_3$ forming $[FeCl_4]^-$ and, when the $FeCl_3$ is in excess, some $[Fe_2Cl_7]^-$.[1494]

5.4.6.2.1 Iron(II)

Tetrahedral [Fe^{II}LCl] with L = hydrotris(3-isopropyl-4-bromopyrazolyl)borate has Fe—Cl = 2.224(2) Å.[686] Five-coordinated Fe^{II} in Fe(**301**)Cl_2 has Fe—Cl = 2.26–2.32 Å.[503,506]



X = NRR', 2,5-dimethylpyrrolyl, 2,6-diisopropylphenyl

(**301**)

Crystallization of $FeCl_2$ from aqueous HCl in the presence of 1,4-dimethylpiperazine (dmpipz) but in the absence of air afforded (dmpipzH_2)[$Fe^{II}_2Cl_4(H_2O_6)$]Cl_2. This anion contains two octahedral Fe^{2+} centers bridged by two chlorides; Fe—$Cl_{terminal}$ = 2.449(1); Fe—Cl_{bridge} = 2.511(1) Å.[1495] The 1,4,7-trimethyl-1,4,7-triazacyclononane complex of formula Fe(tmtacn)Cl_2 is, in the solid state, [Fe_2Cl_3(tmtacn)$_2$][$FeCl_3$(tmtacn)]—whose anion can be generated by reacting $FeCl_4^{2-}$ with tmtacn.[424] The structure of $K_3Na[FeCl_6]$ has been determined at 9.5, 84, and 293 K.[1496]

Equilibrium constants for the displacement of acetonitrile from complexes [$FeL_4(MeCN)_2$], where L_4=($Ph_2PCH_2CH_2PPh_2$)$_2$, P($CH_2CH_2PPh_2$)$_3$, or N($CH_2CH_2PPh_2$)$_3$ by chloride, bromide, or thiocyanate suggest steric control.[910]

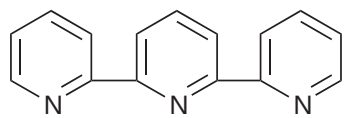
5.4.6.2.2 Iron(III)

The crystal structures and magnetic behavior of the hexachloroferrates(III) of $[Cr(en)_3]^{3+}$ and $[Co(en)_3]^{3+}$ have been described.[1497] Fe^{III}—Cl bond distances in $[FeCl_6]^{3-}$ are 2.40 Å, whereas Fe^{II}—Cl in $[FeCl_6]^{4-}$ is 2.51 Å.[1498] The tetrachloroferrate(III) anion is often the counterion for cationic iron complexes, as for example in the preparation of [Fe(diimine)$_2Cl_2$] [$FeCl_4$],[689] and of complexes of 1,5,9-tris(2-pyridylmethyl)-1,5,9-triazacyclododecane,[728] thiopurine,[983] and the carbothiamide derivative of 2,2′-bipyridyl (**200**).[489] High-spin binuclear $[Fe_2OCl_6]^{2-}$, which may be prepared by reacting iron(III) chloride in toluene with a secondary amine,[1499] is a convenient starting material for, e.g., pyrazolylborate and decanuclear oxoiron(III) complexes, and again is encountered as a counterion for cationic iron complexes, e.g., $[Fe^{II}(thiazole)_6]^{2+}$,[725] and again the 6-carbothioamide derivative of bipy.[489] A crystal structure determination for [Fe(bipy)$_3$][$Cl_3FeOFeCl_3$] showed the di-iron anion to have ∠Fe—O—Fe = 148.9(7)°.[1163]

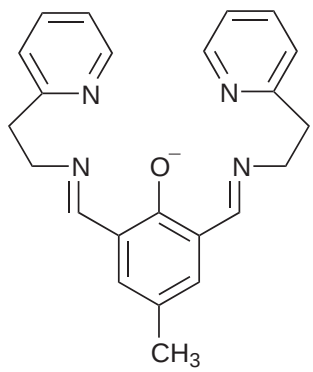
The bis-(ethylenedithio)tetraselenafulvalene (bets) derivative (bets)$_2Fe_xGa_{1-x}Cl_4$ is a superconductor with an insulating magnetic ground state.[1500] Gas phase and fragmentation behavior of binuclear species $[Fe_2Cl_n]^+$, with $n = 1$ to 6, has been probed by sector-field mass spectrometry. An ionization energy of 10.85 eV has been determined for Fe_2Cl_6 from photoionization experiments, and enthalpies of formation derived for the series of $[Fe_2Cl_n]^+$ cations — ΔH_f for $[Fe_2Cl_6]^+$ is 389 kJ mol^{-1}.[1501]

Laser Raman spectroscopic examination of molten $FeCl_3 \cdot 6H_2O$ identified *trans*-$[FeCl_2(H_2O)_4]^+$ and $[FeCl_4]^-$ as the predominant components, consistent with the relatively high conductivity of the melt.[1502] *trans*-$[FeCl_2(H_2O)_4]^+$ has been observed in aqueous iron(III)/chloride solutions by X-ray absorption spectroscopy, which has also been claimed to identify tetrahedral $[FeCl_4]^-$ in media containing 15 mol dm^{-3} chloride.[1020] The *trans*-$[FeCl_4(H_2O)_2]^-$ anion, generated in solution by air oxidation of $FeCl_2$ in HCl, has been isolated as its dabcoH_2^{2+}(dabco = diazabicyclo[2.2.2]octane) salt, $[FeCl_5(H_2O)]^{2-}$ as its enH_2^{2+} salt.[1503] *trans*-$[FeCl_4(H_2O)_2]^-$ has also been obtained as its dmpipzH_2^{2+}(dmpipz = 1,4-dimethylpiperazine) salt, and *mer*-$[FeCl_3(H_2O)_3]$ isolated in the form of [trienH_2][$FeCl_3(H_2O)_3$]Cl_2.[1495] The volume of $[FeCl_4]^-$ has been estimated as 0.155 nm^3.[93]

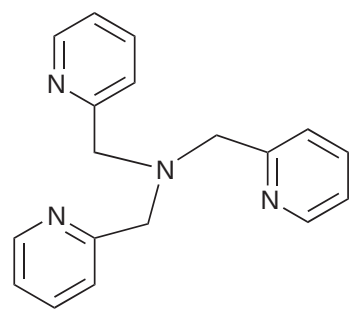
There appears to be a relatively fine balance between *mer* and *fac* geometries for octahedral trichloroiron(III) complexes. Thus it was established some time ago that [Fe(phen)(solvent)Cl_3] adopted the *fac* geometry for solvent = H_2O or MeOH,[1504] but *mer* for solvent = DMF.[1505] The geometric and steric demands of terdentate ligands such as 1,3,5-trimethyltriazacyclohexane,[1506] 1,3,5-trithiacyclononane,[1442] di(2-pyridyl)methylamine,[1507] and bis(2-pyridylmethyl)amine[1508,1509] enforce *fac* geometry; the strong preference of terpy (**302**) for planarity results in *mer* geometry for [Fe(terpy)Cl_3] (see below). Trichloro{2,6-bis(*N*-2-pyridylethyl)iminomethyl)-4-methylphenolate} iron(III) ((**303**), *N*,*N*,*O*-coordinated) is *mer*,[925] as is [Fe(py)$_3Cl_3$] (which has Fe—Cl = 2.326 Å for Cl *trans* to Cl, 2.326 Å for Fe—Cl *trans* to N).[457] The iron(III) complexes of unsymmetrically substituted tris(2-pyridylmethyl)amine (tpa, (**304**)) tripodal ligands, [Fe(**305**)Cl_3] and [Fe(**306**)Cl_3] are again perforce *mer*; they have Fe—Cl bond distances between 2.279 and 2.313 Å.[468] Structures of the iron(III) complexes *mer*-[Fe(pyrazole)$_3Cl_3$], *mer*-[Fe(*N*-methylimidazole)$_3Cl_3$], *mer*-[Fe(terpy)Cl_3], *mer*-[Fe(^{2,4,6}tptz)Cl_3] (^{2,4,6}tptz = (**307**)), and *trans*-[Fe(3-methylpyrazole)$_4Cl_2$]Cl have been determined.[510] Fe—Cl bond distances lie between 2.315 Å and 2.387 Å for Cl *trans* to Fe—Cl, between 2.249 Å and 2.315 Å for Fe—Cl *trans* to N. The structure of *trans*-[Fe(imidazole)$_4Cl_2$]Cl·THF·H_2O has also been reported.[698]



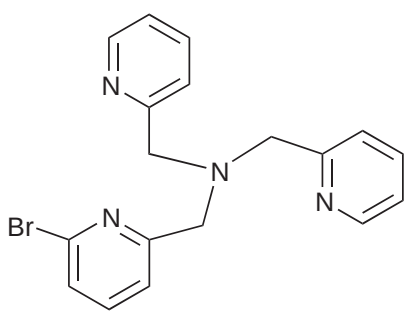
(**302**)



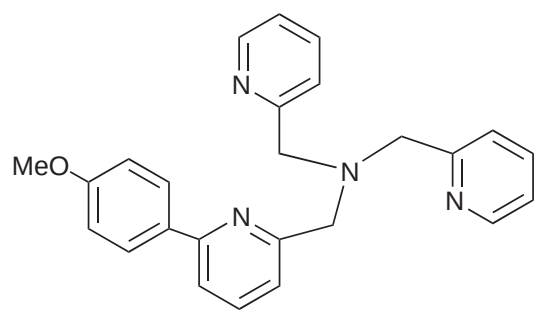
(**303**)



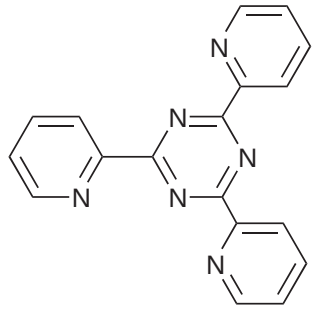
(**304**)



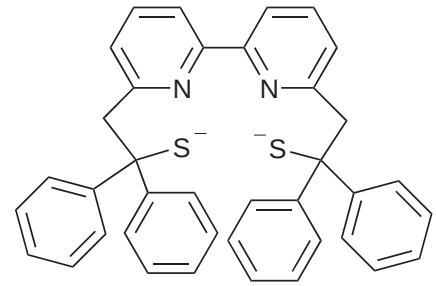
(**305**)



(**306**)

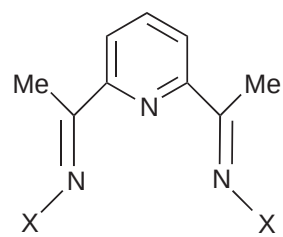


(**307**)



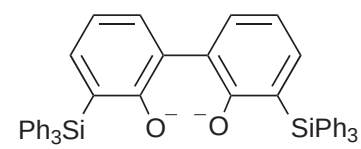
(**308**)

Benzoylacetone-S-*n*-propylisothiosemicarbazonatodichloroiron(III) contains five-coordinated iron(III), with Fe—Cl = 2.244(1) Å and 2.258(1) Å for the axial and in-plane chlorides in the distorted square-pyramidal structure adopted by its ethanol solvate.[974] The chloro-iron(III) complex of the dianion of 6,6′-bis(2,2′-diphenyl-2-sulfanylethyl)-2,2′-bipyridine (**308**) is pentacoordinated (distorted square pyramid) with axial chloride unusually distant from the metal (Fe—Cl = 2.306(3) Å).[529] The terimine complexes [Fe(**309**)Cl_2] also contain five-coordinated iron(II), with Fe—Cl distances between 2.248 and 2.311 Å for the complexes with $NR^1R^2 = NMe_2$, NPh_2, and NMePh.[505] [Fe(**310**)(bipy)Cl] is also a five-coordinate iron(III) complex, with Fe—Cl = 2.249 Å,[437] as is [Fe(**311**)Cl_2], whose geometry is closer to square pyramidal than to trigonal bipyramidal. The Fe—Cl bond distances in [Fe(**311**)Cl_2] are 2.321(2) Å and 2.329(2) Å.[474] In contrast $[Fe(NMe_3)_2Cl_3]$[1510] and $[Fe(4CNpy)_2Cl_3]$[1511] are close to being trigonal bipyramidal, with ∠N—Fe—N = 179.3°, 175.6°, respectively. Fe—Cl bond distances are 2.207(1) Å and 2.228(2) Å in $[Fe(Me_3N)_2Cl_3]$, 2.204(1) Å, 2.216(1) Å and 2.229(1) Å in $[Fe(4CNpy)_2Cl_3]$. The Fe—Cl bond distance in five-coordinate [bis(5-bromosalicylidene)benzene-1,2-diimine]chloroiron(III) is 2.2356(8) Å, in six-coordinate *trans*-[bis(5-bromosalicylidene)benzene-1,2-diimine]chloroaquairon(III) significantly longer at 2.3926(8) Å.[924]

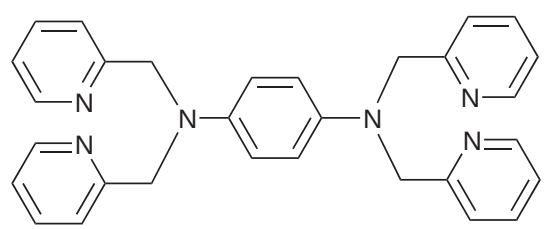


X = NRR', 2,5-dimethylpyrrolyl, 2,6-diisopropylphenyl

(**309**)



(**310**)



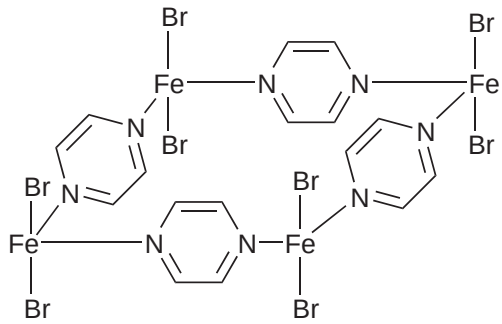
(**311**)

An EXAFS examination of $FeCl^+$aq indicated Fe—Cl = 2.26 Å and Fe—O = 2.05 Å in the $[FeCl(H_2O)_5]^{2+}$ cation; log $K_1 = 3.8$ (±0.4).[1025] A set of best estimates of stability constants for the Fe^{3+}/Cl^- system in aqueous solution[1512] and the formation enthalpy and entropy for $FeCl^+$ formation have been reported.[1513] The ΔH° and ΔS° values are derived from determinations of

K_1 over the range 298–398 K. Partition coefficients for $HFeCl_4$ between water and 1-octanol or dibutyl ether depend markedly on HCl and LiCl concentrations. For dibutyl ether as organic phase there is also a dependence of partition coefficient on Fe^{3+} concentration as there is significant polynuclear complex formation in the ether layer. $[FeCl_4]^-$, in the form of its Et_3BzN^+ salt, acts as a bifunctional or phase transfer catalyst for hydrosilylation of phenylacetylene.[110]

5.4.6.3 Bromide Complexes

$Fe(pz)_2Br_2$ has the layer structure shown as (**312**); Fe—Br = 2.572 Å;[475] compare $FeBr_2$, which has the CdI_2 structure, with Fe—Br = 2.636(2) Å.[1514]



(**312**)

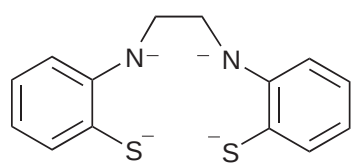
XRD examination of concentrated aqueous solutions of $FeBr_2$ suggested that in a 2.7 mol dm^{-3} solution the average number of bromides coordinated to the Fe^{2+} was 0.325, at an average Fe—Br distance of 2.605 Å, while at 4.5 mol dm^{-3} there were on average 0.747 Br^- per Fe^{2+}, at an average distance of 2.621 Å.[1022]

Crystallization of $FeBr_2$ from aqueous HBr in air in the presence of 1,4-dimethylpiperazine (dmpipz) gives $(dmpipzH_2)[FeBr_4]_2$; in the presence of trien the double salt $(trienH_2)[FeBr_4]Br$ is obtained.[1495] Structures have been reported for $Ba[FeBr_4]_2$[1515] and for its parent $FeBr_3$, which has the BiI_3 structure with pairs of bromide ligands bridging the Fe^{3+} ions, all of which are octahedrally coordinated.[1516]

5.4.6.4 Iodide Complexes

The photochemistry of iron(III)–iodide complexes has been reviewed.[1517] The synthesis and properties of high-purity FeI_2 are relevant to the use of mixtures of this compound with halides of other metals, in other words the use of iodo–iron(II) complexes, in medium-pressure discharge lamps. The enthalpy of dissociation of Fe_2I_4 of 130 kJ mol^{-1} (at 693 K) gives an idea of the strength of the iodide bridges in the dimer.[1518]

FeI_3, first isolated in the pure state as recently as 1988 as a black, fairly stable solid (though unstable in solution),[1519] reacts with iodide to give the previously characterized complex $[FeI_4]^-$.[1520] Iodide appears stable coordinated to iron(III) in ternary porphyrin complexes such as (12,17-diethoxycarbonyl-2,3,6,7,11,18-hexamethylcorrphycenato)-iodo-iron(III), where Fe^{III}—I = 2.600 Å,[851] though it is oxidized by the mono-oxidized form of μ-oxo-di-iron(III) bis-tetraphenylporphyrin.[841] Remarkably, iodide has been reported coordinated to iron(V), in [Fe(**313**)I].[30]



(**313**)

The combined bulk of iodide and of *N*,*N*,*N*′*N*′-tetramethylethylenediamine makes Fe^{2+} tetrahedral in [Fe(tmen)I_2].[442]

5.4.7 HYDRIDE AND DIHYDROGEN COMPLEXES

$[FeH_6]^{4-}$ is a low-spin Fe^{2+} (d^6) complex;[1521] hydride comes between bipy and cyanide in the spectrochemical series for this ion.[1522]

The hydride and the cyanide ligands in *trans*-[Fe(H)(CN){$Ph_2P(CH_2)_nPPh_2$}$_2$], $n = 2$ or 3, can be protonated to give, e.g., the *trans*-[Fe(H_2)(CN){$Ph_2P(CH_2)_nPPh_2$}$_2$]$^+$ and *trans*-[Fe(H_2)(CNH){$Ph_2P(CH_2)_nPPh_2$}$_2$]$^{2+}$ cations.[905,906]

The hydride/dihydrogen complexes *trans*-[Fe(H)(H_2)($R_2PCH_2CH_2PR_2$)$_2$], R = Me, Et, Pr, can be prepared by reversible protonation of the dihydride complexes *cis*-[Fe(H)$_2$($R_2PCH_2CH_2PR_2$)$_2$] in alcoholic solution. The η^2-H_2 can be readily and rapidly replaced by Cl^-, Br^-, or excess of diphosphine.[1523] The $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH_2CH_2PEt_2$ analogues have also been described, and their NMR spectra reported along with NMR data on [Fe(H)(Cl)($Ph_2PCH_2CH_2PEt_2$)].[1524]

cis-[Fe{$P(CH_2CH_2PMe_2)_3$}(H_2)] reacts with EtNCS, PhNCS, or PhNCO to give *cis*-[Fe{$P(CH_2CH_2PMe_2)_3$}(SCHNEt)H], *cis*-[Fe{$P(CH_2CH_2PMe_2)_3$}(SCHNPh)H], or *cis*-[Fe{$P(CH_2CH_2PMe_2)_3$}(OCHNPh)H].[907] *cis*-[Fe(H)(H_2){$P(CH_2CH_2PPh_2)_3$}]$^+$ is unexpectedly stable. The H and H_2 ligands can be distinguished at low temperatures, but at room temperature the structure is more akin to a trigonal bipyramid with an H_3 ligand, bent or triangular, in the axial position *trans* to the bridgehead phosphorus.[909] The $[FeH_3(PR_3)_4]^+$ cation interconverts between this seven-coordinate form and six-coordinate *cis*-$[FeH(H_2)(PR_3)_4]^+$.[914]

5.4.8 ABBREVIATIONS

Abbreviations for ligands which make only one appearance are generally defined at the appropriate point in the text; ligand abbreviations which appear in more than one place are listed and defined below.

ahdx = acethydroxamate
bipy = 2,2′-bipyridyl, (**70**) (4,4′-bipyridyl is abbreviated as 4,4′-bipy)
bipym = 2,2′-bipyrimidine, (**52**)
bipz = 2,2′-bipyrazine, (**40**)
bmi = biacetylbismethyleneimine, MeN=CMeCMe=NMe
bsb = bidentate Schiff base with diimine chelating group, (**73**)
btz = bithiazole (2,2′- (**96**) and 4,4′- (**97**) isomers indicated as $^{2,2'}$btz and $^{4,4'}$btz)
btzn = 2,2′-bi-thiazoline, (**112**)
cat = catenate or catechol
cmi = cyclohexanedionebismethyleneimine, (**105**)
CTAB = cetyltrimethylammonium bromide
cyclam = 1,4,8,11-tetraazacyclotetradecane
cyclen = 1,4,7,10-tetraazacyclododecane
cyst = cysteine
dab = (substituted) 1,4-diazabutadinene, (**74**)
dfo = desferrioxamine
dien = diethylenetriamine
dmg = dimethylglyoxime
dota = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate, (**173**)
dppe = 1,2-bis(diphenylphosphino)ethane
dppp = 1,2-bis(diphenylphosphino)propane
dto = dithiooxalate
dtpa = diethylenetriaminepentacetate
edda = *N*,*N*′-ethylenediaminediacetate
edta = *N*,*N*,*N*′,*N*′-ethylenediaminetetraacetate
en = 1,2-diaminoethane
glygly = glycylglycine
gmi = glyoxalbismethyleneimine, MeN=CHCH=NMe

Hb = hemoglobin
hbedda = *N*,*N*′-di(hydroxybenzyl)ethylenediamine-*N*,*N*′-diacetate
hedta = *N*-(hydroxyethyl)ethylenediamine-*N*,*N*′,*N*′-triacetate
hfac = hexafluoroacetone
hxsb = hexadentate Schiff base with diimine chelating units, e.g., (**76**)
hxsbh = hexadentate Schiff base, (**76**), from pyridine-2-carboxaldehyde and trien
imid = imidazole
L1 = 1,2-dimethyl-3-hydroxy-4-pyridinone, (**24**)
Ln = lanthanide
Mb = myoglobin
Me_2bsb = bidentate Schiff base (**73**) with $R_1 = Ph$, $R_2 = 3,4\text{-}Me_2C_6H_3$
mmi = methylglyoxalbismethyleneimine, MeN=CHCMe=NMe
nta = nitrilotriacetate
oep = octaethylporphyrin
phen = 1,10-phenanthroline, (**71**)
pic = 2-picolylamine = 2-(methylamino)pyridine
py = pyridine
pz = pyrazine
pzc = pyrazine carboxylate
sal = salicylate
salen = *N*,*N*′-ethylene-1,2-salicylidiniminate, (**37**)
sb = Schiff base with diimine chelating unit, (**73**)
SDS = sodium dodecyl sulfate
tacn = 1,4,7-triazacyclononane
terpy = 2,2′,6′,2″-terpyridyl, (**72**)
tpa = tris(2-pyridylmethyl)amine, (**58**)
tpp = tetraphenylporphyrin
tptz = tri(2′-pyridyl)-1,2,4-triazine (2,4,6- (**66**) and 3,5,6- (**67**) isomers indicated as ^{2,4,6}tptz and ^{3,5,6}tptz)
tren = tris(2-aminoethyl)amine = *N*,*N*-bis(2-aminoethyl)-1,2-ethanediamine
trien = 1,8-diamino-3,6-diazaoctane
tsb = terdentate Schiff base with terimine chelating unit, (**69**)
ttcn = ttcn = 1,4,7-triathiacyclononane (**297**)
ttpz = 2,3,5,6-tetrakis(2-pyridyl)pyrazine
tu = thiourea

SOLVENT ABBREVIATIONS

DMAC = *N*,*N*′-dimethylacetamide
DMF = *N*,*N*′-dimethylformamide
DMSO = dimethylsulfoxide
MeCN = acetonitrile
THF = tetrahydrofuran

OTHER ABBREVIATIONS

IVCT = intervalence charge-transfer
LMCT = ligand-to-metal charge-transfer
MLCT = metal-to-ligand charge-transfer
MRI = magnetic resonance imaging

ACKNOWLEDGEMENTS

The authors are most grateful to Dr. J. G. Jones for his valuable assistance with the preparation of the sections on porphyrin and phthalocyanine complexes.

5.4.9 REFERENCES

1. Hawker, P. N.; Twigg, M. V. Iron(II) and lower states. In *Comprehensive Coordination Chemistry;* Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon: Oxford 1987, Chapter 44. 1.
2. Nelson, S. M. Iron(III) and higher states. In *Comprehensive Coordination Chemistry;* Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., Eds.; Pergamon: Oxford, 1987, Chapter 44. 2.
3. Silver, J. Ed. *Chemistry of Iron;* Chapman & Hall: London, 1993.
4. Mielczarek, E. V.; McGrayne, S. B. *Iron, Nature's Universal Element*; Rutgers University Press: New Brunswick, 2000.
5. Melnik, M.; Ondrejkovicová, I.; Vancová, V.; Holloway, C. E. *Rev. Inorg. Chem.* **1997**, *17*, 55.
6. Šima, J.; Makanova, J. *Coord. Chem. Rev.* **1997**, *160*, 161.
7. Kauffman, G. B. Ed. *Coordination Chemistry — A Century of Progress*; ACS Symposium Series, Volume 565; American Chemical Society: Washington 1994.
8. Brock, W. H. *The Fontana History of Chemistry*; Fontana Press: London, 1992.
9. Bratsch, S. G.; Lagowski, J. J. *Polyhedron* **1986**, *5*, 1763.
10. Dodsworth, E.; O'Grady, P. J.; Nicholls, D.; Roberts, D. *Polyhedron* **1987**, *6*, 1191.
11. tom Dieck, H.; Bruder, H. *J. Chem. Soc., Chem. Commun.* **1977**, 24.
12. Ciurli, S.; Meyer, E. M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1987**, 281.
13. Bowmaker, G. A.; Boyd, P. D. W.; Sorrenson, R. J.; Read, C. A.; McDonald, J. W. *Inorg. Chem.* **1987**, *26*, 3.
14. Dietrich-Buchecker, C. O.; Sauvage, J.-P.; Lehn, J.-M. *J. Am. Chem. Soc.* **1989**, *111*, 7791.
15. Braterman, P. S.; Song, J.-I.; Peacock, R. D. *Inorg. Chem.* **1992**, *31*, 555.
16. Masood, M. A.; Zacharias, P. S. *J. Chem. Soc., Chem. Commun.* **1991**, 152.
17. Cai, S.; Walker, F. A.; Licoccia, S. *Inorg. Chem.* **2000**, *39*, 3466.
18. Kamnev, A. A.; Ezhov, B. B. *Koord. Khim.* **1990**, *16*, 1650 (*Chem. Abstr* **1991**, *114*, 134956x).
19. Løgager, T.; Holcman, J.; Sehested, K.; Pedersen, T. *Inorg. Chem.* **1992**, *31*, 3523.
20. Collins, T. J.; Kostka, K. L.; Münck, E.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 5637.
21. Cummins, C. C.; Shrock, R. R. *Inorg. Chem.* **1994**, *33*, 395.
22. Niemoth-Anderson, J. D.; Clark, K. A.; George, T. A.; Ross, C. R. *J. Am. Chem. Soc.* **2000**, *122*, 3977.
23. Yusa, K.; Shikama, K. *Biochemistry* **1987**, *26*, 6684.
24. Tajima, G.; Shikama, K. *Int. J. Biochem.* **1993**, *25*, 101.
25. Hickman, D. L.; Nanthakumar, A.; Goff, H. M. *J. Am. Chem. Soc.* **1988**, *110*, 6384.
26. Nanthakumar, A.; Goff, H. M. *J. Am. Chem. Soc.* **1990**, *112*, 4047.
27. Fujii, H. *Coord. Chem. Rev.* **2002**, *226*, 51.
28. Nakamoto, K. *Coord. Chem. Rev.* **2002**, *226*, 153.
29. Sellmann, D.; Emig, S.; Heinemann, F. W.; Knoch, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1201.
30. Sellmann, D.; Emig, S.; Heinemann, F. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1734.
31. Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504.
32. Read, J. F.; Wy, A. E. H. *Transition Met. Chem.* **1998**, *23*, 755.
33. Weller, M. T.; Hector, A. L. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4162.
34. Kiselev, Yu. M.; Kopelev, N. S.; Spitsyn, V. I. *Doklady* **1987**, *295*, 882.
35. Berglund, G. I.; Carlsson, G. H.; Smith, A. T.; Szöke, H.; Henriksen, A.; Hajdu, J. *Nature* **2002**, *417*, 463.
36. Gütlich, P.; Hauser, A. *Pure Appl. Chem.* **1989**, *61*, 849.
37. Gütlich, P.; Hauser, A. *Coord. Chem. Rev.* **1990**, *97*, 1.
38. Gütlich, P.; Hauser, A.; Spiering, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2024.
39. Real, J. A.; Andrés, E.; Muñoz, M. C.; Julve, M.; Granier, T.; Bousseksou, A.; Varret, F. *Science* **1995**, *268*, 265.
40. Kahn, O.; Martinez, J. C. *Science* **1998**, *279*, 44.
41. Paulsen, H.; Duel, L.; Winkler, H.; Toftlund, H.; Trautwein, A. X. *Inorg. Chem.* **2001**, *40*, 2201.
42. Toftlund, H. *Coord. Chem. Rev.* **1989**, *94*, 67.
43. Gütlich, P.; Garcia, Y.; Goodwin, H. A. *Chem. Soc. Rev.* **2000**, *29*, 419.
44. Real, J. A. *Perspect. Supramol. Chem.* **1999**, *5*, 53.
45. König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527.
46. Hauser, A.; Jeftić, J.; Romstedt, H.; Hinek, R.; Spiering, H. *Coord. Chem. Rev.* **1999**, *190–192*, 471.
47. Turner, J. W.; Schultz, F. A. *Coord. Chem. Rev.* **2001**, *219–221*, 81.
48. König, E. *Struct. Bonding* **1991**, *76*, 51.
49. McGarvey, J. J.; Lawthers, I.; Heremans, K.; Toftlund, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1575.
50. McGarvey, J. J.; Lawthers, I.; Heremans, K.; Toftlund, H. *Inorg. Chem.* **1990**, *29*, 252.
51. DiBenedetto, J.; Arkle, V.; Goodwin, H. A.; Ford, P. C. *Inorg. Chem.* **1985**, *24*, 455.
52. Turner, J. W.; Schultz, F. A. *Inorg. Chem.* **2001**, *40*, 5296.
53. Toftlund, H. *Monatsh.* **2001**, *132*, 1269.
54. Takeda, S.; Ueda, T.; Watanabe, A.; Maruta, G. *Polyhedron* **2001**, *20*, 1263.
55. Linert, W.; Kudryavtsev, A. B. *Coord. Chem. Rev.* **1999**, *190–192*, 405.
56. Boillot, M.-L.; Zarembowitch, J.; Itié, J.-P.; Polian, A.; Bourdet, E.; Haasnoot, J. G. *New J. Chem.* **2002**, *26*, 313.
57. McCusker, J. K.; Zvagulis, M.; Drickamer, H. G.; Hendrickson, D. N. *Inorg. Chem.* **1989**, *28*, 1380.
58. Grey, J. K.; Butler, I. S. *Coord. Chem. Rev.* **2001**, *219–221*, 713.
59. Galyametdinov, Y.; Ksenofontov, V.; Prosvirin, A.; Ovchinnikov, I.; Ivanova, G.; Gütlich, P.; Haase, W. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 4269.
60. Kojima, N.; Aoki, W.; Seto, M.; Kobayashi, Y.; Maeda, Y. *Synth. Met.* **2001**, *121*, 1796.
61. Nakamoto, T.; Miyazaki, Y.; Itoi, M.; Ono, Y.; Kojima, N.; Sorai, M. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 4716.
62. Coucouvanis, D.; Piltingsrud, D. *J. Am. Chem. Soc.* **1973**, *95*, 5556.
63. Holler, F. J.; Coucouvanis, D. *Inorg. Chem.* **1974**, *13*, 2381.
64. Kowal, A. T.; Skarzewski, J. *Spectrochim. Acta* **1985**, *41A*, 563.
65. Bertini, I.; Turano, P.; Vila, A. J. *Chem. Rev.* **1993**, *93*, 2833.
66. Benn, R.; Rufińska, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 861.
67. Mason, J. *Chem. Rev.* **1987**, *87*, 1299.

68. Dechter, J. J. *Prog. Inorg. Chem.* **1985**, *33*, 393 (see p 441).
69. Baltzer, L.; Landergren, M. *J. Chem. Soc., Chem. Commun.* **1987**, 32.
70. Maddock, A. G. *Mössbauer Spectroscopy: Principles and Applications*; Horwood Publishing: Chichester, 1997, Chapters 5, 7, and 8.
71. Münck, E. In *Physical Methods in Bioinorganic Chemistry: Spectroscopy and Magnetism* Que, L., Ed.; University Science Books: Sausalito, California, 2002, Chap. 6.
72. Trautwein, A. X.; Winkler, H.; Schwendy, S.; Grünsteudel, H.; Meyer-Klaucke, W.; Leupold, O.; Rüter, H. D.; Gerdau, E.; Haas, M.; Realo, E.; Mon, D.; Weiss, R. *Pure Appl. Chem.* **1998**, *70*, 917.
73. Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; 2nd ed. VCH: Weinheim, 1991.
74. Tobe, M. L.; Burgess, J. *Inorganic Reaction Mechanisms* **1999**, Addison Wesley Longman: Harlow, U.K.
75. Twigg, M. V (Ed.) *Mechanisms of Inorganic Organometallic Reactions*; Plenum Press: New York, 1986; Vol. 4.
76. Twigg, M. V (Ed.) *Mechanisms of Inorganic Organometallic Reactions*; Plenum Press: New York, 1988; Vol. 5.
77. Twigg, M. V (Ed.) *Mechanisms of Inorganic Organometallic Reactions*; Plenum Press: New York, 1989; Vol. 6.
78. Twigg, M. V (Ed.) *Mechanisms of Inorganic Organometallic Reactions*; Plenum Press: New York, 1991; Vol. 7.
79. Twigg, M. V (Ed.) *Mechanisms of Inorganic Organometallic Reactions*; Plenum Press: New York, 1994; Vol. 8.
80. Lincoln, S. F.; Merbach, A. E. *Adv. Inorg. Chem.* **1995**, *42*, 1.
81. van Eldik, R. In *High Pressure Molecular Science*; Winter, R.; Jonas, J., Eds.; Kluwer, Dordrecht, 1999, p 267.
82. van Eldik, R.; Klärner, F.-G.(Eds.) *High Pressure Chemistry — Synthetic, Mechanistic, and Supercritical Application*; Wiley-VCH: Weinheim, 2002.
83. van Eldik, R.; Hubbard, C. D. *New J. Chem.* **1997**, *21*, 825.
84. Stochel, G.; van Eldik, R. *Coord. Chem. Rev.* **1997**, *159*, 153.
85. Van Eldik, R.; Ford, P. C. *Adv. Photochem.* **1998**, *24*, 61.
86. Drljaca, A.; Hubbard, C. D.; van Eldik, R.; Asano, T.; Basilevsky, M. V.; le Noble, W. J. *Chem. Rev.* **1998**, *98*, 2167.
87. Stochel, G.; van Eldik, R. *Coord. Chem. Rev.* **1999**, *187*, 329.
88. Van Eldik, R.; Hubbard, C. D. *S. Afr. J. Chem.* **2000**, *52*, 139.
89. van Eldik, R.; Dücker-Benfer, C.; Thaler, F. *Adv. Inorg. Chem.* **2000**, *49*, 1.
90. Coe, B. J.; Glenwright, S. J. *Coord. Chem. Rev.* **2000**, *203*, 5.
91. Sinha, U.; Lowery, M. D.; Hammack, W. S.; Hendrickson, D. N.; Drickamer, H. G. *J. Am. Chem. Soc.* **1987**, *109*, 7340.
92. Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1-S83.
93. Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609.
94. Roobottom, H. K.; Jenkins, H. D. B.; Passmore, J.; Glasser, L. *J. Chem. Educ.* **1999**, *76*, 1570.
95. Mingos, D. M. P.; Rohl, A. L.; Burgess, J. *J. Chem. Soc., Dalton Trans.* **1993**, 423.
96. Burgess, J.; Hubbard, C. D.; Patel, M. S.; Radulović, S.; Thuresson, K.; Parsons, S. A.; Guardado, P. *Transition Met. Chem.* **2002**, *27*, 134.
97. Griffin, W. C. *J. Soc. Cosmet. Chem.* **1946**, *1*, 311.
98. Griffin, W. C. *J. Soc. Cosmet. Chem.* **1954**, *5*, 249.
99. Sowada, R.; McGowan, J. C. *Tenside Surf. Det.* **1992**, *29*, 109.
100. Rekker, R. F.; Mannhold, R. (Eds.) *Calculation of Drug Lipophilicity*; VCH: Weinheim, 1992.
101. Blandamer, M. J.; Burgess, J. *Pure Appl. Chem.* **1983**, *55*, 55.
102. Burgess, J.; Pelizzetti, E. *Gazz. Chim. Ital.* **1988**, *118*, 803.
103. Burgess, J. *Pure Appl. Chem.* **1991**, *63*, 1677.
104. Burgess, J.; Pelizzetti, E. *Prog. React. Kinet.* **1992**, *17*, 1; and references therein.
105. Sachinidis, J. I.; Shalders, R. D.; Tregloan, P. A. *Inorg. Chem.* **1994**, *33*, 6180.
106. Swaddle, T. W.; Tregloan, P. A. *Coord. Chem. Rev.* **1999**, *187*, 255.
107. Sachinidis, J. I.; Shalders, R. D.; Tregloan, P. A. *Inorg. Chem.* **1996**, *35*, 2497.
108. Nishide, H.; Hashimoto, Y.; Maeda, H.; Tsuchida, E. *J. Chem. Soc., Dalton Trans.* **1987**, 2963.
109. Goldberg, Yu. Sh.; Iovel, I. G.; Shymanska, M. V. *J. Chem. Soc., Chem. Commun.* **1986**, 286.
110. Iovel, I. G.; Goldberg, Yu. Sh.; Shymanska, M. V.; Lukevics, E. *J. Chem. Soc., Chem. Commun.* **1987**, 31.
111. Micskei, K. *J. Chem. Soc., Dalton Trans.* **1987**, 255.
112. Kragten, J. *Atlas of Metal-Ligand Equilibria in Aqueous Solution;* Ellis Horwood: Chichester, U. K. 1978.
113. Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875.
114. Martell, A. E.; Hancock, R. D. *Metal Complexes in Aqueous Solution*; Plenum: New York, 1996.
115. Collman, J. P.; Fu, L. *Acc. Chem. Res.* **1999**, *32*, 455.
116. Seel, C.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 528.
117. Mikuriya, M.; Ikema, S.; Lim, J.-W. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 99.
118. Mikuriya, M.; Ikenuoe, S.; Nukada, R.; Lim, J.-W. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 101.
119. Ziessel, R. *Coord. Chem. Rev.* **2001**, *216–217*, 195.
120. Leigh, D. A.; Lusby, P. J.; Teat, S. J.; Wilson, A. J.; Wong, J. K. Y. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1538.
121. Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Dupont-Gervais, A.; Van Dorssellaer, A.; Kneisel, B.; Fenske, D. *J. Am. Chem. Soc.* **1997**, *119*, 10956.
122. Fatin-Rouge, N.; Blanc, S.; Leize, E.; Van Dorssellaer, A.; Baret, P.; Pierre, J.-L.; Albrecht-Gary, A. M. *Inorg. Chem.* **2000**, *39*, 5771.
123. Hasenknopf, B.; Lehn, J.-M.; Boumediene, N.; Leize, M.; Van Dorssellaer, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3265.
124. Kimura, M.; Kitamura, T.; Sano, M.; Muto, T.; Hanabusa, K.; Shirai, H.; Kobayashi, N. *New J. Chem.* **2000**, *24*, 113.
125. Hazell, A.; McKenzie, C. J.; Nielsen, L. P.; Schindler, S.; Weitzer, M. *J. Chem. Soc., Dalton Trans.* **2002**, 310.
126. Carrano, C. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1978**, *100*, 5371.
127. Baer, A. J.; Macartney, D. H. *Inorg. Chem.* **2000**, *39*, 1410.
128. Skinner, P. J.; Blair, S.; Kataky, R.; Parker, D. *New J. Chem.* **2000**, *24*, 265.
129. Ogden, M. I.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2001**, 3073.
130. Vögtle, F. *Supramolecular Chemistry*; Wiley: Chichester, U. K. 1991, Section 2.3.
131. Easton, C. J.; Lincoln, S. F. *Modified Cyclodextrins*; Imperial College Press: London, 1999.

132. Schilt, A. A. *Analytical Applications of 1,10-Phenanthroline and Related Compounds*; Pergamon: Oxford, 1969.
133. Luque de Castro, M. D.; Silva, M.; Valcarcel, M. *Analyst* **1984**, *109*, 1375.
134. Garcia de Torres, A.; Valcarcel, M.; Pino, F. *Talanta* **1973**, *20*, 919.
135. Salinas, F.; Jiménez Sánchez, J. C.; Galeano Díaz, T. *Analyt. Chem.* **1986**, *58*, 824.
136. Valcarcel, M.; Luque de Castro, M. D. *Flow Injection Analysis*; Ellis Horwood: Chichester, U.K. 1986.
137. Burguera, M.; Burguera, J. L.; Alarcón, O. M. *Analyt. Chim. Acta* **1986**, *179*, 351.
138. Rocks, B. F.; Sherwood, R. A.; Turner, Z. J.; Riley, C. *Ann. Clin. Biochem.* **1983**, *20*, 72.
139. Burguera, M.; Burguera, J. L.; Cergio Rivas, P.; Alarcón, O. M. *Atom. Spectr.* **1986**, *7*, 79.
140. Burguera, M.; Burguera, J. L.; Alarcón, O. M. *J. Analyt. Atom. Spectrom.* **1986**, *1*, 79.
141. Chen, Y.; Cai, R.; Zeng, Y. *Fenxi Huaxue* **1996**, *24*, 1166*Chem. Abstr.* **1997**, *126*, 54148t.
142. Johnson, D. J.; Williams, H. L. *Clin. Chim. Acta* **1990**, *189*, 199.
143. Safavi, A.; Abdollahi, H.; Hormozinezhad, M. R. *Talanta* **2002**, *56*, 699.
144. Zolgharnein, J.; Abdollahi, H.; Jaefarifar, D.; Azimi, G. H. *Talanta* **2002**, *56*, 1067.
145. Singh, D. K.; Mehrotra, P. *Bull. Soc. Chim. Fr.* **1989**, 348.
146. Andrade, S.; Hypolito, R.; Ulbrich, H. H. G. J.; Silva, M. L. *Chem. Geol.* **2002**, *182*, 85.
147. Habashi, F., Ed. *Handbook of Extractive Metallurgy*; Wiley-VCH: Weinheim, 1997, Section 5. 21.
148. Bartecki, A.; Burgess, J. *The Colour of Metal Compounds*; Gordon Breach: Reading, U.K., 2000.
149. Skelton, H. *Rev. Prog. Coloration* **1999**, *29*, 43.
150. Nassau, K. *The Physics and Chemistry of Colour*; Wiley: Chichester, U.K., 2001.
151. Christie, R. M. *Colour Chemistry*; RSC: Cambridge, 2001.
152. Tilley, R. *Colour and the Optical Properties of Materials*; Wiley: Chichester, U.K, 2000.
153. Volz, H. G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 688.
154. Elvers, B.; Hawkins, S.; Schulz, G. (Eds.) *Ullmann's Encyclopedia of Industrial Chemistry*; 5th ed. Vol. A20, VCH: Weinheim, 1992, p 243.
155. Olsson, K. S.; Säfwenberg, J.; Ritter, B. *Ann. N. Y. Acad. Sci.* **1988**, *526*, 290.
156. Dean, B. S.; Krenzelok, E. P. *Clin. Toxicol.* **1987**, *25*, 221.
157. McCance, R. A.; Widdowson, E. *The Composition of Foods*; 5th ed. Holl, B.; Welch, A. A.; Unwin, I. D.; Buss, D. H.; Paul, A. A.; Southgate, D. A. T., Eds.; 4th reprint, Royal Society of Chemistry: Cambridge, 1995.
158. Wildman, R. E. C. *The Nutritionist — Food, Nutrition, and Optimal Health*; Haworth Press: New York, 2002.
159. Baynes, R. D.; Stipanuk, M. H. Iron. In *Biochemical and Physiological Aspects of Human Nutrition*; Stipanuk, M. H, Ed.; H. Saunders: Philadelphia, U.S.A., 2000; Chap. 31.
160. Bothwell, T. H.; Finch, C. A. *Iron Metabolism*; Churchill: London, 1961.
161. Crichton, R. R. *Inorganic Biochemistry of Iron Metabolism*; 2nd ed. Wiley: New York, 2001.
162. Fairbanks, V. F. In *Hematology*; Williams, W. J.; Butler, E.; Erslev, A. J.; Lichtmann, M. A., Ed.; McGraw-Hill: New York, 1983, p 300.
163. Ferreira, G. C.; Moura, J. J. G.; Franco, R. (Eds.) *Iron Metabolism*; Wiley-VCH: Weinheim, 1999.
164. Halliwell, B.; Gutteridge, J. M. C. *Free Radicals in Biology and Medicine*; 2nd ed. Clarendon Press: Oxford, 1989.
165. Silver, S.; Walden, W. (Eds.) *Metal Ions in Gene Regulation*; Chapman & Hall; London, 1998.
166. Bullen, J. J.; Griffiths, E. (Eds.) *Iron Infection*; 2nd ed. Wiley: Chichester, U.K. 1999.
167. Richardson, D. R.; Ponka, P. *Biochim. Biophys. Acta* **1997**, *1331*, 1.
168. deJong, G.; van Dijk, J. P.; van Eijk, H. G. *Clin. Chim. Acta* **1990**, *90*, 17.
169. Schneider, W. *Arzneim. Forsch.* **1987**, *37*, 92.
170. Schneider, W. *Chimia* **1988**, *42*, 9.
171. Crichton, R. R.; Charloteaux-Wauters, M. *Eur. J. Biochem.* **1987**, *164*, 485.
172. Crichton, R. R. *Adv. Protein Chem.* **1990**, *40*, 281.
173. Winkelmann, G.; van der Helm, F.; Neils, J. B. (Eds.) *Iron Transport in Microbes, Plants and Animals*; VCH: Weinheim, 1987.
174. Albrecht-Gary, A. M.; Crumbliss, A. L. In *Metal Ions in Biological Systems*; Sigel, A.; Sigel, H., Eds.; Marcel Dekker: New York, 1998, Vol. 35, p 239.
175. Mason, P. *Handbook of Dietary Supplements*; Blackwell Science: Oxford, 1995.
176. Boccio, J. R.; Zubillaga, M. B.; Caro, R. A.; Lysionek, A.; Gotelli, C. A.; Gotelli, M. J.; Weill, R. *Biol. Trace Elem. Res.* **1998**, *62*, 65.
177. Thompson, C. J. S *The Lure and Romance of Alchemy*; Bell: New York, 1990, pp 22–23.
178. Dionis, J. B.; Jenny, H.-B.; Peter, H. H. *J. Org. Chem.* **1989**, *54*, 5623.
179. Porter, J. B.; Huehns, E. R.; Hider, R. C. *Baillière's Clin. Hematol.* **1989**, *2*, 257.
180. Grahame-Smith, D. G.; Aronson, J. K. *Oxford Textbook of Clinical Pharmacology and Drug Therapy*; 2nd ed. Oxford University Press: Oxford, 1992.
181. Hider, R. C.; Singh, S. In *Chemistry of Iron*; Silver, J., Ed. Chapman & Hall: London 1993, Chap. 8.
182. Bergeron, R. J.; Brittenham, G. M. (Eds.) *The Development of Iron Chelators for Clinical Use*; CRC Press: Boca Raton, FL, 1994.
183. Bergeron, R. J.; Badman, D. J; Brittenham, G. M. (Eds.) *Iron Chelators: New Development Strategies*; Saratoga Publishers: Ponte Vedra, Florida, 2000.
184. Tilbrook, G. S.; Hider, R. C.; Sigel, A.; Sigel, H., Eds.; *Metal Ions in Biological Systems* **1998**, *35*, 691 Marcel Dekker: New York.
185. Faa, G.; Crisponi, G. *Coord. Chem. Rev.* **1999**, *184*, 291.
186. Martell, A. E.; Motekaitis, R. J.; Murase, I.; Sala, L. F.; Stoldt, R.; Ng, C. Y.; Rosenkrantz, H.; Metterville, J. J. *Inorg. Chim. Acta* **1987**, *138*, 215.
187. Dobbin, P. S.; Hider, R. C. *Chem. Brit.* **1990**, 565.
188. Hershko, C.; Konijn, A. M.; Link, G. *Br. J. Hematol.* **1998**, *101*, 399.
189. Nathan, D. G. *Sem. Hematol.* **1990**, *27*, 83.
190. Giardina, P. J.; Grady, R. W. *Sem. Hematol.* **2001**, *38*, 360.
191. Crichton, R. R.; Florence, A.; Ward, R. J. *Coord. Chem. Rev.* **2002**, *228*, 365.
192. Hider, R. C.; Singh S.; Porter, J. B.; Huehns, E. R. *Ann. N. Y. Acad. Sci.* **1990**, *612*, 327.

193. Callingham, B. A.; Hider, R. C.; Kontoghiorghes, G.; Stockham, M. A. U. K. Patent Application GB 2,157,686: Iron complexes, published 30 Oct 1985 (date of filing 17 April 85) A, 1985.
194. Hider, R. C.; Kontoghiorghes, G.; Silver, J. European Patent Application 0093498: Pharmaceutical compositions containing *N*-substituted-3-hydroxypyrid-2-one or -4-one derivatives, date of filing 24 March 83. 1983.
195. Ahmet, M. T.; Frampton, C. S.; Silver, J. *J. Chem. Soc., Dalton Trans*. **1988**, 1159.
196. Serjeant, G. R. *Sickle Cell Disease*; 2nd ed. Oxford University Press: Oxford, 1992.
197. Kontoghiorghes, G. J. *Analyst* **1995**, *120*, 845.
198. Scarrow, R. C.; Riley, P. E.; Abu-Dari, K.; White, D. L.; Raymond, K. N. *Inorg. Chem*. **1985**, *24*, 954.
199. Kontoghiorghes, G. J.; Sheppard, L.; Hoffbrand, A. V.; Charalambous, J.; Tikerpae, J.; Pippard, M. J. *J. Clin. Pathol*. **1987**, *40*, 404.
200. Kontoghiorghes, G. J.; Aldouri, M.; Sheppard, L.; Hoffbr, A. V. *Lancet* **1987**, *1*, 1294.
201. Kontoghiorghes, G. J.; Goddard, J. G.; Bartlett, A. N.; Sheppard, L. *Clin. Pharmacol. Ther*. **1990**, *48*, 255.
202. Olivieri, N. F.; Brittenham, G. M. *Ann. N. Y. Acad. Sci*. **1998**, *850*, 217.
203. Cohen, A.; Galanello, R.; Piga, A.; Vullo, C.; Tricta, F. *Ann. N. Y. Acad. Sci*. **1998**, *850*, 223.
204. Borgna-Pignatti, C.; Rugulotto, S.; De Stefano, P.; Piga, A.; Di Gregorio, F.; Gamberini, M. R.; Sabato, V.; Melevendi, C.; Cappellini, M. D.; Verlato, G. *Ann. N. Y. Acad. Sci*. **1998**, *850*, 227.
205. Addis, A.; Loebstein, R.; Koren, G.; Einarson, T. R. *Eur. J. Clin. Pharmacol*. **1999**, *55*, 1.
206. Balfour, J. A. B.; Foster, R. H. *Drugs* **1999**, *58*, 553.
207. Cohen, A. R.; Galanello, R.; Piga, A.; DiPalma, A.; Vullo, C.; Tricta, F. *Br. J. Hematol*. **2000**, *108*, 305.
208. Kontoghiorghes, G. J.; Sheppard, L.; Chambers, S. *Arzneim. -Forsch*. **1987**, *37*, 1099.
209. Porter, J. B.; Hoyes, K. P.; Abeysinghe, R.; Huehns, E. R.; Hider, R. C. *Lancet* **1989**, *2*, 156.
210. Molenda, J. J.; Jones, M. M.; Basinger, M. A. *J. Med. Chem*. **1994**, *37*, 93.
211. Burgess, J.; Fawcett, J.; Parsons, S. A. *Acta Crystallogr*. **2001**, *E57*, o1016.
212. Liu, Z. D.; Khodr, H. H.; Lu, S. L.; Hider, R. C. *J. Pharm. Pharmacol*. **2000**, *52*, 263.
213. Galey, J.-B. *Adv. Pharmacol*. **1996**, *38*, 167.
214. Lauffer, R. B. *Chem. Rev*. **1987**, *87*, 901.
215. Epemolu, R. O.; Ackerman, R.; Porter, J. B.; Hider, R. C.; Damani, L. A.; Singh, S. *J. Pharm. Biomed. Anal*. **1994**, *12*, 923.
216. Riaz, M.; Pilpel, N. *J. Pharm. Pharmacol*. **1984**, *36*, 153.
217. Grenier, D.; Huot, M.-P.; Mayr, D. *Antimicrob. Agents Chemother*. **2000**, *44*, 763.
218. Pradines, B.; Rogier, C.; Fusai, T.; Mosnier, J.; Daries, W.; Barret, E.; Parzy, D. *Antimicrob. Agents Chemother*. **2001**, *45*, 1746.
219. Peterson, C. M.; Graziano, J. H.; Grady, R. W.; Jones, R. L.; Vlassara, H. V.; Canale, V. C.; Miller, D. R.; Cerami, A. *Br. J. Hematol*. **1976**, *33*, 477.
220. Heinz, U.; Hegetschweiler, K.; Acklin, P.; Faller, B.; Lattmann, R.; Schebli, H. P. *Angew. Chem., Int. Ed. Engl*. **1999**, *38*, 2568.
221. Hershko, C.; Konijn, A. M.; Nick, H. P.; Breuer, W.; Cabantchik, Z. I.; Link, G. *Blood* **2001**, *97*, 1115.
222. Bergeron, R. J.; Wieg, J.; Brittenham, G. M. *Blood* **1999**, *93*, 370.
223. Borsari, M.; Ferrari, E.; Grandi, R.; Saladini, M. *Inorg. Chim. Acta* **2002**, *328*, 61.
224. De Zwart, M. A. H.; van der Goot, H.; Timmerman, H. *J. Med. Chem*. **1988**, *31*, 716.
225. De Zwart, M. A. H.; van der Goot, H.; Timmerman, H. *J. Med. Chem*. **1989**, *32*, 487.
226. De Zwart, M. A. H.; Bastiaans, H. M. M.; van der Goot, H.; Timmerman, H. *J. Med. Chem*. **1991**, *34*, 1193.
227. Newman, S. L.; Gootee, L.; Stroobant, V.; van der Goot, H.; Boelaert, J. R. *Antimicrob. Agents Chemother*. **1995**, *39*, 1824.
228. Swope, S. K.; Chasteen, N. D.; Weber, K. E.; Harris, D. C. *J. Am. Chem. Soc*. **1988**, *110*, 3835.
229. Sosnovsky, G.; Rao, N. U. M. *Eur. J. Med. Chem*. **1988**, *23*, 517.
230. Wesbey, G. E.; Brasch, R. C.; Engelstadt, B. L.; Moss, A. A.; Crooks, L. E.; Brito, A. C. *Radiology* **1983**, *149*, 175.
231. Lauffer, R. B.; Greif, W. L.; Stark, D. D.; Vincent, A. C.; Saini, S.; Wedeen, V. J.; Brady, T. J. *J. Comput. Assist. Tomogr*. **1985**, *9*, 431.
232. Saini, S.; Hamm, B. In *Clinical Magnetic Resonance Imaging*; Edelman, R. R.; Hesselink, J. R. Eds.; W. B. Saunders: Philadelphia, 1990, Chap. 7, p 252.
233. Merbach, A. E.; Tóth, E. *The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging*; Wiley: New York, 2001.
234. Brooks, R. A.; Vymazal, J.; Goldfarb, R. B.; Bulte, J. W. M.; Aisen, P. *Magn. Reson. Med*. **1998**, *40*, 227.
235. Sadler, P. J.; Guo, Z. *Angew. Chem., Int. Ed. Engl*. **1999**, *38*, 1512.
236. Bjørnerud, A.; Johansson, L. O.; Briley-Sæbø, K.; Ahlström, H. K. *Magn. Res. Med*. **2002**, *47*, 461.
237. Miller, M. J.; Malouin, F. In *The Development of Iron Chelators for Clinical Use*; Bergeron, R. J.; Brittenham, G. M., Eds.; CRC Press: Boca Raton, 1994, p 275.
238. Johnson, G. A.; Benveniste, H.; Engelhardt, R. T.; Qiu, H.; Hedlund, L. W. *Ann. N. Y. Acad. Sci*. **1997**, *820*, 139.
239. Comblin, V.; Gilsoul, D.; Hermann, M.; Humblet, V.; Jacques, V.; Mesbahi, M.; Sauvage, C.; Desreux, J. F. *Coord. Chem. Rev*. **1999**, *185–186*, 451.
240. Short, M. D. In *Textbook of Radiopharmacy*; 2nd ed. Sampson, C.B., Ed.; Gordon Breach: Yverdon, Switzerland, 1994, p 6.
241. Sharman, W. M.; Allen, C. M.; van Lier, J. E. *Drug Design Testing* **1999**, *4*, 507.
242. Ford, P. C.; Bourassa, J.; Mira, K.; Lee, B.; Lorkovic, I.; Boggs, S.; Kudo, S.; Laverman, L. *Coord. Chem. Rev*. **1998**, *171*, 185.
243. Webb, J.; Macey, D. J.; Chua-anusorn, W.; Pierre, T. G.; Brooker, L. R.; Rahman, I.; Noller, B. *Coord. Chem. Rev*. **1999**, *190–192*, 1199.
244. Connell, D. W.; Hawker, D. W.; St, J.; Warne, M.; Vowles, P. P. *Basic Concepts of Environmental Chemistry*; Lewis Publishers: New York, 1997.
245. Clark, R. B.; Frid, C.; Attrill, M. *Marine Pollution*; Clarendon Press: Oxford, 1997.
246. Furness, R. W.; Rainbow, P. S. (Eds.) *Heavy Metals in the Marine Environment*; CRC Press: Boca Raton, Florida, 1990.
247. Stumm, W.; Morgan, J. J. *Aquatic Chemistry*; Wiley-Interscience: New York, 1970.

248. Pankow, J. F. *Aquatic Chemistry Concepts*; Lewis Publishers: Chelsea, Michigan, U. S. A, 1991.
249. Chester, R. *Marine Geochemistry*; Unwin Hyman: London, 1990.
250. Stumm, W. (Ed.) *Aquatic Chemical Kinetics*; Wiley-Interscience: New York, 1990.
251. Olausson, E.; Cato, I. (Eds.) *Chemistry and Biogeochemistry of Estuaries*; Wiley: Chichester, U.K, 1980.
252. Harrison, R. M. (Ed.) *Understanding Our Environment*; 2nd ed., Royal Society of Chemistry: Cambridge, 1992.
253. O'Neill, P. *Environmental Chemistry*, 2nd ed.; Chapman & Hall: London, 1993.
254. Appelo, C. A. J.; Postma, D. *Geochemistry, Groundwater and Pollution*; Balkema: Rotterdam, 1993.
255. Ernst, W. H. O.; Tolsma, D. J. In *Mineral Nutrients in Tropical Forest and Savanna Ecosystems*; Proctor, J., Ed. Blackwell: Oxford, 1989, p 97.
256. Wagh, A. S.; Pinnock, W. R. *Econ. Geol.* **1987**, *82*, 757.
257. Kerr, R. A. *Science* **1994**, *263*, 1089.
258. Corfield, R. *Chem. Brit.* **2003**, *39*, 30.
259. Reid, R. T.; Live, D. H.; Faulkner, D. J.; Butler, A. *Nature* **1993**, *366*, 455.
260. Barbeau, K.; Rue, E. L.; Brul, K. W.; Butler, A. *Nature* **2001**, *413*, 409.
261. Frankel, R. B.; Blakemore, R. P. (Eds.) *Iron Biominerals*; Plenum: New York, 1991.
262. Barry, R. C.; Schnoor, J. L.; Salzberger, B.; Sigg, L.; Stumm, W. *Water Res.* **1994**, *28*, 323.
263. Brown, D. A.; Sherriff, B. L.; Sawicki, J. A.; Sparling, R. *Geochim. Cosmochim. Acta* **1999**, *63*, 2163.
264. Kasama, T.; Murakami, T. *Chem. Geol.* **2001**, *180*, 117.
265. Langford, C. H.; Khan, T. R. *Can. J. Chem.* **1975**, *53*, 2979.
266. Langford, C. H.; Wong, S. M.; Underdown, A. W. *Can. J. Chem.* **1981**, *59*, 181.
267. Lavigne, J. A.; Langford, C. H.; Mak, M. K. S. *Analyt. Chem.* **1987**, *59*, 2616.
268. Hagen, K. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1010.
269. Matsumoto, H.; Smith, E. G.; Sherman, G. D. *Arch. Biochem. Biophys.* **1951**, *33*, 201.
270. Reis, P. J.; Tunks, D. A.; Chapman, R. E. *Aust. J. Biol. Sci.* **1975**, *28*, 69.
271. Reis, P. J. *Aust. J. Biol. Sci.* **1975**, *28*, 483.
272. Stünzi, H.; Harris, R. L. N.; Perrin, D. D.; Teitei, T. *Aust. J. Chem.* **1980**, *33*, 2207.
273. Hardy, J. A.; Aust, A. E. *Chem. Rev.* **1995**, *95*, 97.
274. Wang, X.; Forssberg, K. S. E. *Miner. Process. Extractive Metall. Rev.* **1990**, *6*, 81.
275. Itaya, K.; Uchida, I.; Neff, V. D. *Acc. Chem. Res.* **1986**, *19*, 162.
276. Carrado, K. A.; Kostapapas, A.; Suib, S. L. *Solid State Ionics* **1988**, *26*, 77.
277. Chibwe, K.; Jones, W. *Chem. Mater.* **1989**, *1*, 489.
278. Yang, M.; Thompson, D. W.; Meyer, G. J. *Inorg. Chem.* **2002**, *41*, 1254.
279. Domingo, P. L.; Garcia, B.; Leal, J. M. *Can. J. Chem.* **1987**, *65*, 583.
280. Capone, S.; Robertis, A.; Sammartano, S. *Thermochim. Acta* **1986**, *112*, 1.
281. Sicilia, D.; Rubio, S.; Perez Bendito, D. *Talanta* **1991**, *38*, 1147.
282. Mullica, D. F.; Perkins, H. O.; Sappenfield, E. L. *Inorg. Chim. Acta* **1988**, *142*, 9.
283. Marsh, R. E. *Inorg. Chim. Acta* **1989**, *157*, 1.
284. Mullica, D. F.; Sappenfield, E. L. *Inorg. Chim. Acta* **1989**, *157*, 3.
285. Kitazawa, T.; Takahashi, M.; Takeda, M. *Hyperfine Interact.* **1994**, *84*, 527 (*Chem. Abstr.* **1994**, *121*, 166327d).
286. Zahl, A.; van Eldik, R.; Swaddle, T. W. *Inorg. Chem.* **2002**, *41*, 757.
287. Oh, S. M.; Faulkner, L. R. *J. Electroanal. Chem.* **1989**, *269*, 77.
288. Sieklucka, B. *Prog. React. Kinet.* **1989**, *15*, 175.
289. Hin-Fat, L. *J. Chem. Soc., Dalton Trans.* **1988**, 273.
290. Benko, J.; Vollárová, O.; Alshehri, S.; Burgess, J.; Haines, R. I. *Transition Met. Chem.* **1993**, *18*, 551.
291. Dash, A. C.; Mohanty, P.; Brahma, G. S. *Indian J. Chem.* **1996**, *35A*, 1062.
292. Coddington, J. W.; Wherl, S.; Hurst, J. K. *Inorg. Chem.* **2001**, *40*, 528.
293. Krack, I.; Braun, P.; van Eldik, R. *Physica B + C (Amsterdam)* **1986**, *139–140*, 680.
294. Ašperger, S.; Murati, I.; Pavlovīc, D.; Šustra, A. *J. Chem. Soc., Chem. Commun.* **1986**, 814.
295. Abdel-Khalek, A. A. *Transition Met. Chem.* **1986**, *11*, 67.
296. Baños, J.; Sánchez Burgos, F.; Carmona Guzmán, M. C. *J. Chem. Soc., Dalton Trans.* **1985**, 1975.
297. Rodriguez, A.; Sánchez Burgos, F.; Burgess, J.; Carmona, C. *Can. J. Chem.* **1990**, *68*, 926.
298. Rodriguez, A.; Carmona, C.; Muñoz, E.; Sánchez, F.; Burgess, J. *Transition Met. Chem.* **1991**, *16*, 535.
299. Morillo, M.; Denk, C.; Pérez, P.; López, M.; Sánchez, A.; Prado, R.; Sánchez, F. *Coord. Chem. Rev.* **2000**, *204*, 173.
300. Poonkodi, S. P. R.; Anbalagan, K. *Transition Met. Chem.* **2001**, *26*, 212.
301. Pérez Tejeda, P.; Rodriguez Velasco, J.; Sánchez Burgos, F. *J. Chem. Soc., Dalton Trans.* **1983**, 2679 and references therein.
302. Gokavi, G. S.; Raju, J. R. *Int. J. Chem. Kinet.* **1988**, *20*, 365.
303. Dennis, C. R.; Van Wyk, A. J.; Basson, S. S.; Leipoldt, J. G. *Inorg. Chem.* **1987**, *26*, 270.
304. Al-Subu, M. M.; El-Halawa, R. A.; Abed, H. M. *Int. J. Chem. Kinet.* **1990**, *22*, 1027.
305. Kaziro, R. W.; Beattie, J. K. *Aust. J. Chem.* **1989**, *42*, 1273.
306. Awasthi, A. K.; Upadhyay, S. K. *Transition Met. Chem.* **1985**, *10*, 281.
307. Kumar, P.; Gupta, K. C.; Vehari, K. *React. Kinet. Catal. Lett.* **1985**, *29*, 297.
308. Nath, N.; Singh, L. P. *Rev. Roum. Chim.* **1986**, *31*, 489.
309. Rodriguez, A.; López, S.; Carmona Guzmán, M. C.; Sánchez Burgos, F.; Piazza, C. *J. Chem. Soc., Dalton Trans.* **1986**, 1265.
310. Rodriguez, A.; Muñoz, E.; Jiménez, R.; Carmona, C.; Sánchez, F.; Burgess, J. *Transition Met. Chem.* **1991**, *16*, 102.
311. Kim, Y.; Kim, S.-J.; Nam, W. *Acta Crystallogr.* **2001**, *C57*, 266.
312. Buschmann, W. E.; Miller, J. S. *Inorg. Chem. Commun.* **1998**, *1*, 174.
313. Thétiot, F.; Triki, S.; Pala, J. S. *New J. Chem.* **2002**, *26*, 196.
314. Zhang, S.-W.; Duan, C.-Y.; Sun, W.-Y.; Fu, D.-G.; Tang, W.-X. *Transition Met. Chem.* **2001**, *26*, 127.
315. Lu, T.; Xiang, H.; Su, C.; Cheng, P.; Mao, Z.; Ji, L. *New J. Chem.* **2001**, *25*, 216.
316. Colacio, E.; Domínguez-Vera, J. M.; Ghazi, M.; Kivekäs, R.; Lloret, F.; Moreno, J. M.; Stoeckli-Evans, H. *Chem. Commun.* **1999**, 987.

317. Colacio, E.; Domínguez-Vera, J. M.; Ghazi, M.; Kivekäs, R.; Klinga, M.; Moreno, J. M. *Chem. Commun.* **1998**, 1071.
318. Re, N.; Crescenzi, R.; Floriani, C.; Miyasaka, H.; Matsumoto, N. *Inorg. Chem.* **1998**, *37*, 2717.
319. Darensbourg, D. J.; Adams, M. J.; Yarbrough, J. C. *Inorg. Chem.* **2001**, *40*, 6543.
320. Mullica, D. F.; Sappenfield, E. L.; Tippin, D. B.; Leschnitzer, D. H. *Inorg. Chim. Acta* **1989**, *164*, 99.
321. Kitazawa, T.; Gomi, Y.; Takahashi, M.; Takeda, M.; Enomoto, M.; Miyazaki, A.; Enoki, T. *J. Mater. Chem.* **1996**, *6*, 119.
322. Niel, V.; Martinez-Agudo, J. M.; Muñoz, M. C.; Gaspar, A. B.; Real, J. A. *Inorg. Chem.* **2001**, *40*, 3838.
323. Kitazawa, T.; Sato, Y.; Takahashi, M.; Takeda, M. *J. Phys. Chem. Solids* **1996**, *57*, 1073.
324. Kitazawa, T.; Fukunaga, M.; Takahashi, M.; Takeda, M. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **1994**, *244*, 331 (*Chem. Abstr.* **1994**, *121*, 98251x).
325. Luo, J.; Hong, M.; Chen, C.; Wu, M.; Gao, D. *Inorg. Chim. Acta* **2002**, *328*, 185.
326. Yan, B.; Chen, Z. *Helv. Chim. Acta* **2001**, *84*, 817.
327. Hulliger, F.; Vetsch, H. *Eur. J. Solid State Inorg. Chem.* **1994**, *31*, 363; and references therein.
328. Ali, S. I.; Murtaza, Z. *Ind. J. Chem.* **1984**, *23A*, 258.
329. Bertrán, J. F.; Ruíz, E. R. *Spectrochim. Acta* **1993**, *49A*, 43.
330. Appelt, R.; Vahrenkamp, H. *Z. Anorg. Allg. Chem.* **2003**, *629*, 133.
331. Watson, D. F.; Bocarsly, A. B. *Coord. Chem. Rev.* **2001**, *211*, 177.
332. Gütlich, P.; Garcia, Y.; Woike, T. *Coord. Chem. Rev.* **2001**, *219–221*, 839.
333. Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem.* **1987**, *45*, 283.
334. Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.
335. Clark, R. J. H. *Chem. Soc. Rev.* **1984**, *13*, 219.
336. Pavlishchuk, V. V.; Koval, I. A.; Goreshnik, E.; Addison, A. W.; van Albada, G. A.; Reedijk, J. *Eur. J. Inorg. Chem.* **2001**, 297.
337. Shimamoto, N.; Ohkoshi, S.; Sato, O.; Hashimoto, K. *Inorg. Chem.* **2002**, *41*, 678.
338. Baraldo, L. M.; Forlano, P.; Parise, A. R.; Slep, L. D.; Olabe, J. A. *Coord. Chem. Rev.* **2001**, *219–221*, 881.
339. Bruce, D. W.; Dunmur, D. A.; Maitlis, P. M.; Watkins, J. M.; Tiddy, G. J. T. *Liquid Crystals* **1992**, *11*, 127.
340. Alshehri, S.; Burgess, J.; Morgan, G. H.; Patel, B.; Patel, M. S. *Transition Met. Chem.* **1993**, *18*, 619.
341. Burgess, J.; Patel, M. S. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 783.
342. Benko, J.; Vollárová, O.; Grančićová, O.; Holba, V. *J. Coord. Chem.* **1985**, *14*, 175.
343. Toma, H. E.; Takasugi, M. S. *J. Solution Chem.* **1989**, *18*, 575.
344. Rodriguez, A.; Sánchez, F.; Moyá, M. L.; Burgess, J.; Al-Alousy, A. *Transition Met. Chem.* **1991**, *16*, 445.
345. Burgess, J. *Spectrochim. Acta* **1989**, *45A*, 159.
346. Johnson, C. R.; Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1984**, *23*, 2754.
347. Macartney, D. H. *Rev. Inorg. Chem.* **1988**, *9*, 101.
348. Stochel, G. *Coord. Chem. Rev.* **1992**, *114*, 269.
349. Iha, N. Y. M.; de Lima, J. F. *Inorg. Chem.* **1991**, *30*, 4576.
350. Baran, Y.; Ulgen, A. *Int. J. Chem. Kinet.* **1998**, *30*, 415.
351. Williams, P. A. M.; Aymonino, P. J. *Transition Met. Chem.* **1986**, *11*, 213.
352. Reddy, K. B.; van Eldik, R. *Inorg. Chem.* **1991**, *30*, 596.
353. Chen, C.; Wu, M.; Yeh, A.; Tsai, T. Y. R. *Inorg. Chim. Acta* **1998**, *267*, 81.
354. Stochel, G.; Chatlas, J.; Martinez, P.; van Eldik, R. *Inorg. Chem.* **1992**, *31*, 5480.
355. Alonso, A. M.; Williams, P. A. M.; Aymonino, P. J. *Anal. Asoc. Quím. Argent.* **1988**, *76*, 151.
356. Shi, C.-H.; Wang, S.-T.; Yang, S.-Y.; Yeh, A.; Tien, H.-J. *J. Chin. Chem. Soc. (Taipei)* **1998**, *45*, 77 (*Chem. Abstr.* **1998**, *128*, 252063r).
357. Macartney, D. H.; Warrack, L. J. *Can. J. Chem.* **1989**, *67*, 1774.
358. Lee, G.-H.; Della Ciana, L.; Haim, A. *J. Am. Chem. Soc.* **1989**, *111*, 2535.
359. Das, A.; Bajaj, H. C. *Polyhedron* **1997**, *16*, 1023.
360. Huang, H.-Y.; Chen, W.-J.; Yang, C.-C.; Yeh, A. *Inorg. Chem.* **1991**, *30*, 1862.
361. Almaraz, A. E.; Gentil, L. A.; Baraldo, L. M.; Olabe, J. A. *Inorg. Chem.* **1996**, *35*, 7718.
362. Blandamer, M. J.; Burgess, J.; Fawcett, J.; Radulović, S.; Russell, D. R. *Transition Met. Chem.* **1988**, *13*, 120.
363. Blandamer, M. J.; Briggs, B.; Burgess, J.; Elvidge, D.; Guardado, P.; Hakin, A. W.; Radulović, S.; Hubbard, C. D. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2703.
364. Blandamer, M. J.; Burgess, J.; Duce, P. P.; Elvidge, D. L.; Guardado, P.; Hubbard, C. D.; Ibechem, J. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 215.
365. Al-Alousy, A.; Alshehri, S.; Blandamer, M. J.; Blundell, N. J.; Burgess, J.; Cowles, H. J.; Radulović, S.; Guardado, P.; Hubbard, C. D. *J. Chem. Soc. Faraday Trans. 1* **1993**, *89*, 1041.
366. Blandamer, M. J.; Burgess, J.; Hakin, A. W.; Guardado, P.; Nuttall, S.; Radulović, S. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 559.
367. Blandamer, M. J.; Burgess, J.; Fawcett, J.; Guardado, P.; Hubbard, C. D.; Nuttall, S.; Prouse, L. J. S.; Radulovīč, S.; Russell, D. R. *Inorg. Chem.* **1992**, *31*, 1383.
368. Alshehri, S.; Blandamer, M. J.; Burgess, J.; Guardado, P.; Hubbard, C. D. *Polyhedron* **1993**, *12*, 445.
369. Blandamer, M. J.; Burgess, J.; Guardado, P.; Hubbard, C. D. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 735.
370. Blandamer, M. J.; Burgess, J.; Elvidge, D. L.; Guardado, P.; Hakin, A. W.; Prouse, L. J. S.; Radulović, S.; Russell, D. R. *Transition Met. Chem.* **1991**, *16*, 82.
371. Al Alousy, A.; Burgess, J. *Transition Met. Chem.* **1987**, *12*, 565.
372. Yeh, A.; Haim, A. *J. Am. Chem. Soc.* **1985**, *107*, 369.
373. Toma, H. E.; Rocha, R. C. *Croat. Chem. Acta* **2001**, *74*, 499.
374. Hoddenbagh, J. M. A.; Macartney, D. H. *Inorg. Chem.* **1986**, *25*, 2099.
375. Toma, H. E.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 176.
376. Maciejowska, I.; van Eldik, R.; Stochel, G.; Stasicka, Z. *Inorg. Chem.* **1997**, *36*, 5409.
377. Alshehri, S.; Burgess, J. *Inorg. Chim. Acta* **1991**, *181*, 153.
378. Alshehri, S.; Burgess, J.; Van Eldik, R.; Hubbard, C. D. *Inorg. Chim. Acta* **1995**, *240*, 305.
379. Abu-Gharib, E. A.; Razak bin Ali, M.; Blandamer, M. J.; Burgess, J. *Transition Met. Chem.* **1987**, *12*, 371.

380. Moyá, M. L.; Barrios, A.; Graciani, M. del, M.; Jiménez, R.; Muñoz, E.; Sánchez, F.; Burgess, J. *Transition Met. Chem.* **1991**, *16*, 165.
381. Tejera, I.; Rodriguez, A.; Sánchez, F.; Moyá, M. L.; Burgess, J. *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 2573.
382. Tejera, I.; Jiménez, R.; Rodríguez, A.; Sánchez, F.; Moyá, M. L. *React. Kinet. Catal. Lett.* **1992**, *46*, 427.
383. Barrios, A.; Graciani, M. del M.; Jiménez, R.; Muñoz, E.; Sánchez, F.; Moyá, M. L.; Alshehri, S.; Burgess, J. *Transition Met. Chem.* **1992**, *17*, 231.
384. Al-Alousy, A.; Alshehri, S.; Burgess, J.; Graciani, M. del M.; Moyá, M.-L.; Muñoz, E.; Rodriguez, A.; Sánchez, F. *Transition Met. Chem.* **1993**, *18*, 179.
385. Muriel-Delgado, F.; Jiménez, R.; Gómez-Herrera, C.; Sánchez, F. *Langmuir* **1999**, *15*, 4344.
386. Muriel-Delgado, F.; Jiménez, R.; Gómez-Herrera, C.; Sánchez, F. *New J. Chem.* **1999**, *23*, 1203.
387. Rodríguez, A.; Moyá, M. L.; López, P.; Muñoz, E. *Int. J. Chem. Kinet.* **1990**, *22*, 1017.
388. Stochel, G.; van Eldik, R.; Hejmo, E.; Stasicka, Z. *Inorg. Chem.* **1988**, *27*, 2767.
389. Stochel, G.; van Eldik, R. *Inorg. Chim. Acta* **1989**, *155*, 95.
390. Stochel, G.; van Eldik, R. *Inorg. Chim. Acta* **1991**, *190*, 55.
391. Bradley, S. M.; Doine, H.; Krouse, H. R.; Sisley, M. J.; Swaddle, T. W. *Aust. J. Chem.* **1988**, *41*, 1323.
392. Hrepic, N. V.; Malin, J. M. *Inorg. Chem.* **1979**, *18*, 409.
393. Coelho, A. L.; Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1983**, *22*, 2703.
394. Roncaroli, F.; Olabe, J. A.; van Eldik, R. *Inorg. Chem.* **2002**, *41*, 5417.
395. Bennett, D. A.; Dasgupta, T. P.; Stedman, G. *Transition Met. Chem.* **1998**, *23*, 749.
396. Guardado, P.; van Eldik, R. *Inorg. Chem.* **1990**, *29*, 3473.
397. Gotor, R. P.; López, P.; Pérez, P.; Jiménez, R.; Sánchez, F.; Burgess, J. *Transition Met. Chem.* **2002**, *27*, 127.
398. Moyá, M. L.; Burgess, J.; Sánchez, F. *Int. J. Chem. Kinet.* **1993**, *25*, 469.
399. Muriel, F.; Sánchez, F.; Burgess, J. *Transition Met. Chem.* **2000**, *25*, 537.
400. Razak bin Ali, M.; Blandamer, M. J.; Burgess, J.; Guardado, P.; Sánchez, F. *Inorg. Chim. Acta* **1987**, *131*, 59.
401. Prado-Gotor, R.; Jiménez, R.; Pérez-Tejeda, P.; López-López, M.; Sánchez, F. *Chem. Phys.* **2001**, *263*, 139.
402. Galán, M.; Domínguez, M.; Moyá, M. L.; Sánchez, F.; Burgess, J. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 937.
403. Moyá, M. L.; Sánchez, F.; Burgess, J. *Int. J. Chem. Kinet.* **1993**, *25*, 891.
404. Sasaki, Y.; Ninomiya, T.; Nagasawa, A.; Endo, K.; Saito, K. *Inorg. Chem.* **1987**, *26*, 2164.
405. Glöckle, M.; Kaim, W.; Klein, A.; Roduner, E.; Hübner, G.; Zalis, S.; van Slageren, J.; Renz, F.; Gütlich, P. *Inorg. Chem.* **2001**, *40*, 2256.
406. Narain, G.; Agnihotri, T. M.; Shukla, P. R. *Indian J. Chem. Sect. A* **1984**, *23*, 243.
407. Casado, J.; Mosquera, M.; Rodríguez Prieto, M. F.; Vázquez Tato, J. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 735.
408. Narain, G.; Shakya, A. K.; Shukla, P. R. *Thermochim. Acta* **1983**, *64*, 373.
409. Narain, G.; Shakya, A. K.; Shukla, P. R. *Thermochim. Acta* **1983**, *67*, 377.
410. Smith, J. N.; Dasgupta, T. P. *Inorg. React. Mech.* **2001/2**, *3*, 181.
411. Shishido, S. M.; Ganzarolli de Oliveira, M. *Prog. React. Kinet. Mech.* **2001**, *26*, 239.
412. Janiak, C.; Dorn, T.; Paulsen, H.; Wrackmeyer, B. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1663.
413. Wanner, M.; Scheiring, T.; Kaim, W.; Slep, L. D.; Baroldo, L. M.; Olabe, J. A.; Záliš, S.; Baerends, E. J. *Inorg. Chem.* **2001**, *40*, 5704.
414. Rauhala, P.; Oh, T.; Yeh, K.; Chiueh, C. C. *Ann. N. Y. Acad. Sci.* **2002**, *962*, 60.
415. Kuroda, Y.; Tanaka, N.; Goto, M.; Sakai, T. *Inorg. Chem.* **1989**, *28*, 997.
416. Jiang, J.; Acunzo, A.; Koch, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 12109.
417. Jiang, J.; Koch, S. A. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2629.
418. Rauchfuss, T. B.; Contakes, S. M.; Hsu, S. C. N.; Reynolds, M. A.; Wilson, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 6933.
419. Jiang, J.; Koch, S. A. *Inorg. Chem.* **2002**, *41*, 158.
420. Contakes, S. M.; Hsu, S. C. N.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2002**, *41*, 1670.
421. Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.
422. Bley, B.; Willner, H.; Aubke, F. *Inorg. Chem.* **1997**, *36*, 158.
423. Bernhardt, E.; Bley, B.; Wartchow, R.; Willner, H.; Bill, E.; Kuhn, P.; Sham, I. H. T.; Bodenbinder M.; Brochler, R.; Aubke, F. *J. Am. Chem. Soc.* **1999**, *121*, 7188.
424. Morel, A. C.; Rauchfuss, T. B. *Inorg. Chem.* **2000**, *39*, 3029.
425. Volbeda, A.; Charon, M.-H.; Piras, C.; Hatchikian, E. C.; Frey, M.; Fontecilla-Camps, J. C. *Nature* **1995**, *373*, 580.
426. Freemantle, M. *Chem. Eng. News* **2002**, July 22, 35.
427. Peters, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853.
428. Nicolet, Y.; Piras, C.; Legrand, P.; Hatchikian, E. C.; Fontecilla-Camps, J. C. *Structure* **1999**, *7*, 13.
429. Lemon, B. J.; Peters, J. W. *Biochemistry* **1999**, *38*, 12969.
430. Schmidt, M.; Contakes, S. M.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 9736.
431. Le Cloiret, A.; Best, S. P.; Borg, S.; Davies, S. C.; Evans, D. J.; Hughes, D. L.; Pickett, C. J. *Chem. Commun.* **1999**, 2285.
432. Lyon, E. J.; Georgakaki, I. P.; Reibenspies, J. H.; Darensbourg, M. Y. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3178.
433. Gloaguen, F.; Lawrence, J. D.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **2001**, *123*, 9476.
434. Bruschi, M.; Fantucci, P.; De Gioia, L. *Inorg. Chem.* **2002**, *41*, 1421.
435. Razavet, M.; Davies, S. C.; Hughes, D. L.; Pickett, C. J. *Chem. Commun.* **2001**, 847.
436. Viefhaus, T.; Schwarz, W.; Hübler, K.; Locke, K.; Weidlein, J. *Z. Anorg. Allg. Chem.* **2001**, *627*, 715.
437. Kayal, A.; Lee, S. C. *Inorg. Chem.* **2002**, *41*, 321.
438. Simonneaux, G.; Kobeissi, M. *J. Chem. Soc., Dalton Trans.* **2001**, 1587.
439. Hirano, M.; Akita, M.; Morikita, T.; Kubo, H.; Fukuoka, A.; Komiya, S. *J. Chem. Soc., Dalton Trans.* **1997**, 3453.
440. Schimek, G. L.; Kolis, J. W.; Long, G. J. *Chem. Mater.* **1997**, *9*, 2776.
441. Chen, Z.; Wang, R.-J.; Huang, X.-Y.; Li, J. *Acta Crystallogr.* **2000**, *56C*, 1100.
442. Calderazzo, F.; Englert, U.; Pampaloni, G.; Vanni, E. *C. R. Acad. Sci. Ser. IIc : Chim.* **1999**, 311.
443. Stubbe, J.; Kozarich, J. W. *Chem. Rev.* **1987**, *87*, 1107.
444. Loeb, K. E.; Zalseki, J. M.; Hess, C. D.; Hecht, S. M.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 53.

445. Hecht, S. M. *Acc. Chem. Res.* **1986**, *19*, 383.
446. Claussen, C. A.; Long, E. C. *Chem. Rev.* **1999**, *99*, 2797.
447. Turner, S. S.; Michaut, C.; Durot, S.; Day, P.; Gelbrich, T.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **2000**, 905.
448. De Munno, G.; Poerio, T.; Viau, G.; Julve, M.; Lloret, F.; Journaux, Y.; Rivière, E. *J. Chem. Soc., Chem. Commun.* **1996**, 2587.
449. Drummond, J.; Wood, J. S. *J. Chem. Soc., Chem. Commun.* **1969**, 1373.
450. Kornath, A. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3135.
451. De Munno, G.; Poerio T.; Viau, G.; Julve, M.; Lloret, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1459.
452. Hao, X.; Wei, Y.; Zhang, S. *Chem. Commun.* **2000**, 2271.
453. Shen, H.-Y.; Bu, W.-M.; Gao, E.-Q.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Wang, G.-L. *Inorg. Chem.* **2000**, *39*, 396.
454. Fukui, H.; Ito, M.; Moro-oka, Y.; Kitajima, N. *Inorg. Chem.* **1990**, *29*, 2868.
455. Sheriff, S.; Hendrickson, W. A. Smith J. L. *J. Mol. Biol.* **1987**, *197*, 273.
456. Singh, B.; Long, J. R.; de Biani, F. F.; Gatteschi, D.; Stavropoulos, P. *J. Am. Chem. Soc.* **1997**, *119*, 7030.
457. Januszczyk, M.; Janicki, J.; Wojakowska, H.; Krzyminiewski, R.; Pietrzak, J. *Inorg. Chim. Acta* **1991**, *186*, 27.
458. Kiani, S.; Tapper, A.; Staples, R. J.; Stavropoulos, P. *J. Am. Chem. Soc.* **2000**, *122*, 7503.
459. Kaji, K.; Sorai, M. *Thermochim. Acta* **1985**, *88*, 185.
460. Nakamoto, T.; Tan, Z.-C.; Sorai, M. *Inorg. Chem.* **2001**, *40*, 3805.
461. Wiehl, L.; Kiel, G.; Köhler, C. P.; Spiering, H.; Gütlich, P. *Inorg. Chem.* **1986**, *25*, 1565.
462. Kamiyama, A.; Noguchi, T.; Kajiwara, T.; Ito, T. *Inorg. Chem.* **2002**, *41*, 507.
463. Ugalde-Saldívar, V. M.; Sosa-Torres, M. E.; Ortiz-Frade, L.; Bernès, S.; Höpfl, H. *J. Chem. Soc., Dalton Trans.* **2001**, 3099.
464. Anderson, P. A.; Astley, T.; Hitchman, M. A.; Keene, F. R.; Moubaraki, B.; Murray, K. S.; Skelton, B. W.; Tiekink, E. R. T.; Toftlund, H.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2000**, 3505.
465. Ogo, S.; Wada, S.; Watanabe, Y.; Iwase, M.; Wada, A.; Harata, M.; Jitsukawa, K.; Masuda, H.; Einage, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2102.
466. Wada, A.; Ogo, S.; Watanabe, Y.; Mukai, M.; Kitagawa, T.; Jitsukawa, K.; Masuda, H.; Einage, H. *Inorg. Chem.* **1999**, *38*, 3592.
467. Wada, A.; Ogo, S.; Nagatomo, S.; Kitagawa, T.; Watanabe, Y.; Jitsukawa, K.; Masuda, H. *Inorg. Chem.* **2002**, *41*, 616.
468. Mandon, D.; Nopper, A.; Litrol, T.; Goetz, S. *Inorg. Chem.* **2001**, *40*, 4803.
469. Matouzenko, G. S.; Létard, J.-F.; Lecocq, S.; Bousseksou, A.; Capes, L.; Salmon, L.; Perrin, M.; Kahn, O.; Collet, A. *Eur. J. Inorg. Chem.* **2001**, 2935.
470. Riley, D. P. *Chem. Rev.* **1999**, *99*, 2573 (see Section 4B); and references therein.
471. Pascaly, M.; Duda, M.; Schweppe, F.; Zurlinden, K.; Müller, F. K.; Krebs, B. *J. Chem. Soc., Dalton Trans.* **2001**, 828.
472. Kryatov, S. V.; Nazarenko, A. Y.; Robinson, P. D.; Rybak-Akimova, E. V. *Chem. Commun.* **2000**, 921.
473. Duel, L.; Hazell, R.; McKenzie, C. J.; Nielsen, L. P.; Toftlund, H. *J. Chem. Soc., Dalton Trans.* **2001**, 152.
474. Batten, S. R.; McKenzie, C. J.; Nielsen, L. P. *Acta Crystallogr.* **2001**, *C57*, 156.
475. James, M. *Aust. J. Chem.* **2002**, *55*, 219.
476. Rarig, R. S.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2001**, 3446.
477. Marczenko, Z. *Spectrophotometric Determination of Elements*; Ellis Horwood: Chichester, U. K, 1976.
478. Granifo, J. *Polyhedron* **1995**, *14*, 1593.
479. Granifo, J. *Polyhedron* **1996**, *15*, 203.
480. Grammenudi, S.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1122.
481. Constable, E. C. *Adv. Inorg. Chem.* **1989**, *34*, 1.
482. Constable, E. C. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 69.
483. Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: San Diego, 1992.
484. Chelucci, G.; Thummel, R. P. *Chem. Rev.* **2002**, *102*, 3129.
485. Mudasir, N.; Yoshioka, Inoue H. *Transition Met. Chem.* **1999**, *24*, 210.
486. Collomb, M.-N.; Deronzier, A.; Gorgy, K.; Leprêtre, J.-C. *New J. Chem.* **2000**, *24*, 455.
487. Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1987**, 1292.
488. Ziessel, R.; Lehn, J.-M. *Helv. Chim. Acta* **1990**, *73*, 1149.
489. Childs, B. C.; Goodwin, H. A. *Aust. J. Chem.* **2001**, *54*, 685.
490. Rawle, S. C.; Moore, P.; Alcock, N. W. *J. Chem. Soc., Chem. Commun.* **1992**, 684.
491. Sakai, S.; Sasaki, T. *J. Am. Chem. Soc.* **1994**, *116*, 1587.
492. Ion, A.; Moutet, J.-C.; Saint-Aman, E.; Royal, G.; Tingry, S.; Pecaut, J.; Menage, S.; Ziessel, R. *Inorg. Chem.* **2001**, *40*, 3632.
493. Batten, S. R.; Murray, K. S.; Sinclair, N. J. *Acta Crystallogr.* **2000**, *C56*, e320.
494. Decurtins, S.; Schmalle, H. W.; Schneuwly, P.; Oswald, H. R. *Inorg. Chem.* **1993**, *32*, 1888.
495. Hoshina, G.; Ohba, S.; Tsuchiya, N.; Isobe, T.; Senna, M. *Acta Crystallogr.* **2000**, *C56*, e191.
496. Deng, R. M. K.; Simon, S.; Dillon, K. B.; Goetha, A. E. *Acta Crystallogr.* **2001**, *C57*, 4.
497. De Munno, G.; Julve, M.; Real, J. A. *Inorg. Chim. Acta* **1997**, *255*, 185.
498. De Munno, G.; Poerio, T.; Viau, G.; Julve, M.; Lloret, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1459.
499. Horn, C.; Scudder, M.; Dance, I. *Cryst. Eng. Commun.* **2001**, *3*, 9.
500. Fun, H.-K.; Raj, S. S. S.; Fang, X.; Zheng, L.-M.; Xin, X.-Q. *Acta Crystallogr.* **1999**, *55C*, 903.
501. Bron, M.; Radnik, J.; Fieber-Erdmann, M.; Bogdanoff, P.; Fiechter, S. *J. Electroanal. Chem.* **2002**, *535*, 113.
502. Kreischer, K.; Kipke, J.; Bauerfeind, M.; Sundermeyer, J. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1023.
503. Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1998**, 849.
504. Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Strömberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.

505. Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Mastroianni, S.; Redshaw, C.; Solan, G. A.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2001**, 1639.
506. Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.
507. Khorshun, D. V.; Musaev, D. G.; Vreven, T.; Morokuma, K. *Organometallics* **2001**, *20*, 2007.
508. Suhr, D.; Lötscher, D.; Stoeckli-Evans, H.; von Zelewsky, A. *Inorg. Chim. Acta* **2002**, *341*, 17.
509. Constable, E. C.; Holmes, J. M. *Inorg. Chim. Acta* **1987**, *126*, 187.
510. Cotton, S. A.; Franckevicius, V.; Fawcett, J. *Polyhedron* **2002**, *21*, 2055.
511. Alshehri, S.; Burgess, J.; Shaker, A. *Transition Met. Chem.* **1998**, *23*, 689.
512. Alshehri, S.; Burgess, J.; Fawcett, J.; Russell, D. R.; Shaker, A. M. *Transition Met. Chem.* **2000**, *25*, 691.
513. Rothin, A. S.; Banbery, H. J.; Berry, F. J.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *Polyhedron* **1989**, *8*, 491.
514. Thomson, A. J.; Skarda, V.; Cook, M. J.; Robbins, D. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1781.
515. Daul, C.; Schlaepfer, C. W. *J. Chem. Soc., Dalton Trans.* **1988**, 393.
516. Ruminski, R. R.; Petersen, J. D. *Inorg. Chim. Acta* **1985**, *97*, 129.
517. Constable, E. C.; Baum, G.; Bill, E.; Dyson, R.; van Eldik, R.; Fenske, D.; Kaderli, S.; Morris, D.; Neubrand, A.; Neuburger, M.; Smith, D. R.; Wieghardt, K.; Zehnder, M.; Zuberbühler, A. D. *Chem. Eur. J.* **1999**, *5*, 498.
518. Schenker, S.; Stein, P. C.; Wolney, J. A.; Brady, C.; McGarvey, J. J.; Toftlund, H.; Hauser, A. *Inorg. Chem.* **2001**, *40*, 134.
519. Erlenmeyer, H.; Schmid, E. H. *Helv. Chim. Acta* **1941**, *24*, 869.
520. Craig, D. C.; Goodwin, H. A.; Onggo, D.; Rae, A. D. *Aust. J. Chem.* **1988**, *41*, 1625.
521. Baker, A. T.; Goodwin, H. A. *Aust. J. Chem.* **1985**, *38*, 851.
522. Enamullah, M. *J. Coord. Chem.* **1997**, *42*, 231.
523. Addison, A. W.; Burman, S.; Wahlgren, C. G.; Rajan, O. A.; Rowe, T. M.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1987**, 2621.
524. Boča, R.; Boča, M.; Dlháň, L.; Falk, K.; Fuess, H.; Haase, W.; Jaroščiak, R.; Papánková, B.; Renz, F.; Vrbová, M.; Werner, R. *Inorg. Chem.* **2001**, *40*, 3025.
525. Baker, A. T.; Goodwin, H. A.; Rae, A. D. *Inorg. Chem.* **1987**, *26*, 3513.
526. Sugiyarto, K. H.; Craig, D. C.; Rae, A. D.; Goodwin, H. A. *Aust. J. Chem.* **1993**, *46*, 1269.
527. Sugiyarto, K. H.; Craig, D. C.; Goodwin, H. A. *Aust. J. Chem.* **1996**, *49*, 497.
528. Sugiyarto, K. H.; Craig, D. C.; Rae, A. D.; Goodwin, H. A. *Aust. J. Chem.* **1996**, *49*, 505.
529. Kopf, M.-A.; Varech, D.; Tuchagues, J.-P.; Mansuy, D.; Artaud, I. *J. Chem. Soc., Dalton Trans.* **1998**, 991.
530. Blandamer, M. J.; Burgess, J.; Balon, M.; Guardado, P.; Maestre, A. *Transition Met. Chem.* **1988**, *13*, 313.
531. Tarui, T. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2481.
532. El-Samahy, A. A.; Abu-Gharib, E.-E. A.; Eltaher, A.-E.; El-Khatib, R. M.; Burgess, J. *Transition Met. Chem.* **1992**, *17*, 438.
533. Blundell, N. J.; Burgess, J. *Inorg. Chim. Acta* **1990**, *173*, 5.
534. Enamullah, M.; Linert, W. *J. Coord. Chem.* **1996**, *40*, 193.
535. Leidner, C. R.; Sullivan, B. P.; Reed, R. A.; White, B. A.; Crimmins, M. T.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 882.
536. de Carvalho, I. N.; Tubino, M. *J. Braz. Chem. Soc.* **1991**, *2*, 56.
537. Lucie, J.-M.; Stranks, D. R.; Burgess, J. *J. Chem. Soc., Dalton Trans.* **1975**, 245.
538. Burgess, J.; Galema, S. A.; Hubbard, C. D. *Polyhedron* **1991**, *10*, 703.
539. Blandamer, M. J.; Burgess, J.; Cowles, H. J.; Horn, I. M.; Engberts, J. B. F. N.; Galema, S. A.; Hubbard, C. D. *J. Chem. Soc. Faraday Trans. 1* **1989**, *85*, 3733.
540. Blandamer, M. J.; Burgess, J.; Engberts, J. B. F. N.; Sanchez, F. *Faraday Discuss. Chem. Soc.* **1988**, *85*, 309.
541. Burgess, J.; Hubbard, C. D. *Comments Inorg. Chem.* **1995**, *17*, 283.
542. Tubino, M.; Vichi, E. J. S. *Inorg. Chim. Acta* **1987**, *131*, 175.
543. Tubino, M.; Vichi, E. J. S.; Lauff, I. K. *Chem. Scripta* **1989**, *29*, 2015.
544. Milde, S. P.; Blandamer, M. J.; Burgess, J.; Engberts, J. B. F. N.; Galema, S. A.; Hubbard, C. D. *J. Phys. Org. Chem.* **1999**, *12*, 227.
545. Abu-Gharib, E. A.; Burgess, J. *Transition Met. Chem.* **1993**, *18*, 623.
546. Blandamer, M. J.; Burgess, J.; Cowles, H. J.; De Young, A. J.; Engberts, J. B. F. N.; Galema, S. A.; Hill, S. J.; Horn, I. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1141.
547. Blandamer, M. J.; Burgess, J.; Cowles, H. J.; Horn, I. M.; Blundell, N. J.; Engberts, J. B. F. N. *J. Chem. Soc., Chem. Commun.* **1989**, 1233.
548. Blandamer, M. J.; Blundell, N. J.; Burgess, J.; Cowles, H. J.; Engberts, J. B. F. N.; Horn, I. M.; Warrick, P. *J. Am. Chem. Soc.* **1990**, *112*, 6854.
549. Priimov, G. U.; Moore, P.; Maritim, P. K.; Butalanyi, P. K.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **2000**, 445.
550. Rao, G. V.; Sridhar, Y.; Hela, P. G.; Padhi, T.; Anipindi, N. R. *Transition Met. Chem.* **1999**, *24*, 566.
551. Gillard, R. D. *Coord. Chem. Rev.* **1975**, *16*, 67.
552. Nord, G. *Comments Inorg. Chem.* **1976**, *4*, 15, 1921 .
553. Serpone, N.; Ponterini, G.; Jamieson, M. A.; Bolletta, F.; Maestri, M. *Coord. Chem. Rev.* **1983**, *50*, 209.
554. Constable, E. C. *Polyhedron* **1983**, *2*, 551.
555. Burgess, J.; Duke, D. L.; Hubbard, C. D. *Transition Met. Chem.* **1987**, *12*, 460.
556. Clack, D. W.; Gillard, R. D. *Transition Met. Chem.* **1985**, *10*, 419.
557. Clack, D. W.; Gillard, R. D. *Inorg. Chim. Acta* **1988**, *141*, 37.
558. Zhang, X.-M.; Tong, M-L.; Chen, X.-M. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 1029.
559. Shaker, A. M.; Alshehri, S.; Burgess, J. *Transition Met. Chem.* **1998**, *23*, 683.
560. Abu Gharib, E. A.; Gosal, N.; Burgess, J. *Croat. Chem. Acta* **2001**, *74*, 545.
561. Alousy, A.; Burgess, J.; Elvidge, D.; Hubbard, C. D.; Radulović, S. *Inorg. React. Mech.* **2000**, *2*, 249.
562. Alshehri, S.; Burgess, J. *Int. J. Chem. Kinet.* **1993**, *25*, 113.
563. Burgess, J.; Hubbard, C. D. *Inorg. Chem.* **1988**, *27*, 2548.
564. Burgess, J.; Hubbard, C. D. *Int. J. Chem. Kinet.* **2000**, *32*, 263.
565. Burgess, J.; Hubbard, C. D. *J. Am. Chem. Soc.* **1984**, *106*, 1717.

566. Blandamer, M. J.; Burgess, J.; Clark, B.; Duce, P. P.; Hakin, A. W.; Gosal, N.; Radulović, S.; Guardado, P.; Sanchez, F.; Hubbard, C. D.; Abu-Gharib, E. A. *J. Chem. Soc. Faraday Trans. 1* **1986**, *82*, 1471.
567. Alshehri, S.; Burgess, J.; Hubbard, C. D. *Transition Met. Chem.* **1993**, *18*, 228.
568. Haines, R. I.; Hutchings, D. R.; Strickland, D. W. *Inorg. React. Mech.* **2000**, *2*, 223.
569. Puri, B. K.; Satake, M.; Kano, G.; Usami, S. *Analyt. Chem.* **1987**, *59*, 1850.
570. Rodger, A.; Nordén, B.; Rodger, P. M.; Bates, P. J. *Eur. J. Inorg. Chem.* **2002**, 49.
571. Carter, M. T.; Rodriguez, M.; Bard, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 8901.
572. Mudasir Yoshioka N.; Inoue, H. *J. Inorg. Biochem.* **1999**, *77*, 239.
573. Davies, N. R.; Dwyer, F. P. *Trans. Faraday Soc.* **1952**, *48*, 244.
574. Davies, N. R.; Dwyer, F. P. *Trans. Faraday Soc.* **1953**, *49*, 180.
575. Davies, N. R.; Dwyer, F. P. *Trans. Faraday Soc.* **1954**, *50*, 24, 820, 1325 .
576. Basolo, F.; Hayes, J. C.; Neumann, H. M. *J. Am. Chem. Soc.* **1954**, *76*, 3807.
577. Seiden, L.; Basolo, F.; Neumann, H. M. *J. Am. Chem. Soc.* **1959**, *81*, 3809.
578. Serpone, N.; Bickley, D. G. *Prog. Inorg. Chem.* **1972**, *17*, 391.
579. Blinn, E. L.; Wilkins, R. G. *Inorg. Chem.* **1976**, *15*, 2952.
580. Montgomery, C. D.; Shorrock, C. J. *Inorg. Chim. Acta* **2002**, *328*, 259.
581. Tachiyashiki, S.; Yamatera, H. *Polyhedron* **1983**, *2*, 9.
582. Arora, K.; Bhargava, A. P.; Gupta, Y. K. *J. Chem. Soc., Dalton Trans.* **1990**, 1257.
583. Burgess, J.; Sánchez, F.; Morillo, E.; Gil, A.; Tejera, J. I.; Galán, A.; García, J. M. *Transition Met. Chem.* **1986**, *11*, 166.
584. Lengyel, I.; Barna, T.; Basza, G. *J. Chem. Soc. Faraday Trans.* **1988**, *84*, 229.
585. Tikhanova, L. P.; Moshkovich, F. S.; Kovalenko, A. S. *Ukr. Khim. Zh.* **1988**, *54*, 1045.
586. Cyfert, M. *Z. Phys. Chem. (Leipzig)*, **1990**, *271*, 117.
587. Kjaer, A. M.; Ulstrup, J. *Inorg. Chem.* **1982**, *21*, 3490.
588. Parasher, P.; Hussain, J.; Sharma, P. D. *Int. J. Chem. Kinet.* **1991**, *23*, 473.
589. Burgess, J.; Shraydeh, B. *Polyhedron* **1992**, *11*, 2015.
590. Nord, G. *Comments Inorg. Chem.* **1992**, *13*, 221.
591. Ojo, J. F.; Hasegawa, Y.; Sasaki, Y.; Kunimasa, K.; Abe, M.; Ohta, N. *Inorg. React. Mech.* **2000**, *2*, 301.
592. Schmid, R.; Kirchner, K.; Dickert, F. L. *Inorg. Chem.* **1988**, *27*, 1530.
593. Doine, H.; Swaddle, T. W. *Can. J. Chem.* **1988**, *66*, 2763.
594. Mønsted, O.; Nord, G. *Adv. Inorg. Chem.* **1991**, *37*, 381.
595. Iha, N. Y. M.; Chum, H. L. *Inorg. Chim. Acta* **1985**, *97*, 151.
596. tom Dieck, H.; Diercks, R.; Stamp, L.; Bruder, H.; Schuld, T. *Chem. Ber.* **1987**, *120*, 1943.
597. Haiduc, I.; Silaghi-Dumitrescu, I. *Coord. Chem. Rev.* **1986**, *74*, 127.
598. tom Dieck, H.; Stamp, L.; Diercks, R.; Müller, C. *Nouv. J. Chim.* **1985**, *9*, 289.
599. Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1984**, 1005.
600. Stufkens, D. J.; Kokkes, M. W.; Oskam, A. *J. Mol. Struct.* **1984**, *114*, 61.
601. Trogler, W. C.; Johnson, C. E.; Ellis, D. E. *Inorg. Chem.* **1981**, *20*, 980.
602. Johnson, C. E.; Trogler, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6352.
603. Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1983**, 439.
604. Frühauf, H.-W. *J. Chem. Res.* **1983**, *(S)* 218, *(M)*, 2035.
605. Squizani, F.; Stein, E.; Vichi, E. J. S. *J. Braz. Chem. Soc.* **1996**, *7*, 127.
606. Brewer, K. J.; Murphy, W. R.; Petersen, J. D. *Inorg. Chim. Acta* **1989**, *159*, 93.
607. Brewer, K. J.; Murphy, W. R.; Petersen, J. D. *Inorg. Chem.* **1986**, *26*, 3376.
608. Triki, S.; Thétiot, F.; Galán-Mascarós, J.-R.; Pala, J. S.; Dunbar, K. R. *New J. Chem.* **2001**, *25*, 954.
609. Real, J. A.; Castro, I.; Bousseksou, A.; Verdaguer, M.; Burriel, R.; Castro, M.; Linares, J.; Varret, F. *Inorg. Chem.* **1997**, *36*, 455.
610. Chastanet, G.; Gaspar, A. B.; Real, J. A.; Létard, J.-F. *Chem. Commun.* **2001**, 819.
611. Real, J. A.; Bolvin, H.; Bousseksou, A.; Dworkin, A.; Kahn, O.; Varret, F.; Zarembowitch, J. *J. Am. Chem. Soc.* **1992**, *114*, 4650.
612. Létard, J.-F.; Real, J. A.; Moliner, N.; Gaspar, A. B.; Capes, L.; Cador, O.; Kahn, O. *J. Am. Chem. Soc.* **1999**, *121*, 10630.
613. Waldhör, E.; Poppe, J.; Kaim, W.; Cutin, E. H.; Garcia Posse, M. E.; Katz, N. E. *Inorg. Chem.* **1995**, *34*, 3093.
614. Stratton, W. J.; Busch, D. H. *J. Am. Chem. Soc.* **1958**, *80*, 1286, 3191 .
615. Stratton, W. J.; Busch, D. H. *J. Am. Chem. Soc.* **1960**, *82*, 4834.
616. Garg, A.; Tandon, J. P. *Transition Met. Chem.* **1988**, *13*, 395.
617. Owens, C.; Drago, R. S.; Bertini, I.; Luchinat, C.; Banci, L. *J. Am. Chem. Soc.* **1986**, *108*, 3298.
618. Bertini, I.; Owens, C.; Luchinat, C.; Drago, R. S. *J. Am. Chem. Soc.* **1987**, *109*, 5208.
619. Valcarcel, M.; Martinez, M. P.; Pino, F. *Analyst* **1975**, *100*, 33.
620. Youinov, M.-T.; Ziessel, R.; Lehn, J.-M. *Inorg. Chem.* **1991**, *30*, 2144.
621. Barragan de la Rosa, F. J.; Gómez Ariza, J. L.; Pino, F. *Talanta* **1983**, *30*, 555.
622. Montaña González, M. T.; Gómez Ariza, J. L.; Garcia de Torres, A. *An. Quim.* **1984**, *80B*, 129.
623. Barragan de la Rosa, F. J.; Gómez Ariza, J. L.; Pino, F. *Mikrochim. Acta (Wien), III* **1983**, 159.
624. Gómez Ariza, J. L.; Montana González, M. T. *Microchem. J.* **1982**, *27*, 290.
625. Zurita, D.; Baret, P.; Pierre, J.-L. *New J. Chem.* **1994**, *18*, 1143.
626. Stratton, W. J. *Inorg. Chim. Acta* **1969**, *3*, 97.
627. Stratton, W. J. *Inorg. Chem.* **1970**, *9*, 517.
628. Meistermann, I.; Moreno, V.; Prieto, M. J.; Moldrheim, E.; Sletten, E.; Khalid, S.; Rodger, P. M.; Peberdy, J. C.; Isaac, C. J.; Rodger, A.; Hannon, M. J. *Proc. Natl. Acad. Sci. USA* **2002**, *89*, 5069.
629. Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1938**, 1672.
630. Bergh, P. A.; Offenhartz, O'D.; George, P.; Haight, G. P. *J. Chem. Soc.* **1964**, 1533.
631. Dell'Amico, D. B.; Calderazzo, F.; Englert, U.; Labella, L.; Marchetti, F. *J. Chem. Soc., Dalton Trans.* **2001**, 357.
632. Che, C.-M.; Chan, C.-W.; Yang, S.-M.; Guo, C.-X.; Lee, C.-Y.; Peng, S.-M. *J. Chem. Soc., Dalton Trans.* **1995**, 2961.
633. Branca, M.; Pispisa, B.; Aurisicchio, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1543.

634. Cerdonio, M.; Mogno, F.; Pispisa, B.; Romani, G. L.; Vitale, S. *Inorg. Chem.* **1977**, *16*, 400.
635. Pispisa, B.; Barteri, M.; Farinella, M. *Inorg. Chem.* **1983**, *22*, 3166 and references therein.
636. Constable, E. C. *Adv. Inorg. Chem. Radiochem.* **1986**, *30*, 69.
637. Calderazzo, F.; Labella, L.; Marchetti, F. *J. Chem. Soc., Dalton Trans.* **1998**, 1485.
638. Constable, E. C.; Ward, M. D.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1675.
639. Crane, J. D.; Sauvage, J.-P. *New J. Chem.* **1992**, *16*, 649.
640. Constable, E. C.; Phillips, D. *Chem. Commun.* **1997**, 827.
641. Maddock, A. G. *J. Chem. Soc., Dalton Trans.* **1986**, 2349.
642. Agarwala, B. V.; Ramanathan, K. V.; Khetrapal, C. L. *J. Coord. Chem.* **1985**, *14*, 133.
643. Burgess, J.; Drasdo, D. N.; Singh, K. *Transition Met. Chem.* **1994**, *19*, 113.
644. Benko, J.; Burgess, J.; López Cornejo, P.; Vollárová, O. *Croat. Chem. Acta* **2001**, *74*, 607.
645. Byfield, M. P.; Frost, V. L.; Pemberton, J. L. J.; Pratt, J. M. *J. Chem. Soc. Faraday Trans.* **1989**, *85*, 2713.
646. Burgess, J.; Maguire, S.; McGranaghan, A.; Parsons, S. A.; Nowicka, B.; Samotus, A. *Transition Met. Chem.* **1998**, *23*, 615.
647. Blundell, N. J.; Burgess, J.; Guardado, P.; Hubbard, C. D. *J. Chem. Soc., Dalton Trans.* **1991**, 1743.
648. Burgess, J.; Drasdo, D. N.; Shraydeh, B. *J. Chem. Res. (S)*, **1992**, 288.
649. Burgess, J.; Radulović, S.; Sánchez, F. *Transition Met. Chem.* **1987**, *12*, 529.
650. Linert, W.; Fukuda, Y.; Camard, A. *Coord. Chem. Rev.* **2001**, *218*, 113.
651. Migron, Y.; Marcus, Y. *J. Phys. Org. Chem.* **1990**, *4*, 310.
652. Apostoluk, W.; Tłaczała, T.; Duda, L. L. *Polish J. Chem.* **2000**, *74*, 321.
653. Tłaczała, T.; Bartecki, A. *Monatsh.* **1997**, *128*, 225.
654. Shraydeh, B.; Burgess, J. *Spectr. Lett.* **1993**, *26*, 129.
655. Shraydeh, B.; Burgess, J. *Monatsh.* **1993**, *124*, 877.
656. Linert, W.; Bauer, G.; Jameson, R. F.; Taha, A. *J. Coord. Chem.* **1997**, *42*, 211.
657. Al-Alousy, A.; Burgess, J. *Inorg. Chim. Acta* **1990**, *169*, 167.
658. Gameiro, P.; Maia, A.; Pereira, E.; de Castro, B.; Burgess, J. *Transition Met. Chem.* **2000**, *25*, 283.
659. Blandamer, M. J.; Burgess, J.; Shraydeh, B. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 531.
660. Ahmed, S.; Burgess, J.; Capper, G.; Fellowes, N. C.; Patel, M. S. *Polyhedron* **1993**, *12*, 1145.
661. Burgess, J.; Patel, M. S.; Tindall, C. *Spectr. Lett.* **1993**, *26*, 1469.
662. Burgess, J.; Lane, R. C.; Singh, K.; de Castro, B.; Gameiro dos Santos, A. P. *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 3071.
663. Gameiro, P.; Pereira, E.; Garcia, P.; Breia, S.; Burgess, J.; de Castro, B. *Eur. J. Inorg. Chem.* **2001**, 2755.
664. Garcia, P.; Marques, J.; Pereira, E.; Gameiro, P.; Salema, R.; de Castro, B. *Chem. Commun.* **2001**, 1298.
665. Kotowski, M.; van Eldik, R.; Razak bin Ali, M.; Burgess, J.; Radulović, S. *Inorg. Chim. Acta* **1987**, *131*, 225.
666. Alousy, A.; Blundell, N. J.; Burgess, J.; Hubbard, C. D.; van Eldik, R. *Transition Met. Chem.* **2002**, *27*, 244.
667. Razak bin Ali, M.; Burgess, J.; Smith, A. E. *Transition Met. Chem.* **1988**, *13*, 107.
668. Burgess, J.; Shraydeh, B. *Polyhedron* **1992**, *11*, 2015.
669. Blundell, N. J.; Burgess, J.; Hubbard, C. D. *Inorg. Chim. Acta* **1989**, *155*, 165.
670. Benko, J.; Vollárová, O.; Burgess, J.; López, P. *Transition Met. Chem.* **2000**, *25*, 674.
671. Hubbard, C. D.; Bajaj, H. C.; van Eldik, R.; Burgess, J.; Blundell, N. J. *Inorg. Chim. Acta* **1991**, *183*, 1.
672. Takagi, H. D.; Kagayama, N.; Matsumoto, M.; Tarumi, T.; Funahashi, S. *J. Mol. Liq.* **1995**, *65/66*, 277.
673. Haines, R. I.; Pieda, D.; Goulding, W. *Transition Met. Chem.* **1998**, *23*, 763.
674. Gillard, R. D.; Hummel, H.-U. *Transition Met. Chem.* **1985**, *10*, 348.
675. Beck, M. T.; Porzsolt, E. C. *J. Coord. Chem.* **1971**, *1*, 57.
676. Beck, M. T. In *Coordination Chemistry in Solution*; Högfeldt, E., Eds.; Swedish National Research Council: Lund, 1972, p 241.
677. Lescouëzec, R.; Lloret, F.; Julve, M.; Vaissermann, J.; Verdaguer, M.; Llusar, R.; Uriel, S. *Inorg. Chem.* **2001**, *40*, 2065.
678. Lescouëzec, R.; Lloret, F.; Julve, M.; Vaissermann, J.; Verdaguer, M. *Inorg. Chem.* **2002**, *41*, 818.
679. Nelson, S. M.; McIlroy, D. P. A.; Stevenson, C. S.; König, E.; Ritter, G.; Waigel, J. *J. Chem. Soc., Dalton Trans.* **1986**, 991.
680. Schilt, A. A.; Fritsch, K. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2677.
681. Teodorescu, M. *Rev. Roum. Chim.* **1976**, *21*, 1031.
682. Savage, S.; Jia-Long, Z.; Maddock, A. G. *J. Chem. Soc., Dalton Trans.* **1985**, 991.
683. Baker, W. A.; Bobonich, H. M. *Inorg. Chem.* **1963**, *2*, 1071.
684. Lee, J.-J.; Sheu, H.-S.; Lee, C.-R.; Chen, J.-M.; Lee, J.-F.; Wang, C.-C.; Wang, Y. *J. Am. Chem. Soc.* **2000**, *122*, 5742.
685. Inoue, H.; Nakajima, H.; Takahashi, T.; Uchida, H.; Shirai, T.; Fluck, E. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3483.
686. Kulshreshtha, S. K.; Iyer, R. M. *Chem. Phys. Lett.* **1984**, *108*, 501.
687. Kulshreshtha, S. K.; Sasikala, R.; König, E. *Chem. Phys. Lett.* **1986**, *123*, 215.
688. Coronel, P.; Barraud, A.; Claude, R.; Kahn, O.; Ruaudel-Teixier, A.; Zarembowitch, J. *J. Chem. Soc., Chem. Commun.* **1989**, 193.
689. Figgis, B. N.; Patrick, J. M.; Reynolds, P. A.; Skelton, B. W.; White, A. H.; Healy, P. C. *Aust. J. Chem.* **1983**, *36*, 2043.
690. Goodwin, H. J.; McPartlin, M.; Goodwin, H. A. *Inorg. Chim. Acta* **1977**, *25*, L74.
691. Toma, H. E.; Morino, L. A. *Transition Met. Chem.* **1990**, *15*, 66.
692. Lefko, P.; Stynes, D. V. *J. Coord. Chem.* **1988**, *16*, 383.
693. Mohan, M.; Kumar, M. *Polyhedron* **1985**, *4*, 1929.
694. Saha, B.; Ali, M.; Gangopadhyay, S.; Shaikh, N.; Banerjee, P. *Inorg. React. Mech.* **2001/2002**, *3*, 173.
695. Toma, H. E.; Silva, A. C. C. *Can. J. Chem.* **1986**, *64*, 1280.
696. Cohen, S. M.; Halper, S. R. *Inorg. Chim. Acta* **2002**, *341*, 12.
697. Sini, G.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **2002**, *41*, 602.
698. Obrey, S. J.; Bott, S. G.; Barron, A. R. *J. Chem. Cryst.* **2000**, *30*, 61.
699. Yang, S.-P.; Tong, Y.-X.; Zhu, H. L.; Cao, H.; Chen, X.-M.; Ji, L.-N. *Polyhedron* **2001**, *20*, 223.
700. Patrick, B. O.; Reiff, W. M.; Sánchez, V.; Storr, A.; Thompson, R. C. *Polyhedron* **2001**, *20*, 1577.

701. Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.
702. Brunker, T. J.; Hascall, T.; Cowley, A. R.; Rees, L. H.; O'Hare, D. *Inorg. Chem.* **2001**, *40*, 3170.
703. Trofimenko, S.; Calabrese, J. C.; Domaille, P. J.; Thompson, J. S. *Inorg. Chem.* **1989**, *28*, 1091.
704. Reger, D. L.; Little, C. A.; Rheingold, A. L.; Lam, M.; Liable-Ss, L. M.; Rhagitan, B.; Concolino, T.; Mohan, A.; Long, G. J.; Briois, V.; Grandjean, F. *Inorg. Chem.* **2001**, *40*, 1508.
705. Reger, D. L.; Little, C. A.; Young, V. G.; Pink, M. *Inorg. Chem.* **2001**, *40*, 2870.
706. Manikandan, P.; Padmakumar, K.; Justin Thomas, K. R.; Varghese, B.; Onodera, H.; Manoharan, P. T. *Inorg. Chem.* **2001**, *40*, 6930.
707. Suemura, N.; Ohama, M.; Kaisaki, S. *Chem. Commun.* **2001**, 1538.
708. Garcia, Y.; Kahn, O.; Rabardel, L.; Chansou, B.; Salmon, L.; Tuchagues, J. P. *Inorg. Chem.* **1999**, *38*, 4663.
709. Garcia, Y.; Van Koningsbruggen, P. J.; Lapouyade, R.; Fournes, L.; Rabardel, L.; Kahn, O.; Ksenofontov, V.; Levchenko, G.; Gütlich, P. *Chem. Mater.* **1998**, *10*, 2426.
710. Garcia, Y.; Van Koningsbruggen, P. J.; Lapouyade, R.; Rabardel, L.; Kahn, O.; Wieczorek, M.; Bronisz, R.; Ciunik, Z.; Rudolf, M. F. *C. R. Acad. Sci. Ser. IIc : Chim.* **1998**, 523.
711. Vreugdenhil, W.; van Diemen, J. H.; de Graaf, A. G.; Hasnoot, J. G.; Reedijk, J.; van der Kraan, A. M.; Kahn, O.; Zarembowitch, J. *Polyhedron* **1990**, *9*, 2971.
712. Ozarowski, A.; Shunzhong, Y.; McGarvey, B. R.; Mislankar, A.; Drake, J. E. *Inorg. Chem.* **1991**, *30*, 3167.
713. Biangi Cingi, M.; Manotti, A. M.; Tiripicchio, A.; Cornelissen, J. P.; Hasnoot, J. P.; Reedijk, J. *Acta Crystallogr.* **1986**, *C42*, 1296.
714. Kunkeler, P. J.; van Koningsbruggen, P. J.; Cornelissen, J. P.; van der Horst, A. N.; van der Kraan, A. M.; Spek, A. L.; Haasnoot, J. G.; Reedijk, J. *J. Am. Chem. Soc.* **1996**, *118*, 2190.
715. Kolnaar, J. J. A.; de Heer, M. I.; Kooijman, H.; Spek, A. L.; Schmitt, G.; Ksenofontov, V.; Gütlich, P.; Haasnoot, J. G.; Reedijk, J. *Eur. J. Inorg. Chem.* **1999**, 881.
716. Thomann, M.; Kahn, O.; Guilhem, J.; Varret, F. *Inorg. Chem.* **1994**, *33*, 6029.
717. Kolnaar, J. J. A.; van Dijk, G.; Kooijman, H.; Spek, A. L.; Ksenofontov, V. G.; Gütlich, P.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1997**, *36*, 2433.
718. Janiak, C. *J. Chem. Soc., Chem. Commun.* **1994**, 545.
719. Lavrenova, L. G.; Larionov, S. V. *Koord. Khim.* **1998**, *24*, 403.
720. Lavrenova, L. G.; Larionov, S. V. *Russ. J. Coord. Chem.* **1998**, *24*, 379.
721. Decurtins, S.; Gütlich, P.; Köhler, C. P.; Spiering, H.; Hauser, A. *Chem. Phys. Lett.* **1984**, *105*, 1.
722. van Koningsbruggen, P. J.; Garcia, Y.; Kahn, O.; Fournès, L.; Kooijman, H.; Spek, A. L.; Haasnoot, J. G.; Moscovici, J.; Provost, K.; Michalowicz, A.; Renz, F.; Gütlich, P. *Inorg. Chem.* **2000**, *39*, 1891.
723. Stassen, A. F.; Roubeau, O.; Gramage, I. F.; Linarès, J.; Varret, F.; Mutikainen, I.; Turpeinen, U.; Haasnoot, J. G.; Reedijk, J. *Polyhedron* **2001**, *20*, 1699.
724. van Koningsbruggen, P. J.; Garcia, Y.; Kooijman, H.; Spek, A. L.; Haasnoot, J. G.; Kahn, O.; Linares, J.; Codjovi, E.; Varret, F. *J. Chem. Soc., Dalton Trans.* **2001**, 466.
725. James, M.; Kawaguchi, H.; Tatsumi, K. *Polyhedron* **1997**, *16*, 4279.
726. Chaudhuri, P.; Wieghardt, K. *Prog. Inorg. Chem.* **1987**, *35*, 329.
727. Zhang, D.; Busch, D. H. *Inorg. Chem.* **1994**, *33*, 5138.
728. Alcock, N. W.; Zhang, D.; Busch, D. H. *Acta Crystallogr.* **1999**, *55C*, 886.
729. Spiccia, L.; Fallon, G. D.; Grannas, M. J.; Nichols, P. J.; Tiekink, E. R. T. *Inorg. Chim. Acta* **1998**, *279*, 192.
730. Blakesley, D. W.; Payne, S. C.; Hagen, K. S. *Inorg. Chem.* **2000**, *39*, 1979.
731. Schlager, O.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1995**, *34*, 6449.
732. Schlager, O.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1995**, *34*, 6456.
733. Mountford, H. S.; Spreer, L. O.; Otvos, J. W.; Calvin, M.; Brewer, K. J.; Richter, M.; Scott, B. *Inorg. Chem.* **1992**, *31*, 717.
734. Mountford, H. S.; MacQueen, D. B.; Li, A.; Otvos, J. W.; Calvin, M.; Frankel, R. B.; Spreer, L. O. *Inorg. Chem.* **1994**, *33*, 1748.
735. Spreer, L. O.; Li, A.; MacQueen, D. B.; Allan, C. B.; Otvos, J. W.; Calvin, M.; Frankel, R. B.; Papaefthymiou, G. C. *Inorg. Chem.* **1994**, *33*, 1753.
736. Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230.
737. Sessler, J. L.; Sibert, J. W.; Lynch, V. *Inorg. Chem.* **1990**, *29*, 4143.
738. Paschke, J.; Kirsch, M.; Korth, H.-G.; de Groot, H.; Sustmann, R. *J. Am. Chem. Soc.* **2001**, *123*, 11099.
739. Vasconcellos, L. C. G.; Oliveira, C. P.; Castellano, E. E.; Ellena, J.; Moreira, I. S. *Polyhedron* **2001**, *20*, 493.
740. Baran, Y.; Yilmaz, I.; Erk, B. *Transition Met. Chem.* **2001**, *26*, 36.
741. McAuley, A.; Subramanian, S. *Coord. Chem. Rev.* **2000**, *200–202*, 75.
742. Seibig, S.; van Eldik, R. *Inorg. Chem.* **1997**, *36*, 4115.
743. Schrodt, A.; van Eldik, R. *Inorg. React. Mech.* **1998**, *1*, 57.
744. *Chem. Rev.* **1996**, *96*, 2239–3042.
745. Guiliard, R.; Kadish, K. M. *Chem. Rev.* **1988**, *88*, 1121.
746. Latos-Grażyński, L.; Rachelwicz, K.; Wojaczynski, J. *Coord. Chem. Rev.* **1999**, *192*, 109.
747. Traylor, T. G. *Acc. Chem. Res.* **1997**, *30*, 251.
748. Wojaczynski, J.; Latos-Grażyński, L. *Inorg. Chem.* **1995**, *34*, 1044.
749. Burrell, A. K.; Officer, D. L.; Plieger, P. G.; Reid, D. C. W. *Chem. Rev.* **2001**, *101*, 2751.
750. Wijeskera, T.; Matsumoto, A.; Dolphin, D.; Lexa, D. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1028.
751. Dawson, J. H.; Bracete, A. M.; Huff, A. M.; Kadkhodayan, S.; Chang, C. K.; Sono, M. *ACS Adv. Chem. Series* **1995**, *246*, 351.
752. Andersson, L. A.; Dawson, J. H. *Struct. Bonding* **1991**, *74*, 1.
753. Bertini, I.; Turacco, P.; Vila, A. J. *Chem. Rev.* **1993**, *93*, 2823.
754. Walker, F. A. *Coord. Chem. Rev.* **1999**, *186*, 471.
755. Walker, F. A.; Montfort, W. R.; Czernuszewicz, R. S. *J. Am. Chem. Soc.* **2001**, *123*, 11664.
756. Clusen, M. R.; Greenwood, C.; Thomson, A. J. *Adv. Inorg. Chem.* **1991**, *36*, 201.
757. Bottomley, L. A.; Olson, L.; Kadish, K. M. *Adv. Chem. Ser.* **1982**, *201*, 279.

758. Kadish, K. M. *Prog. Inorg. Chem.* **1986**, *34*, 435.
759. Kadish, K. M.; Mu, X. H. *Pure Appl. Chem.* **1990**, *62*, 1051.
760. Alexiou, C.; Lever, A. B. P. *Coord. Chem. Rev.* **2001**, *216*, 45.
761. Momenteau, M.; Reed, C. A. *Chem. Rev.* **1994**, *94*, 659.
762. Klotz, I. M.; Kurtz, D. M. *Chem. Rev.* **1994**, *94*, 567.
763. Moro-Oha, Y.; Fujisawa, K.; Kitajuma, N. *Pure Appl. Chem.* **1995**, *67*, 241.
764. Busch, D. H.; Alcock, N. W. *Chem. Rev.* **1994**, *94*, 585.
765. Shikama, K. *Coord. Chem. Rev.* **1988**, *83*, 73.
766. Nasri, H.; Ellison, M. K.; Krebs, C.; Huyhn, B. H.; Scheidt, W. R. *J. Am. Chem. Soc.* **2000**, *122*, 10795.
767. Ellison, M. K.; Shang, M.; Kim, J.; Scheidt, W. R. *Acta Cryst.* **1996**, *C52*, 3040.
768. Galla, H.-J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 378.
769. Caldwell, K.; Noel, L. J.; Ciccone, J. D.; Traylor, T. G. *ACS Symp. Ser.* **1986**, *321*, 182.
770. Walker, J. R.; Malmstrœm, B. E.; Gray, H. B. *Biophys. Chem.* **1995**, *544*, 199.
771. Maldotti, A.; Molinari, A.; Amadelli, R. *Chem. Rev.* **2002**, *102*, 3811.
772. Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369.
773. Sono, M.; Roach, M. P.; Coulter, E. D.; Dawson, J. H. *Chem. Rev.* **1996**, *96*, 2841.
774. Watanabe, Y.; Fujii, H. *Struct. Bonding* **2000**, *97*, 61.
775. Ozaki, S.; Matsui, T.; Roach, M. P.; Watanabe, Y. *Coord. Chem. Rev.* **2000**, *198*, 61.
776. Loew, G. H.; Harris, D. L. *Chem. Rev.* **2000**, *100*, 407.
777. Newcomb, M.; Toy, P. H. *Acc. Chem. Res.* **2000**, *33*, 449.
778. Wertz, D. L.; Valentine, J. S. *Struct. Bonding* **2000**, *97*, 37.
779. Groves, J. T. *J. Porph. Phthalocyanines* **2000**, *4*, 350.
780. Ogliaro, F.; deVisser, S. P.; Groves, J. T.; Shaik, S. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2874.
781. Momenteau, M.; Loock, B.; Tetreau, C.; Lavalette, D.; Croisy, A.; Schaeffer, C.; Huel, C.; Lhoste, J.-M. *J. Chem. Soc. Perkin 2* **1987**, 249.
782. Pfeiffer, H.-P.; Sander, H.; Breitmaier, E. *Liebigs Ann. Chem.* **1987**, 725.
783. Feig, A. L.; Lippard, S. J. *Chem. Rev.* **1994**, *94*, 759.
784. Bytheway, I.; Hall, M. B. *Chem. Rev.* **1994**, *94*, 639.
785. Koerner, R.; Wright, J. L.; Ding, X. D.; Nesset, M. J. M.; Aubrecht, K.; Watson, R. A.; Barber, R. A.; Mink, L. M.; Tipton, A. R.; Norvell, C. J.; Skidmore, K.; Simonis, U.; Walker, F. A. *Inorg. Chem.* **1998**, *37*, 733.
786. Zingg, A.; Felber, B.; Gramlich, V.; Fu, L.; Collman, J. P.; Diederich, F. *Helv. Chim. Acta* **2002**, *85*, 333.
787. Weyermann, P.; Diederich, F.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *Helv. Chim. Acta* **2002**, *85*, 571.
788. Weyermann, P.; Diederich, F. *Helv. Chim. Acta* **2002**, *85*, 599.
789. Robert, A.; Coppel, Y.; Meunier, B. *Inorg. Chim. Acta* **2002**, *339*, 488.
790. Kalisch, H. R.; Latos-Grazynski, L.; Balch, A. L. *J. Am. Chem. Soc.* **2000**, *122*, 12478.
791. Kim, Y.; Nam, W.; Lim, M. H.; Jin, S. W.; Lough, A. J.; Kim, S.-J. *Acta Crystallogr.* **2001**, *C57*, 556.
792. Ohgo, Y.; Saito, T.; Nakamura, M. *Acta Crystallogr.* **2001**, *C57*, 233.
793. Barkigia, K. M.; Renner, M. W.; Fajer, J. *J. Porph. Phthalocyanines* **2001**, *5*, 415.
794. Gerothanassis, I. P.; Loock, B.; Momenteau, M. *J. Chem. Soc., Chem. Commun.* **1992**, 598.
795. Safo, M. K.; Nesset, M. J. M.; Walker, F. A.; Debrunner, P. G.; Scheidt, W. R. *J. Am. Chem. Soc.* **1997**, *119*, 9438.
796. Munro, O. Q.; Serth-Guzzo, J. A.; Turowska-Tyrk, I.; Mohanrao, K.; Shokhireva, T. Kh.; Walker, F. A.; Debrunner, P. G.; Scheidt, W. R. *J. Am. Chem. Soc.* **1999**, *121*, 11144.
797. Shokhirev, N. V.; Shokhireva, T. Kh.; Polam, J. P.; Watson, C. T.; Raffii, K.; Simonis, U.; Walker, F. A. *J. Phys. Chem. A* **1997**, *101*, 2778.
798. Murshudov, G. N.; Melik-Adamyan, W. R.; Grebenko, A. I.; Barynin, U. V.; Vagin, A. A.; Vainshtein, B. K.; Dauter, Z.; Wilson, K. S. *FEBS Lett.* **1992**, *312*, 127.
799. Simonato, J.-P.; Pécaut, J.; Le Pape, L.; Oddou, J.-L.; Jeey, C.; Shang, M.; Scheidt, W. R.; Wojaczyński, J.; Wołowiec, S.; Latos-Grażyński, L.; Marchon, J.-C. *Inorg. Chem.* **2000**, *39*, 3978.
800. Ikeue, T.; Saitoh, T.; Yamaguchi, T.; Ohgo, Y.; Nakamura, M.; Takahashi, M.; Takeda, M. *Chem. Commun.* **2000**, 1989.
801. Ikeue, T.; Ohgo, Y.; Yamaguchi, T.; Takahashi, M.; Takeda, M.; Nakamura, M. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2617.
802. Summerville, D. A.; Cohen, I. A.; Hatano, K.; Scheidt, W. R. *Inorg. Chem.* **1978**, *17*, 2906.
803. Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.
804. Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Yoshida, Z. I.; Ogoshi, H. *Inorg. Chem.* **1980**, *19*, 950.
805. Barkigia, K. M.; Berber, M. D.; Fajer, J.; Medforth, C. J.; Renner, M. W.; Smith, K. M. *J. Am. Chem. Soc.* **1990**, *112*, 8851.
806. Cheng, R.-J.; Chen, P.-Y.; Gau, P.-R.; Chen, C.-C.; Peng, S.-M. *J. Am. Chem. Soc.* **1997**, *119*, 2563.
807. Schünemann, V.; Gerdan, M.; Trautwein, A. X.; Haoudi, N.; Mandon, D.; Fischer, J.; Weiss, R.; Tabard, A.; Guilard, R. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3181.
808. Ogura, H.; Yatsunyk, L.; Medforth, C. J.; Smith, K. M.; Barkigia, K. M.; Renner, M. W.; Melamed, D.; Walker, F. A. *J. Am. Chem. Soc.* **2001**, *123*, 6564.
809. Burstyn, J. N.; Roe, J. A.; Miksztal, A. R.; Shaevitz, B. A.; Lang, G.; Valentine, J. S. *J. Am. Chem. Soc.* **1988**, *110*, 1382.
810. Mazumdar, S.; Medhi, O. K.; Mitra, S. *Inorg. Chem.* **1988**, *27*, 2541.
811. Medhi, O. K.; Houlton, A.; Silver, J. *Inorg. Chim. Acta* **1989**, *161*, 213.
812. Medhi, O. K.; Mazumdar, S.; Mitra, S. *Inorg. Chem.* **1989**, *28*, 3243.
813. Mazumdar, S.; Medhi, O. K. *J. Chem. Soc., Dalton Trans.* **1990**, 2633.
814. Mazumdar, S.; Medhi, O. K.; Mitra, S. *J. Chem. Soc., Dalton Trans.* **1990**, 1057.
815. Medhi, O. K.; Silver, J. *Inorg. Chim. Acta* **1988**, *153*, 133.
816. Levey, G.; Sweigart, D. A.; Jones, J. G.; Prignano, A. L. *J. Chem. Soc., Dalton Trans.* **1992**, 605.
817. Paneque, A.; Fernández-Bertran, J.; Reguera, E.; Yee-Madeira, H. *Transition Met. Chem.* **2001**, *26*, 76.

818. Byers, W.; Cossham, J. A.; Edwards, J. O.; Gordon, A. T.; Jones, J. G.; Kenny, E. T. P.; Mahmood, A.; McKnight, J.; Sweigart, D. A.; Tondreau, G. A.; Wright, T. *Inorg. Chem.* **1986**, *25*, 4767.
819. Woo, K.; Sweigart, D. A. *Inorg. Chem.* **1993**, *32*, 4979.
820. Schneppensieper, T.; Zahl, A.; van Eldik, R. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1678.
821. Laverman, L. E.; Ford, P. C. *J. Am. Chem. Soc.* **2001**, *123*, 11614.
822. Andersen, M. B.; Hsuanyu, Y.; Welinder, K. G.; Schneider, P.; Dunford, H. B. *Acta Chem. Sc.* **1991**, *45*, 206.
823. Buchalova, M.; Warburton, P. R.; van Eldik, R.; Busch, D. H. *J. Am. Chem. Soc.* **1997**, *119*, 5867.
824. Buchalova, M.; Busch, D. H.; van Eldik, R. *Inorg. Chem.* **1998**, *37*, 1116.
825. Projahn, H.-D.; van Eldik, R. *Inorg. Chem.* **1991**, *30*, 3288.
826. Projahn, H.-D.; Schindler, S.; van Eldik, R.; Fortier, D. G.; Andrew, C. R.; Sykes, A. G. *Inorg. Chem.* **1995**, *34*, 5935.
827. David, S.; James, B. R.; Dolphin, D.; Traylor, T. G.; Lopez, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 6.
828. Bruice, T. C.; Dicken, C. M.; Balasubramanian, P. N.; Woon, T. C.; Lu, F.-L. *J. Am. Chem. Soc.* **1987**, *109*, 3436.
829. Ostović, D.; Knobler, C. B.; Bruice, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 3444.
830. Ferreira, G. C. *J. Biol. Chem.* **1994**, *269*, 4396.
831. Sawyer, D. T. *Comments Inorg. Chem.* **1990**, *10*, 129.
832. Crawford, P. W.; Ryan, M. D. *Inorg. Chim. Acta* **1991**, *179*, 25.
833. Crawford, P. W.; Ryan, M. D. *Inorg. Chim. Acta* **2002**, *328*, 13.
834. Kim, Y. O.; Song, B.; Goff, H. M. *Inorg. Chem.* **1993**, *32*, 1304.
835. Feng, D.; Ryan, M. D. *Inorg. Chem.* **1987**, *26*, 2480.
836. Choi, I.-K.; Liu, Y.; Feng, D.; Paeng, K.-J.; Ryan, M. D. *Inorg. Chem.* **1991**, *30*, 1832.
837. Liu, Y.; Ryan, M. D. *J. Electroanal. Chem.* **1994**, *368*, 209.
838. Fernes, J. B.; Feng, D.; Chang, A.; Keyser, A.; Ryan, M. D. *Inorg. Chem.* **1986**, *25*, 2606.
839. Bartoli, J.-F.; Le Barch, K.; Palacio, M.; Battioni, P.; Mansuy, D. *Chem. Commun.* **2001**, 1718.
840. Hubbard, C. D.; Jones, J. G. *Inorg. Chim. Acta* **1986**, *125*, 71.
841. Hubbard, C. D.; Jones, J. G.; McKnight, J. *J. Chem. Soc., Dalton Trans.* **2000**, 3143.
842. Modi, S.; Shedbalkar, V. P.; Behere, D. V. *Inorg. Chim. Acta* **1990**, *173*, 9.
843. Dickerson, L. D.; Sauer-Masarwa, A.; Herron, N.; Fendrick, C. M.; Busch, D. H. *J. Am. Chem. Soc.* **1993**, *115*, 3623.
844. Satoh, Y.; Shikama, K. *J. Biol. Chem.* **1981**, *256*, 10272.
845. Shikama, K. *Biochem. J.* **1984**, *223*, 279.
846. Shikama, K. *Chem. Rev.* **1998**, *98*, 1357.
847. Shikama, K. *Biol. Rev. (Cambridge)*, **1990**, *65*, 517.
848. Sitter, A. J.; Reczek, C. M.; Terner, J. *Biochim. Biophys. Acta* **1985**, *828*, 229.
849. Tsukahara, K.; Kiguchi, K.; Mizoguchi, C.; Matsui, M.; Kubota, N.; Arakawa, R.; Sakurai, T. *Inorg. React. Mech.* **2000**, *2*, 49.
850. Vogel, E. *J. Heterocycl. Chem.* **1996**, *33*, 1461.
851. Ohgo, Y.; Neya, S.; Funasaki, N.; Nakamura, M. *Acta Crystallogr.* **2001**, *C57*, 694.
852. Gisselbrecht, J. P.; Gross, M.; Köcher, M.; Lausmann, M.; Vogel, E. *J. Am. Chem. Soc.* **1990**, *112*, 8618.
853. Lausmann, M.; Zimmer, I.; Lex, J.; Lueken, H.; Wieghardt, K.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 736.
854. Kadisch, K. M.; Boulas, P.; D'Souza, F.; Aukaloo, A. M.; Guilard, R.; Lausmann, M.; Vogel, E. *Inorg. Chem.* **1994**, *33*, 471.
855. Rachlewicz, K.; Latos-Grażyński, L.; Vogel, E. *Inorg. Chem.* **2000**, *39*, 3247.
856. Ohgo, Y.; Neya, S.; Ikeue, T.; Funasaki, N.; Nakamura, M. *Acta Crystallogr.* **2001**, *C57*, 1046.
857. Licoccia, S.; Paolesse, R.; Tassoni, E.; Boschi, T. *J. Chem. Soc., Dalton Trans.* **1995**, 3617.
858. Cai, S.; Licoccia, S.; Walker, F. A. *Inorg. Chem.* **2001**, *40*, 5795.
859. Michel, S. L. J.; Hoffman, B. M.; Baum, S. M.; Barrett, A. G. M. *Prog. Inorg. Chem.* **2001**, *50*, 473 (see p 488).
860. Farrington, D. J.; Jones, J. G.; Robinson, N. D.; Twigg, M. V. *Transition Met. Chem.* **1999**, *24*, 697.
861. Baldacchini, T.; Monacelli, F. *Inorg. Chim. Acta* **1999**, *295*, 200.
862. Jones, J. G.; Farrington, D. J.; McDonald, F. M.; Mooney, P. M.; Twigg, M. V. *Transition Met. Chem.* **1998**, *23*, 693.
863. Ozoemena, K.; Nyokong, T. *J. Chem. Soc., Dalton Trans.* **2002**, 1806.
864. Ascenzi, P.; Brunori, M.; Pennesi, G.; Ercolani, C.; Monacelli, F. *J. Chem. Soc., Dalton Trans.* **1987**, 369.
865. Glover, R. E.; Koshkin, V.; Dunford, H. B.; Mason, R. P. *Nitric Oxide* **1999**, *3*, 439.
866. Scheidt, W. R.; Ellison, M. K. *Acc. Chem. Res.* **1999**, *32*, 350.
867. Wylie, G. R. A.; Scheidt, W. R. *Chem. Rev.* **2002**, *102*, 1067.
868. Hoshino, M.; Laverman, L.; Ford, P. C. *Coord. Chem. Rev.* **1999**, *187*, 75.
869. Wolak, M.; van Eldik, R. *Coord. Chem. Rev.* **2002**, *230*, 263.
870. Littlejohn, D.; Chang, S. G. *J. Phys. Chem.* **1982**, *86*, 537.
871. Zang, V.; Kotowski, M.; van Eldik, R. *Inorg. Chem.* **1988**, *27*, 3279.
872. Zang, V.; van Eldik, R. *Inorg. Chem.* **1990**, *29*, 4462.
873. Wolak, M.; Stochel, G.; Hamza, M.; van Eldik, R. *Inorg. Chem.* **2000**, *39*, 2018.
874. Wanat, A.; Schneppensieper, T.; Stochel, G.; van Eldik, R.; Bill, E.; Wieghardt, K. *Inorg. Chem.* **2002**, *41*, 4.
875. Zhang, Y.; Pavlosky, M. A.; Brown, C. A.; Westre, T. E.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1992**, *114*, 9189.
876. Schneppensieper, T.; Wanat, A.; Stochel, G.; Goldstein, S.; Meyerstein, D.; van Eldik, R. *Eur. J. Inorg. Chem.* **2001**, 2317.
877. Schneppensieper, T.; Finkler, S.; Czap, A.; van Eldik, R.; Heus, M.; Nieuwenhuizen, P.; Wreesmann, C.; Abma, W. *Eur. J. Inorg. Chem.* **2001**, 491.
878. Schneppensieper, T.; Wanat, A.; Stochel, G.; van Eldik, R. *Inorg. Chem.* **2002**, *41*, 2565.
879. Fernez, B. O.; Lorković, I. M.; Ford, P. C. *Inorg. Chem.* **2003**, *42*, 2.
880. Lorković, I. M.; Ford, P. C. *Inorg. Chem.* **2000**, *39*, 632.
881. Kosaka, H.; Sawai, Y.; Sakaguchi, H.; Kumura, E.; Harada, N.; Watanabe, M.; Shiga, T. *Am. J. Physiol.* **1994**, *266*, C1400.
882. Westenberger, U.; Thanner, S.; Ruf, H. H.; Gersonde, K.; Sutter, G.; Trentz, O. *Free Radic. Res. Commun.* **1990**, *11*, 167.

883. Hall, D. M.; Buettner, G. R.; Matthes, R. D.; Gisolfi, C. V. *J. Appl. Physiol.* **1994**, *77*, 548.
884. Eich, R. F.; Li, T.; Lemon, D. D.; Doherty, D. H.; Curry, S. R.; Aitken, J. F.; Mathews, A. J.; Johnson, K. A.; Smith, R. D.; Phillips, G. N. J.; Olson, J. S. *Biochemistry* **1996**, *35*, 6976.
885. Liu, X.; Miller, M. J. S.; Joshi, M. S.; Sadowska-Krowicka, H; Clark, D. A.; Lancaster, J. R. *J. Biol. Chem.* **1998**, *273*, 18709.
886. Lancaster, J. R. *Proc. Natl. Acad. Sci. USA* **1994**, *91*, 8137.
887. Lancaster, J. R. *Nitric Oxide* **1997**, *1*, 18.
888. Richardson, D. R.; Ponka, P. *Methods Neurosci.* **1996**, *31*, 329.
889. Reif, D. W.; Simmons, R. D. *Arch. Biochem. Biophys.* **1990**, *283*, 537.
890. Carmichael, A. J.; Steelgoodwin, L.; Gray, B.; Arroyo, C. M. *Free Radic. Res. Commun.* **1993**, *19*, S201.
891. Watts, R. N.; Richardson, D. R. *J. Lab. Clin. Med.* **2000**, *136*, 149.
892. Glover, R. E.; Ivy, E. D.; Orringer, E. P.; Maeda, H.; Mason, R. P. *Mol. Pharmacol.* **1999**, *55*, 1006.
893. Gladwin, M. T.; Schechter, A. N. *Sem. Hematol.* **2001**, *38*, 333.
894. Lee, M.; Arosio, P.; Cozzi, A.; Chasteen, N. D. *Biochemistry* **1994**, *33*, 3679.
895. Stamler, J. S.; Jia, L.; Eu, J. P.; McMahon, T. J.; Demchenko, I. T.; Bonaventura, J.; Gernert, K.; Piantadosi, C. A. *Science* **1997**, *276*, 2034.
896. Wardrop, S. L.; Watts, R. N.; Richardson, D. R. *Biochemistry* **2000**, *39*, 2748.
897. Franz, K. J.; Lippard, S. J. *Inorg. Chem.* **2000**, *39*, 3722.
898. George, A. V.; Field, L. D.; Malouf, E. Y.; McQueen, A. E. D.; Pike, S. R.; Purches, G. D.; Hambley, T. W.; Buys, I. E.; White, A. H.; Hockless, D. C. R.; Skelton, B. W. *J. Organomet. Chem.* **1997**, *538*, 101.
899. Gao, Y.; Golah, D. G.; Hughes, A. N.; Spivak, G. J.; Havighurst, M. D.; Magnuson, V. R. *Polyhedron* **1998**, *17*, 3881.
900. Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031.
901. Foley, S. R.; Yap, G. P. A.; Richeson, D. S. *Inorg. Chem.* **2002**, *41*, 4149.
902. Cotton, F. A.; Daniels, L. M.; Favello, L. R.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 269.
903. Cotton, F. A.; Daniels, L. M.; Matonic, J. H.; Murillo, C. A. *Inorg. Chim. Acta* **1997**, *256*, 277.
904. Baudler, M.; Akpapoglou, S. Ouzonis D.; Wasgestian, F.; Meinigke, B.; Budzikiewicz, H.; Münster, H. *Angew. Chem. Internat. Ed.* **1988**, *27*, 280.
905. Rocchini, E.; Rigo, P.; Mezzetti, A.; Stephan, T.; Morris, R. H.; Lough, A. J.; Forde, C. E.; Fong, T. P.; Drouin, S. D. *J. Chem. Soc., Dalton Trans.* **2000**, 3591.
906. Fong, P.; Forde, C. E.; Lough, A. J.; Morris, R. H.; Rigo, P.; Rocchini, E.; Stephan, T. *J. Chem. Soc., Dalton Trans.* **2000**, 4475.
907. Field, L. D.; Shaw, W. J.; Turner, P. *Organometallics* **2001**, *20*, 3491.
908. Field, L. D.; Thomas, I. P.; Turner, P.; Hambley, T. W. *Aust. J. Chem.* **2000**, *53*, 541.
909. Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19.
910. Angeles Máñez, M.; Fernández-Trujillo, M. J.; Basalotte, M. G. *Polyhedron* **1996**, *15*, 2305.
911. Field, L. D.; Messerle, B. A.; Smernik, R. J.; Hambley, T. W.; Turner, P. *Inorg. Chem.* **1997**, *36*, 2884.
912. Jeffery, J. C.; Odell, B.; Stevens, N.; Talbot, R. E. *Chem. Commun.* **2000**, 101.
913. Courtney, D.; Cromhout, N. L.; Cunningham, D.; Gallagher, J. F.; Manning, A. R.; McArdle, P.; Pratt, S. I. *Inorg. Chim. Acta* **2002**, *327*, 98.
914. Gusev, D. G.; Huebner, R. Burger P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716.
915. Buys, I. E.; Field, L. D.; George, A. V.; Hambley, T. W. *Aust. J. Chem.* **1997**, *50*, 159.
916. Kang, B.-S.; Chen, X.-M.; Gao, H.-R.; Wu, B.-M.; Mak, T. C. W. *Synth. React. Inorg. Met.-Org. Chem.* **1996**, *26*, 1651.
917. Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1988**, 509.
918. Basallote, M. G.; Durán, J.; Fernández-Trujillo, M. J.; González, G.; Máñez, M. A.; Martínez, M. *Inorg. Chem.* **1998**, *37*, 1623.
919. Jian, F.; Wang, Y.; Lu, L.; Yang, X.; Wang, X.; Chantrapromma, S.; Fun, H.-K.; Razak, I. A. *Acta Crystallogr.* **2001**, *C57*, 714.
920. Burgess, J.; Drasdo, D. S.; Patel, M. S. *J.Pharm. Sci.* **1994**, *83*, 54.
921. Boukhalfa, H.; Thomas, F.; Serratrice, G.; Béguin, C. G. *Inorg. React. Mech.* **2001/2002**, *3*, 153.
922. Hämäläinen, R.; Turpeinen, U. *Acta Chem. Sc.* **1989**, *43*, 15.
923. Shetti, U. N.; Revankar, V. K.; Mahale, V. B. *Indian J. Chem.* **1998**, *37A*, 540.
924. Elmali, A.; Kavlakoglu, E.; Elerman, Y.; Svoboda, I. *Acta Crystallogr.* **2000**, *C56*, 1097.
925. Muikuriya, M.; Kushida, K.; Nakayama, H.; Mori, W.; Kishita, M. *Inorg. Chim. Acta* **1989**, *165*, 35.
926. Furutachi, H.; Ōkawa, H. *Inorg. Chem.* **1997**, *36*, 3911.
927. Haikarainen, A.; Sipilä, J.; Pietikäinen, P.; Pajunen, A.; Mutikainen, I. *J. Chem. Soc., Dalton Trans.* **2001**, 991.
928. Hernández-Molina, R.; Mederos, A.; Gili, P.; Domínguez, S.; Núñez, P. *Polyhedron* **1997**, *16*, 4191.
929. Das, A.; Dash, A. C. *Indian J. Chem.* **2001**, *40A*, 65.
930. Das, A.; Dash, A. C. *Inorg. React. Mech.* **2000**, *2*, 101.
931. Šima, J. *Croat. Chem. Acta* **2001**, *74*, 593.
932. Shyu, H.-L.; Wei, H.-H.; Lee, G.-H.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **2000**, 915.
933. König, E.; Ritter, G.; Dengler, J.; Nelson, S. M. *Inorg. Chem.* **1987**, *26*, 3582.
934. Ohshio, H.; Maeda, Y.; Takashima, Y. *Inorg. Chem.* **1983**, *22*, 2684.
935. Maeda, Y.; Tsutsumi, T.; Takashima, Y. *Inorg. Chem.* **1984**, *23*, 2440.
936. Federer, W. D.; Hendrickson, D. N. *Inorg. Chem.* **1984**, *23*, 3861–3870.
937. Hyami, S.; Gu, Z.-Z.; Yoshiki, H.; Fujishima, A.; Sato, O. *J. Am. Chem. Soc.* **2001**, *123*, 11644.
938. Timken, M. D.; Abdel-Mawgoud, A. M.; Hendrickson, D. N. *Inorg. Chem.* **1986**, *25*, 160.
939. Timken, M. D.; Strouse, C. E.; Soltis, S. M.; Daverio, S. A.; Hendrickson, D. N.; Abdel-Mawgoud, A. M.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 395.
940. Petrouleas, V.; Tuchagues, J. P. *Chem. Phys. Lett.* **1987**, *137*, 21.
941. Hayami, S.; Gu, Z.-Z.; Yoshiki, H.; Fujishima, A.; Sato, O. *J. Am. Chem. Soc.* **2001**, *123*, 11644.
942. Hovey, J. K.; Tremaine, P. R. *J. Phys. Chem.* **1985**, *89*, 5541.
943. Nakasuska, N.; Kunimatsu, M.; Kunimatsu, K.; Tanaka, M. *Inorg. Chem.* **1985**, *24*, 10.

944. Dervan, P. B. *Science* **1986**, *232*, 464.
945. Barton, J. K. *Science* **1986**, *233*, 727.
946. Lin, W.; Welsh, W. J.; Harris, W. R. *Inorg. Chem.* **1994**, *33*, 884.
947. Rodriguez, M.-C.; Morgenstern-Badarau, I.; Cesario, M.; Guilhem, J.; Keita, B.; Nadjo, L. *Inorg. Chem.* **1996**, *35*, 7804.
948. Rana, T. M.; Meares, C. F. *J. Am. Chem. Soc.* **1990**, *112*, 2457.
949. Serratice, G.; Galey, J.-B.; Aman, E. S.; Dumats, J. *Eur. J. Inorg. Chem.* **2001**, 471.
950. Bailey, N. A.; Cummins, D.; McKenzie, E. D.; Worthington, J. M. *Inorg. Chim. Acta* **1981**, *50*, 111.
951. Turowski, P. N.; Rodgers, S. J.; Scarrow, R. C.; Raymond, K. N. *Inorg. Chem.* **1988**, *27*, 474.
952. Zang, V.; van Eldik, R. *Inorg. Chem.* **1990**, *29*, 1705.
953. Seibig, S.; van Eldik, R. *Eur. J. Inorg. Chem.* **1999**, 447.
954. Seibig, S.; van Eldik, R. *Inorg. React. Mech.* **1999**, *1*, 91.
955. Francis, K. C.; Cummins, D.; Oakes, J. *J. Chem. Soc., Dalton Trans.* **1985**, 493.
956. Gilbert, B. C.; Stell, J. K. *J. Chem. Soc. Perkin Trans. 2* **1990**, 1281.
957. Gilbert, B. C.; Stell, J. K. *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 3261.
958. Gilbert, B. C.; Stell, J. K.; Jeff, M. *J. Chem. Soc. Perkin Trans. 2* **1988**, 1867.
959. Van Eldik, R.; Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1994**, *33*, 1566.
960. Galey, J.-B.; Destrée, O.; Dumats, J.; Génard, S.; Tachon, P. *J. Med. Chem.* **2000**, *43*, 1418.
961. Chang, C. A.; Francesconi, L. C.; Malley, M. F.; Kumar, K. Gougoutas J. Z.; Tweedle, M. F.; Lee, D. W.; Wilson, L. J. *Inorg. Chem.* **1993**, *32*, 3501.
962. Fábián, I.; Diebler, H. *Inorg. Chem.* **1987**, *26*, 925.
963. Sun, Y.; Martell, A. E.; Motekaitis, R. J. *Inorg. Chem.* **1986**, *25*, 4780.
964. Fitzsimmons, B. W.; Hume, A.; Larkworthy, L. F.; Turnbull, M. H.; Yavari, A. *Inorg. Chim. Acta* **1985**, *106*, 109.
965. Djurdjević, P. *Transition Met. Chem.* **1990**, *15*, 345.
966. Djurdjević, P.; Jelić, R. *Transition Met. Chem.* **1997**, *22*, 284.
967. Sóvágó, I.; Kiss, T.; Gergely, A. *Pure Appl. Chem.* **1993**, *65*, 1029.
968. Nawar, N. A.; Shallaby, A.-H. M.; Hosny, N. M.; Mostafa, M. M. *Transition Met. Chem.* **2001**, *26*, 180.
969. Färber, M.; Osiander, H.; Severin, T. *J. Heterocyclic Chem.* **1994**, *31*, 947.
970. Marlin, D. S.; Mascharak, P. K. *Chem. Soc. Rev.* **2000**, *29*, 69.
971. Moratal, J.; Julve, M.; Faus, J. *Rev. Chim. Minér.* **1982**, *19*, 72.
972. García-España, E.; Julve, M.; Moratal, J. M.; Faus, J.; Guillin, J.; Zarembowitch, J. *New J. Chem.* **1988**, *12*, 59.
973. Basu, P.; Choudhury, S. B.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1989**, *28*, 2680.
974. Argay, G.; Kálmán, A.; Leovac, V. M. *Acta Crystallogr.* **1999**, *55C*, 1440.
975. Ivanovic-Burmazovic, I.; Hamza, M. S. A.; van Eldik, R. *Inorg. Chem.* **2002**, *41*, 5150.
976. Clemente-Juan, J. M.; Mackiewicz, C.; Verelst, M.; Dahan, F.; Bousseksou, A.; Sanakis, Y.; Tuchagues, J.-P. *Inorg. Chem.* **2002**, *41*, 1478.
977. Martell, A. E.; Perutka, J.; Kong, D. *Coord. Chem. Rev.* **2001**, *216–217*, 55.
978. Lah, M. S.; Kirk, M. L.; Hatfield, W.; Pecoraro, V. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1606.
979. Lah, M. S.; Pecoraro, V. L. *Comments Inorg. Chem.* **1990**, *11*, 59.
980. Lin, S.; Liu, S.-X.; Lin, B.-Z. *Inorg. Chim. Acta* **2002**, *328*, 69.
981. Liu, S.-X.; Lin, S.; Lin, B.-Z.; Lin, C.-C.; Huang, J.-Q. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1084.
982. Hahn, F. E.; McMurry, T. J.; Hugi, A.; Raymond, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 1854.
983. Schmalle, H. W.; Gyr, E.; Dubler, E. *Acta Crystallogr.* **2000**, *C56*, 957.
984. Padhyé, S.; Kauffmann, G. B. *Coord. Chem. Rev.* **1985**, *63*, 127.
985. Chattopadhyay, S. K.; Hossain, M.; Ghosh, S.; Guha, A. K. *Transition Met. Chem.* **1990**, *15*, 473.
986. Cooper, L.; Davies, S. C.; Dilworth, J. R.; Hughes, D. L.; Konkol, M.; Richards, R. L.; Sers, J. R.; Sobota, P. *Can. J. Chem.* **2001**, *79*, 490.
987. Davies, S. C.; Hughes, D. L.; Richards, R. L.; Sers, J. R. *Chem. Commun.* **1998**, 2699.
988. Barclay, J. E.; Davies, S. C.; Evans, D. J.; Fairhurst, S. A.; Fowler, C.; Henderson, R. A.; Hughes, D. L.; Oglieve, K. E. *Transition Met. Chem.* **1998**, *23*, 701.
989. Grapperhaus, C. A.; Patra, A. K.; Mashuta, M. S. *Inorg. Chem.* **2002**, *41*, 1039.
990. Huang, W.; Jia, J.; Cummings, J.; Nelson, M.; Schneider, G.; Lindqvist, Y. *Structure* **1997**, *5*, 691.
991. Nakasako, M.; Odaka, M.; Yohda, M.; Dohmae, N.; Takio, K.; Kamiya, N.; Endo, I. *Biochemistry* **1999**, *38*, 9887.
992. Boone, A. J.; Cory, M. G.; Scott, M. J.; Zerner, M. C.; Richards, N. G. J. *Inorg. Chem.* **2001**, *40*, 1837; and references therein.
993. Noguchi, T.; Hoshino, M.; Tsujimura, M.; Odaka, M.; Endo, I. *Biochemistry* **1996**, *35*, 16777.
994. Odaka, M.; Fujii, K.; Hoshino, M.; Noguchi, T.; Tsujimura, M.; Nagashima, S.; Yohda, M.; Nagamune, T.; Inoue, Y.; Endo, I. *J. Am. Chem. Soc.* **1997**, *119*, 3785.
995. Noveron, J. C.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **2001**, *123*, 3247.
996. Davies, S. C.; Durrant, M. C.; Hughes, D. L.; Richards, R. L.; Sanders, J. R. *J. Chem. Soc., Dalton Trans.* **2000**, 4694.
997. Shearer, J.; Nehring, J.; Lovell, S.; Kaminsky, W.; Kovacs, J. A. *Inorg. Chem.* **2001**, *40*, 5483.
998. Beissel, T.; Bürger, K. S.; Voigt, G.; Wieghardt, K.; Butzlaff, C.; Trautwein, A. X. *Inorg. Chem.* **1993**, *32*, 124.
999. Garg, A.; Tandon, J. P. *Transition Met. Chem.* **1987**, *12*, 42.
1000. Elmali, A.; Elerman, Y.; Svoboda, I. *Acta Crystallogr.* **2001**, *C57*, 375.
1001. Jones, P. *J. Biol. Chem.* **2001**, *276*, 13791.
1002. Cornell, R. M.; Schwertmann, U. *The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses* 1996, VCH: Weinheim.
1003. Powell, A. K. *Struct. Bonding* **1997**, *88*, 1.
1004. Powell, A. K.; Heath, S. L. *Comments Inorg. Chem.* **1994**, *15*, 255.
1005. Feitknecht, W.; Giovanoli, R.; Michaelis, W.; Müller, M. *Z. Anorg. Allg. Chem.* **1975**, *417*, 114.
1006. Danesi, P. R.; Chiarizia, R.; Scibona, G.; Riccardi, R. *Inorg. Chem.* **1973**, *12*, 2089.
1007. Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 344.

1008. Nielson, G. W.; Enderby, J. E., Eds.; *Water and Aqueous Solutions* 1986, Adam Hilger: Bristol.
1009. Enderby, J. E.; Cummings, S.; Herdman, G. J.; Nielson, G. W.; Salmon, P. S.; Skipper, N. *J. Phys. Chem.* **1987**, *91*, 5851.
1010. Ishiguro, S.-I.; Ohtaki, H. *Coord. Chem.* **1987**, *15*, 237.
1011. Magini, M. (Ed.) *X-Ray Diffraction of Ions in Aqueous Solution: Hydration and Complex Formation*; CRC Press: Florida, 1988.
1012. Richens, D. T. *The Chemistry of Aqua Ions* **1997**, Wiley: Chichester, U.K. Chap. 8.
1013. Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.
1014. Marcus, Y. *Chem. Rev.* **1988**, *88*, 1475.
1015. Herdman, G. J.; Nielson, G. W. *J. Phys. Condens. Matter* **1992**, *4*, 649.
1016. Ohtaki, H.; Yamaguchi, T.; Maeda, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 701.
1017. Kalman, E.; Radnai, T.; Palinkas, G.; Hajdu, F.; Vertes, A. *Electrochim. Acta* **1988**, *33*, 1223.
1018. Sham, T. J.; Hastings, B. K.; Perlman, M. L. *Chem. Phys. Lett.* **1981**, *83*, 391.
1019. Herdman, G. J.; Nielson, G. W. *J. Phys. Condens. Matter* **1992**, *4*, 627.
1020. Apted, M. J.; Waychunas, G. A.; Brown, G. E. *Geochim. Cosmochim. Acta* **1985**, *49*, 2081.
1021. Kálmán, E.; Radnai, T.; Pálinkás, G.; Hajdu, F.; Vértes, A. *Electrochim. Acta* **1988**, *33*, 1223.
1022. Ichihashi, M.; Wakita, H.; Masuda, I. *J. Solution Chem.* **1984**, *13*, 505.
1023. Herdman, G. J.; Salmon, P. S. *J. Am. Chem. Soc.* **1991**, *113*, 2930.
1024. Salmon, P. S.; Lond, P. B. *Physica B* **1992**, *182*, 421.
1025. Inada, Y.; Funahashi, S. *Z. Naturforsch.* **1999**, *54B*, 1518.
1026. Combes, J. M.; Manceau, A.; Calas, G.; Bottero, J. Y. *Geochim. Cosmochim. Acta* **1989**, *53*, 583.
1027. Figgis, B. N.; Kucharski, B. N.; Reynolds, P. A.; Tasset, F. *Acta Crystallogr.* **1989**, *C45*, 942.
1028. Figgis, B. N.; Forsyth, J. B.; Kucharski, B. N.; Reynolds, P. A.; Tasset, F. *Proc. Roy. Soc. London* **1990**, *428*, 113.
1029. Figgis, B. N.; Kepert, C. J.; Kucharski, B. N.; Reynolds, P. A. *Acta Crystallogr.* **1992**, *B48*, 753.
1030. Chandler, G. S.; Christos, G. A.; Figgis, B. N.; Reynolds, P. A. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 1961.
1031. Best, S. P.; Forsyth, J. B. *J. Chem. Soc., Dalton Trans.* **1990**, 395.
1032. Armstrong, R. S.; Beattie, J. K.; Best, S. P.; Braithwaite, G. P.; Del Favero, P.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1990**, *43*, 393.
1033. Nielson, G. W.; Tromp, R. H. *Annu. Rep. Prog. Chem. Sect. C* **1991**, *88*, 45.
1034. Åkesson, R.; Pettersson, L. G. M.; Sandström, M.; Wahlgren, U. *J. Am. Chem. Soc.* **1994**, *116*, 8691.
1035. Åkesson, R.; Pettersson, L. G. M.; Sandström, M.; Wahlgren, U. *J. Am. Chem. Soc.* **1994**, *116*, 8705.
1036. Rotzinger, F. P. *J. Am. Chem. Soc.* **1997**, *119*, 5230.
1037. Rotzinger, F. P. *Helv. Chim. Acta* **2000**, *83*, 3006.
1038. Cusanelli, A.; Frey, U.; Richens, D. T.; Merbach, A. E. *J. Am. Chem. Soc.* **1996**, *118*, 5265.
1039. Jolley, W. H.; Stranks, D. R.; Swaddle, T. W. *Inorg. Chem.* **1990**, *29*, 1948.
1040. Furholz, U.; Haim, A. *Inorg. Chem.* **1985**, *24*, 3091.
1041. Friedman, H. L.; Newton, M. D. *J. Electroanal. Chem. Interfac. Chem.* **1986**, *204*, 21.
1042. Buda, F.; Ensing, B.; Gribnau, M. C. M.; Baerends, E. J. *Chem. Eur. J.* **2001**, *7*, 2775.
1043. Bakac, A.; Wang, W.-D. *Inorg. React. Mech.* **1998**, *1*, 65.
1044. Bakač, A. *Croat. Chem. Acta* **2001**, *74*, 633.
1045. Pogue, R. F.; Atkinson, G. *J. Chem. Eng. Data* **1989**, *34*, 227.
1046. Sengupta, D.; Pal, A.; Lahiri, S. C. *J. Chem. Soc., Dalton Trans.* **1983**, 2685.
1047. Blandamer, M. J.; Burgess, J. *J. Chem. Soc., Dalton Trans.* **1985**, 867.
1048. Sengupta, D.; Pal, A.; Lahiri, S. C. *J. Chem. Soc., Dalton Trans.* **1985**, 868.
1049. Kalidas, C.; Hefter, G.; Marcus, Y. *Chem. Rev.* **2000**, *100*, 819.
1050. Hefter, G.; Marcus, Y.; Waghorne, W. E. *Chem. Rev.* **2002**, *102*, 2773.
1051. Micskei, K.; Nagypal, I. *J. Chem. Soc., Dalton Trans.* **1990**, 743.
1052. Benjarvongkulchai, S.; Cannon, R. D. *Polyhedron* **1992**, *11*, 517.
1053. Barnés, C. M.; Theil, E. C.; Raymond, K. N. *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5195.
1054. Biruš, M.; Kujundžić, N.; Pribanić, M. *Prog. React. Kinet.* **1993**, *18*, 171.
1055. Lente, G.; Fábián, I. *Inorg. Chem.* **2002**, *41*, 1306.
1056. Flynn, C. M. *Chem. Rev.* **1984**, *84*, 31.
1057. Schneider, W. *Comments Inorg. Chem.* **1984**, *3*, 205.
1058. Cornell, R. M.; Giovanoli, R.; Schneider, W. *J. Chem. Tech. Biotechnol.* **1989**, *46*, 115.
1059. Schneider, W.; Schwyn, B. Stumm, W., Eds.; *Aquatic Surface Chemistr* **1987**, 167. Wiley: New York.
1060. Feitknecht, W.; Michaelis, W. *Helv. Chim. Acta* **1962**, *45*, 212.
1061. Musić, S.; Popović, S.; Orehoveć, Z.; Czako-Nagy, I. *J. Colloid Interface Sci.* **1993**, *160*, 479.
1062. Musić, S.; Orehoveć, Z.; Popović, S.; Czako-Nagy, I. *J. Mater. Sci.* **1994**, *29*, 1991.
1063. Gotić, M.; Popović, S.; Ljubesić, N.; Musić, S. *J. Mater. Sci.* **1994**, *29*, 2474.
1064. Murphy, P. J.; Posner, A. M.; Quirk, J. P. *J. Colloid Interface Sci.* **1976**, *56*, 270, 298, 312; and references therein.
1065. Khoe, G. H.; Brown, P. L.; Sylva, R. N.; Robins, R. G. *J. Chem. Soc., Dalton Trans.* **1986**, 1901.
1066. Rustad, J. R.; Hay, B. P.; Halley, J. W. *J. Chem. Phys.* **1995**, *102*, 427.
1067. Martinez, P.; van Eldik, R.; Kelm, H. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 81.
1068. Pozdnyakov, I. P.; Glebov, E. M.; Plyusnin, V. F.; Grivin, V. P.; Ivanov, Y. V.; Voroyev, D. Yu.; Bashin, N. M. *Pure Appl. Chem.* **2000**, *72*, 2187.
1069. Khan, A. I.; O'Hare, D. *J. Mater. Chem.* **2002**, *12*, 3191.
1070. Carlino, S.; Hudson, M. J. *Solid State Ionics* **1998**, *110*, 153.
1071. Jordan, R. B. *Reaction Mechanisms of Inorganic and Organometallic Systems* 1991, Oxford University Press: New York; Chap. 3. 8. b.
1072. Grant, M.; Jordan, R. B. *Inorg. Chem.* **1981**, *20*, 55.
1073. Grace, M. R.; Swaddle, T. W. *Inorg. Chem.* **1992**, *31*, 4674.
1074. Jameson, R. F.; Linert, W.; Tschinkowitz, A.; Gutmann, V. *J. Chem. Soc., Dalton Trans.* **1988**, 943.
1075. Blanco, C. A.; Romero, J. M.; Verdu, J. *Int. J. Chem. Kinet.* **1993**, *25*, 1005.

1076. Blanco, C. A.; Sumillera, J. *New J. Chem.* **1994**, *18*, 223.
1077. Biruš, M.; Bradić, Z.; Krznarić, G.; Kujundzić, N.; Pribanić, M.; Wilkins, P. C.; Wilkins, R. G. *Inorg. Chem.* **1987**, *26*, 1000.
1078. Biruš, M.; Krznarić, G.; Kujundzić, N.; Pribanić, M. *Croat. Chem. Acta* **1988**, *61*, 33.
1079. Biruš, M.; van Eldik, R. *Inorg. Chem.* **1991**, *30*, 4559.
1080. Dash, A. C.; Mohammed, S. S. *Indian J. Chem.* **1992**, *31A*, 412.
1081. Dash, A. C.; Mohammed, S. S. *Indian J. Chem.* **1992**, *31A*, 166.
1082. Martinez, P.; van Eldik, R. *Ber Bunsenges. Phys. Chem.* **1985**, *89*, 728.
1083. Martinez, P.; Mohr, R.; van Eldik, R. *Ber. Bunsenges. Phys. Chem.* **1986**, *90*, 609.
1084. Abrahams, B. F.; Lu, K. D.; Moubaraki, B.; Murray, K. S.; Robson, R. *J. Chem. Soc., Dalton Trans.* **2000**, 1793.
1085. Wisniewska, J.; van Eldik, R. *Inorg. Chem.* **2002**, *41*, 3802.
1086. Pelizzetti, E.; Mentasti, E. *Inorg. Chem.* **1979**, *18*, 583.
1087. Bansch, B.; Martinez, P.; Uribe, D.; Zulunga, J.; van Eldik, R. *Inorg. Chem.* **1991**, *30*, 4555.
1088. Bengtsson, G.; Fronæus, S.; Bengtsson-Kloo, L. *J. Chem. Soc., Dalton Trans.* **2002**, 2548.
1089. Rudgewick-Brown, N.; Cannon, R. D. *Inorg. Chem.* **1985**, *24*, 2463.
1090. Abe, Y.; Shirai, K.; Kurokawa, A.; Kinoshita, M. *Inorg. React. Mech.* **2001**, *3*, 107.
1091. Jameson, R. F.; Linert, W.; Tschinkowitz, A. *J. Chem. Soc., Dalton Trans.* **1988**, 2109.
1092. Eiki, T.; Tagaki, W. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1235.
1093. Brandt, C.; van Eldik, R. *Transition Met. Chem.* **1998**, *23*, 667.
1094. Carbone, A. I.; Cavasino, F. P.; Sbriziolo, C.; Pelizzetti, E. *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 31.
1095. Morrison, T. I.; Reis, A. H.; Knapp, G. S.; Fradin, F. Y.; Chen, H.; Klippert, T. E. *J. Am. Chem. Soc.* **1978**, *100*, 3262.
1096. Knudsen, J. M.; Larsen, E.; Moreira, J. E.; Furskov-Neilson, O. *Acta Chem. Sc.* **1975**, *A29*, 833.
1097. Meagher, A. *Inorg. Chim. Acta* **1988**, *146*, 19.
1098. Ramsay, J. D. F. In *Water and Aqueous Solutions*; Nielson, G.W.; Enderby, J. E. ; Eds.; Adam Hilger: Bristol 1986, pp 207–218.
1099. Lente, G.; Fábián, I. *Inorg. Chem.* **1999**, *38*, 603.
1100. Smoukov, S. K.; Quaroni, L.; Wang, X.; Doan, P. E.; Hoffman, B. M.; Que, L. *J. Am. Chem. Soc.* **2002**, *124*, 2595.
1101. Melikov, I. V.; Kozlovskaya, L. B.; Berliner, L. B.; Prokofiev, M. A. *J. Colloid Interfac. Sci.* **1987**, *117*, 1.
1102. Henry, M.; Jolivet, J. P.; Livage, J. *Struct. Bonding* **1992**, *77*, 153.
1103. Bradley, S. M.; Kydd, R. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2407.
1104. O'Keefe, B. J.; Monnier, S. M.; Hillmeyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2001**, *123*, 339.
1105. Kovács, T.; Speier, G.; Réglier, M.; Giorgi, M.; Vértes, A.; Vankó, G. *Chem. Commun.* **2000**, 469.
1106. Taube, H. *Prog. Inorg. Chem.* **1986**, *34*, 607.
1107. Que, L.; Watanabe, Y. *Science* **2001**, *292*, 651.
1108. Wada, A.; Ogo, S.; Watanabe, Y.; Mukai, M.; Kitagawa, T.; Jitsukawa, K.; Masuda, H.; Einage, H. *Inorg. Chem.* **1999**, *38*, 3592.
1109. Simaan, A. J.; Banse, F.; Girerd, J.-J.; Wieghardt, K.; Bill, E. *Inorg. Chem.* **2001**, *40*, 6538.
1110. Solomon, E. I.; Tuczek, F.; Root, D. E.; Brown, CA. *Chem. Rev.* **1994**, *94*, 827.
1111. Cowley, A. R.; Chippindale, A. M. *J. Chem. Soc., Dalton Trans.* **2000**, 3425.
1112. Wang, K.; Yu, J.; Song, Y.; Xu, R. *J. Chem. Soc., Dalton Trans.* **2003**, 99.
1113. Lente, G.; Magalhães, M. E. A.; Fábián, I. *Inorg. Chem.* **2000**, *39*, 1950.
1114. Rankin, B. J.; Thewles, A.; Lote, C. J.; Webb, M.; Roberts, N. B. *J. Pharm. Pharmacol.* **2001**, *53*, 513; and references therein.
1115. Bellitto, C.; Federici, F.; Colapietro, M.; Portalone, G.; Caschera, D. *Inorg. Chem.* **2002**, *41*, 709.
1116. Altomare, A.; Bellito, C.; Ibrahim, S. A.; Mahmoud, M. R.; Rizzi, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3913.
1117. Kraft, J.; van Eldik, R. *Atmos. Environ.* **1989**, *23*, 2709.
1118. Kraft, J.; van Eldik, R. *Inorg. Chem.* **1989**, *28*, 2297.
1119. Kraft, J.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1989**, 790.
1120. Kraft, J.; van Eldik, R. *Inorg. Chem.* **1989**, *28*, 2306.
1121. Lee, C. K.; Tavlarides, L. L. *Polyhedron* **1985**, *4*, 47.
1122. Alguacil, F. J.; Amer, S. *Polyhedron* **1986**, *5*, 1755.
1123. Wilkinson, E. C.; Dong, Y. H.; Que, L. *J. Am. Chem. Soc.* **1994**, *116*, 8394.
1124. Gupta, A.; Crumbliss, A. L. *J. Lab. Clin. Med.* **2000**, *136*, 371.
1125. Cowart, R. E.; Swope, S.; Loh, T. T.; Chasteen, N. D.; Bates, G. W. *J. Biol. Chem.* **1986**, *261*, 4607.
1126. Harris, W. R.; Rezvani, A. B.; Bali, P. K. *Inorg. Chem.* **1987**, *26*, 2711.
1127. Katz, E.; Sheeney-Haj-Ichia, L.; Willner, I. *Chem. Eur. J.* **2002**, *8*, 4138.
1128. Coronado, E.; Gómez-García, C. J. *Comments Inorg. Chem.* **1995**, *17*, 255.
1129. Müller, A.; Kögerler, P.; Dress, A. W. M. *Coord. Chem. Rev.* **2001**, *222*, 193.
1130. Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R. *Science* **1994**, *265*, 1054.
1131. Keita, B.; Girard, F.; Nadjo, L.; Contant, R.; Canny, J.; Richet, M. *J. Electroanal. Chem.* **1999**, *478*, 76.
1132. Keita, B.; Belhouari, A.; Nadjo, L.; Contant, R. *J. Electroanal. Chem.* **1998**, *442*, 49.
1133. Contant, R.; Abbessi, M.; Canny, J.; Belhouari, A.; Keita, B.; Nadjo, L. *Inorg. Chem.* **1997**, *36*, 4961.
1134. Zhang, X.; Chen, Q.; Duncan, D. C. Lachicotte R. J.; Hill, C. L. *Inorg. Chem.* **1997**, *36*, 4381.
1135. Zhang, X.; Chen, Q.; Duncan, D. C.; Campana, C. F.; Hill, C. L. *Inorg. Chem.* **1997**, *36*, 4208.
1136. Bösing, M.; Loose, I.; Pohlmann, H.; Krebs, H. *Chem. Eur. J.* **1997**, *3*, 1232.
1137. Loose, I.; Droste, E.; Bösing, M.; Pohlmann, H.; Dickman, M. H.; Rosu, C.; Pope, M. T.; Krebs, H. *Inorg. Chem.* **1999**, *38*, 2688.
1138. Kortz, U.; Savelieff, M. G.; Bassil, B. S.; Keita, B.; Nadjo, L. *Inorg. Chem.* **2002**, *41*, 783.
1139. Musić, S.; Furić, K.; Bajs, Z.; Mohaćek, V. *J. Mater. Sci.* **1992**, *27*, 5269.
1140. Musić, S.; Gotić, M.; Popović, S.; Furić, K.; Mohaćek, V. *J. Mater. Sci.* **1994**, *29*, 1227.

1141. Musić, S.; Gotić, M.; Popović, S.; Czako-Nagy, I. *Mater. Lett.* **1994**, *20*, 143 (*Chem. Abstr.* **1994**, *121*, 115760g).
1142. Qureshi, M. S.; Kazmi, S. A. *J. Chem. Soc. Pak.* **1998**, *20*, 175 (*Chem. Abstr.* **1999**, *130*, 187657n).
1143. Calderazzo, F.; Englert, U.; Pampaloni, G.; Passarelli, V.; Serni, G.; Wang, R. *Can. J. Chem.* **2001**, *79*, 495.
1144. Martin, R. B. *J. Inorg. Biochem.* **1986**, *28*, 181.
1145. Ribas, X.; Salvadó, V.; Valiente, M. *J. Chem. Res.* **1989**, *(S)* 332, *(M)*, 2533.
1146. Escot, M.-T.; Martre, A.-M.; Pouillen, P.; Martinet, P. *Bull. Soc. Chim. Fr.* **1989**, 316.
1147. Otsuki, H.; Brunetti, A.; Owens, E. S.; Finn, R. D.; Blasberg, R. G. *J. Nucl. Med.* **1989**, *30*, 1676.
1148. Martin, R. B.; Savory, J.; Brown, S.; Bertholf, R. L.; Wills, M. R. *Clin. Chem.* **1987**, *33*, 405.
1149. Nissenson, A. R.; Lindsay, R. M.; Swan, S.; Seligman, P. A.; Strobos, J. *Am. J. Kidney Dis.* **1999**, *33*, 471.
1150. Seligman, P. A.; Schleicher, R. B. *Clin. Chem.* **1999**, *45*, 898.
1151. Jacobs, J. C.; Alexander, N. M. *Clin. Chem.* **1990**, *36*, 1803.
1152. Randhawa, B. S.; Sweety, K. J. *J. Radioanal. Nucl. Chem.* **1999**, *242*, 675.
1153. Powell, A. K.; Charnock, J. M.; Flood, A. C.; Garner, D. C.; Ware, M. J.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1992**, 203.
1154. Loginov, A. V.; Katenin, S. B.; Voyakin, I. V.; Shagisultanova, G. A. *Koord. Khim.* **1986**, *12*, 1621 (*Chem. Abstr.* **1987**, *106*, 75999y).
1155. Lloret, F.; Julve, M.; Faus, J.; Solans, X.; Journaux, Y.; Morgenstern-Badarau, I. *Inorg. Chem.* **1990**, *29*, 2232.
1156. Graham, A. W.; Kurmoo, M.; Day, P. *J. Chem. Soc., Chem. Commun.* **1995**, 2061.
1157. Coronado, E.; Galán-Mascaros, J. R.; Gómez-García, C. J. *J. Chem. Soc., Dalton Trans.* **2000**, 205.
1158. Davies, G.; Fataftah, A.; Cherkasskiy, A.; Ghabbour, E. A.; Radwan, A.; Jansen, S. A.; Kolla, S.; Paciolla, M. D.; Sein, L. T.; Buermann, W.; Balasubramanian, M.; Budnick, J.; Xing, B. *J Chem. Soc., Dalton Trans.* **1997**, 4047.
1159. Tavadyan, L. A.; Tonikyan, H. G.; Minasyan, S. H.; Harutyunyan, L. A.; Greenaway, F. T.; Williams, S.; Gray-Kaufman, R. A.; Sorenson, J. R. J. *Inorg. Chim. Acta* **2002**, *328*, 1.
1160. Escot, M.-T.; Pouillen, P.; Martinet, P. *Bull. Soc. Chim. Fr.* **1989**, 321.
1161. Lee, D.; Lippard, S. J. *Inorg. Chim. Acta* **2002**, *341*, 1.
1162. Gaines, A.; Hammett, L. P.; Walden, G. H. *J. Am. Chem. Soc.* **1936**, *58*, 1668.
1163. Healy, P. C.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 2057.
1164. Plowman, J. E.; Loehr, T. M.; Schauer, C. K.; Anderson, O. P. *Inorg. Chem.* **1984**, *23*, 3553.
1165. Healy, P. C.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* **1984**, *37*, 1405.
1166. Pascaly, M.; Duda, M.; Rompel, A.; Sift, B. H.; Mayer-Klauke, W.; Krebs, B. *Inorg. Chim. Acta* **1999**, *291*, 298.
1167. Kurtz, D. M. *Chem. Rev.* **1990**, *90*, 585.
1168. Walczack, M. M.; Flynn, N. T. *J. Electroanal. Chem.* **1998**, *441*, 43.
1169. Ménage, S.; Vincent, J.-M.; Lambeaux, C.; Chottard, G.; Fontecave, M. *Inorg. Chem.* **1993**, *32*, 4766.
1170. Duboc-Toia, C.; Ménage, S.; Lambeaux, C.; Fontecave, M. *Tetrahedron Lett.* **1997**, *38*, 3727.
1171. Dunand-Sauthier, M.-N. C.; Deronzier, A.; Toia, C. D.; Fontecave, M.; Gorgy, K.; Leprêtre, J.-C.; Ménage, S. *J. Electroanal. Chem.* **1999**, *469*, 53.
1172. Wilkinson, E. C.; Dong, Y.; Zang, Y.; Fujii, H.; Fraczkiewicz, R.; Fraczkiewicz, G.; Czernuszewicz, R. S.; Que, L. *J. Am. Chem. Soc.* **1998**, *120*, 954.
1173. Hazell, A.; Jensen, K. B.; McKenzie, C. J.; Toftlund, H. *Inorg. Chem.* **1994**, *33*, 3127.
1174. Kryatov, S. V.; Rybak-Akimova, E. V.; MacMurdo, V. L.; Que, L. *Inorg. Chem.* **2001**, *40*, 2220.
1175. Kodera, M.; Taniike, Y.; Itoh, M.; Tanahashi, Y.; Shimakoshi, H.; Kano, K.; Hirota, S.; Ijima, S.; Ohba, M.; Okawa, H. *Inorg. Chem.* **2001**, *40*, 4821.
1176. Powell, A. K.; Heath, S. L.; Gatteschi, D.; Pardi, L.; Sessoli, R.; Spina, G.; Del Giallo, F.; Pieralli, F. *J. Am. Chem. Soc.* **1995**, *117*, 2491.
1177. Veith, M.; Grätz, F.; Huch, V. *Eur. J. Inorg. Chem.* **2001**, 367.
1178. Lee, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 12153.
1179. Lee, D.; Lippard, S. J. *Inorg. Chem.* **2002**, *41*, 827.
1180. Lee, D.; Krebs, C.; Huynh, B. H.; Hendrich, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **2000**, *122*, 5000.
1181. Lee, D.; Du Bois, J.; Petasis, D.; Hendrich, M. P.; Krebs, C.; Huynh, B. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1999**, *121*, 9893.
1182. Hagadorn, J. R.; Que, L.; Tolman, W. B. *J. Am. Chem. Soc.* **1998**, *120*, 13531.
1183. Vincent, J. B.; Huffman, J. C.; Christou, G.; Li, Q.; Nanny, M. A.; Hendrickson, D. N.; Fong, R. H.; Fish, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 6898.
1184. Armstrong, W. H.; Spool, A.; Papaefthymiou, G. C.; Frankel, R.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 3653.
1185. Wieghardt, K.; Pohl, K.; Ventur, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 392.
1186. Gomez-Romero, P.; Casan-Pastor, N.; Ben-Hussein, A.; Jameson, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 1988.
1187. Mimmi, M. C.; Miccichè, F.; Kooijman, H.; Spek, A. L.; Warzewska, S. T.; Bouwman, E. *Inorg. Chim. Acta* **2002**, *340*, 197.
1188. Dick, S.; Weiss, A.; Wagner, U.; Wagner, F.; Grosse, G. *Z. Naturforsch.* **1997**, *52B*, 372.
1189. Oberhausen, K. J.; Richardson, J. F.; O'Brien, R. J.; Buchanan, R. M.; McCusker, J. K.; Hendrickson, D. N. *Inorg. Chem.* **1992**, *31*, 1125.
1190. Toftlund, H.; Murray, K.; Zwack, P. R.; Taylor, L. F.; Anderson, O. P. *J. Chem. Soc., Chem. Commun.* **1986**, 191.
1191. Beer, R. H.; Tolman, W. B.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1991**, *30*, 2082.
1192. Mizoguchi, T. J.; Kuzelka, J.; Spingler, B.; DuBois, J. L.; Davydov, R. M.; Hedman, B.; Hodgson, K. O.; Lippard, S. J. *Inorg. Chem.* **2001**, *40*, 4662.
1193. Wilkins, R. G. *Chem. Soc. Rev.* **1992**, *21*, 171.
1194. Stenkamp, R. E. *Chem. Rev.* **1994**, *94*, 715.
1195. Lee, D.; Lippard, S. J. *J. Am. Chem. Soc.* **2001**, *123*, 4611.
1196. Scarpellini, M.; Naves, A.; Bortoluzzi, A. J.; Vencato, I.; Drago, V.; Ortiz, W. A.; Zucco, C. *J. Chem. Soc., Dalton Trans.* **2001**, 2616.
1197. Hagadorn, J. R.; Que, L.; Tolman, W. B. *J. Am. Chem. Soc.* **1999**, *121*, 9760.
1198. Mashuta, M. S.; Webb, R. J.; Oberhausen, K. J.; Richardson, J. F.; Buchanan, R. M.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1989**, *111*, 2745.

1199. Borovik, A. S.; Que, L.; Papaefthymiou, V.; Münck, E.; Taylor, L. F.; Anderson, O. P. *J. Am. Chem. Soc.* **1988**, *110*, 1986.
1200. Mikuriya, M.; Kakuta, Y.; Nukada, R.; Kotera, T.; Tokii, T. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1425.
1201. Suzuki, M.; Uehara, A. *Inorg. Chim. Acta* **1986**, *123*, L9.
1202. Suzuki, M.; Uehara, A.; Oshio, H.; Endo, K.; Yanaga, M.; Kida, S.; Saito, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3547.
1203. Borovik, A. S.; Que, L. *J. Am. Chem. Soc.* **1988**, *110*, 2345.
1204. Borovik, A. S.; Murch, B. P.; Que, L.; Papaefthymiou, V.; Münck, E. *J. Am. Chem. Soc.* **1987**, *109*, 7190.
1205. Murch, B. P.; Bradley, F. C.; Que, L. *J. Am. Chem. Soc.* **1986**, *108*, 5027.
1206. Cohen, J. D.; Payne, S.; Hagen, K. S.; Sers-Loehr, J. *J. Am. Chem. Soc.* **1997**, *119*, 2960.
1207. He, C.; Lippard, S. J. *Inorg. Chem.* **2001**, *40*, 1414.
1208. Cannon, R. D.; White, R. P. *Prog. Inorg. Chem.* **1988**, *36*, 195.
1209. Nakamoto, T.; Katada, M.; Endo, K.; Sano, H. *Polyhedron* **1998**, *17*, 3507.
1210. Woehler, S. E.; Wittebort, R. J.; Oh, S. M.; Kambara, T.; Hendrickson, D. N.; Inniss, D.; Strouse, C. E. *J. Am. Chem. Soc.* **1987**, *109*, 1063.
1211. Meesuk, L.; Jayasooriya, U. A.; Cannon, R. D. *Spectrochim. Acta* **1987**, *43A*, 687.
1212. Meesuk, L.; Jayasooriya, U. A.; Cannon, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 2009.
1213. White, R. P.; Al-Basseet, J. O.; Cannon, R. D.; Kearley, G. J.; Jayasooriya, U. A. *Physica B (Amsterdam)* **1989**, *156–157*, 367(*Chem. Abs.* **1989**, *110*, 241362q).
1214. White, R. P.; Sa-ard, N. C.; Bollen, S. K.; Cannon, R. D.; Jayasooriya, U. A.; Robertson, S. T.; Steigenberger, U.; Tomkinson, J. *Spectrochim. Acta* **1990**, *46A*, 903.
1215. Cannon, R. D.; Jayasooriya, U. A.; arapKoske, S. K.; White, R. P.; Williams, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 4158.
1216. Cannon, R. D.; Jayasooriya, U. A.; White, R. P.; arapKoske, S. K. *Spectrochim. Acta* **1993**, *49A*, 1787.
1217. Oh, S. M.; Kambara, T.; Hendrickson, D. N.; Sorai, M.; Kaji, K.; Woehler, S. E.; Wittebort, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 5540.
1218. Sorai, M.; Kaji, K.; Hendrickson, D. N.; Oh, S. M. *J. Am. Chem. Soc.* **1986**, *108*, 702.
1219. Montri, L.; Cannon, R. D. *Spectrochim. Acta* **1985**, *41A*, 643.
1220. Oh, S. M.; Hendrickson, D. N.; Hassett, K. L.; Davis, R. E. *J. Am. Chem. Soc.* **1984**, *106*, 7984.
1221. Hendrickson, D. N.; Oh, S. M.; Dong, T. Y.; Kambara, T.; Cohn, M. J.; Moore, M. F. *Comments Inorg. Chem.* **1985**, *4*, 329.
1222. Oh, S. M.; Hendrickson, D. N.; Hassett, K. L.; Davis, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 8009.
1223. Bond, A. M.; Clark, R. J. H.; Humphrey, D. G.; Panayiotopoulos, P.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1998**, 1845.
1224. Cannon, R. D.; Montri, L.; Brown, D. B.; Marshall, K. M.; Elliott, C. M. *J. Am. Chem. Soc.* **1984**, *106*, 2591.
1225. White, R. P.; Wilson, L. M.; Williamson, D. J.; Moore, G. R.; Jayasooriya, U. A.; Cannon, R. D. *Spectrochim. Acta* **1990**, *46A*, 917.
1226. Woehler, S. E.; Wittebort, R. J.; Oh, S. M.; Hendrickson, D. N.; Inniss, D.; Strouse, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 2938.
1227. Cannon, R. D.; Jayasooriya, U. A.; Wu, R.; arapKoske, S. K.; Stride, J. A.; Nielsen, O. F.; White, R. P.; Kearley, G. J.; Summerfield, D. *J. Am. Chem. Soc.* **1994**, *116*, 11869.
1228. Sowrey, F. E.; Tilford, C.; Wocadlo, S.; Anson, C. E.; Powell, A. K.; Bennington, S. M.; Montfrooij, W.; Jayasooriya, U. A.; Cannon, R. D. *J. Chem. Soc., Dalton Trans.* **2001**, 862.
1229. Kaneko, Y.; Nakano, M.; Sorai, M.; Jang, H. G.; Hendrickson, D. N. *Inorg. Chem.* **1989**, *28*, 1067.
1230. Sorai, M.; Shiomi, Y.; Hendrickson, D. N.; Oh, S. M.; Kambara, T. *Inorg. Chem.* **1987**, *26*, 223.
1231. Stadler, C.; Daub, J.; Köhler, J.; Saalfrank, R. W.; Coropceanu, V. Schünemann V.; Ober, C.; Trautwein, A. X.; Parker, S. F.; Poyraz, M.; Inomata, T.; Cannon, R. D. *J. Chem. Soc., Dalton Trans.* **2001**, 3373.
1232. Jovmir, T. C.; Turta, C. I.; Shova, S. G.; Simonov, Yu. A.; Gdaniec, M.; Bulgac, I. I.; Cadelnic, I. G.; Filoti, G. *J. Struct. Chem.* **1999**, *40*, 905.
1233. Silva, M. R.; Beja, A. M.; Paixão, J. A.; Alte da Veiga, L.; Martin-Gil, J. *Acta Crystallogr.* **2001**, *C57*, 542.
1234. Tong, M.-L.; Chen, X.-M.; Sun, Z.-M.; Hendrickson, D. N. *Transition Met. Chem.* **2001**, *26*, 195.
1235. Micklitz, W.; Bott, S. G.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 372.
1236. Harding, C. J.; Henderson, R. K.; Powell, A. K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 570.
1237. Seddon, E. J.; Huffman, J. C.; Christou, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4446.
1238. Mal, S. K.; Young, V. G.; Que, L. *Inorg. Chem.* **2000**, *39*, 1831.
1239. Cotton, F. A.; Daniels, L. M.; Jordan, G. T.; Murillo, C. A.; Pascual, I. *Inorg. Chim. Acta* **2000**, *297*, 6.
1240. Horn, A.; Neves, A.; Bortoluzzi, A. J.; Drago, V.; Ortiz, W. A. *Inorg. Chem. Commun.* **2001**, *4*, 173.
1241. Boudalis, A. K.; Lalioti, N.; Spyroulias, G. A.; Raptopoulou, C. P.; Terzis, A.; Tangoulis, V.; Perlepes, S. *J. Chem. Soc., Dalton Trans.* **2001**, 955.
1242. Yan, B.; Chen, Z.-D. *Inorg. Chem. Commun.* **2001**, *4*, 138.
1243. Ammala, P. S.; Cashion, J. D.; Kepert, C. M.; Murray, K. S.; Moubaraki, B.; Spiccia, L.; West, B. O. *J. Chem. Soc., Dalton Trans.* **2001**, 2032.
1244. Brechin, E. K.; Knapp, M. J.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chim. Acta* **2000**, *297*, 389.
1245. Wieghardt, K.; Pohl, K.; Jibril, I.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 77.
1246. Barra, A.-L.; Debrunner, P.; Gatteschi, D.; Schulz, C. E.; Sessoli, R. *Europhys. Lett.* **1996**, *35*, 133.
1247. Maccagnano, S.; Achey, R.; Negusse, E.; Lussier, A.; Mola, M. M.; Hill, S.; Dalal, N. S. *Polyhedron* **2001**, *20*, 1441.
1248. Nair, V. S.; Hagen, K. S. *Inorg. Chem.* **1994**, *33*, 185.
1249. Schake, A. R.; Tsai, H.-L.; Webb, R. J.; Folting, K.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1994**, *33*, 6020.
1250. Gautier-Lumeau, I.; Fouquard, C.; Merle, C.; Pierre, J.-L.; Luneau, D. *J. Chem. Soc., Dalton Trans.* **2001**, 2127.
1251. Bino, A.; Shweky, I.; Cohen, S.; Bauminger, E. R.; Lippard, S. J. *Inorg. Chem.* **1998**, *37*, 5168.
1252. Benelli, C.; Parsons, S.; Solan, G. A.; Winpenny, R. E. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1825.

1253. Taft, K. L.; Delfs, C. D.; Papefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 823.
1254. Gatteschi, D.; Sessoli, R.; Cornia, A. *Chem. Commun.* **2000**, 725.
1255. Abbati, G. L.; Caneschi, A.; Cornia, A.; Fabretti, A. C.; Gatteschi, D. *Inorg. Chim. Acta* **2000**, *297*, 291.
1256. Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 3337.
1257. Gorun, S. M.; Lippard, S. J. *Nature* **1986**, *319*, 666.
1258. Micklitz, W.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6856.
1259. Benelli, C.; Cano, J.; Journaux, Y.; Sessoli, R.; Solan, G. A.; Winpenny, R. E. P. *Inorg. Chem.* **2001**, *40*, 188.
1260. Dell'Amico, D. B.; Boschi, D.; Calderazzo, F.; Ianelli, S.; Labella, L.; Marchetti, F.; Pelizzi, G.; Quadrelli, E. G. F. *Inorg. Chim. Acta* **2000**, *300-302*, 882.
1261. Asirvatham, S.; Khan, M. A.; Nicholas, K. M. *Inorg. Chem.* **2000**, *39*, 2006.
1262. Taft, K. L.; Papefthymiou, G. C.; Lippard, S. J. *Science* **1993**, *259*, 1302.
1263. Heath, S. L.; Powell, A. K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 191.
1264. Goodwin, J. C.; Sessoli, R.; Gatteschi, D.; Wernsdorfer, W.; Powell, A. K.; Heath, S. L. *J. Chem. Soc., Dalton Trans.* **2000**, 1835.
1265. Schmitt, W.; Murugesu, M.; Goodwin, J. C.; Hill, J. P.; Mandel, A.; Bhalla, R.; Anson, C. E.; Heath, S. L.; Powell, A. K. *Polyhedron* **2000**, *20*, 1687.
1266. Gatteschi, D.; Caneschi, A.; Sessoli, R.; Cornia, A. *Chem. Soc. Rev.* **1996**, *25*, 101.
1267. Urs, U. K.; Shalini, K.; Shivashankar, S. A.; Row, T. N. G. *Acta Crystallogr.* **2000**, *56C*, 448.
1268. Hu, M.-L.; Jin, Z.-M.; Miao, Q.; Fang, L. P. *Z. Kristallogr. New Cryst. Struct.* **2001**, *216*, 597.
1269. Al-Alousy, A.; Burgess, J. *Polyhedron* **1992**, *11*, 531.
1270. Caneschi, A.; Cornia, A.; Lippard, S. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 467.
1271. Caneschi, A.; Cornia, A.; Fabretti, A. C.; Foner, S.; Gatteschi, D.; Grandi, R.; Schenetti, L. *Chem. Eur. J.* **1996**, *2*, 1379.
1272. Secco, F.; Venturini, M. *Polyhedron* **1999**, *18*, 3289.
1273. Nelson, W. O.; Karpishin, T. B.; Rettig, S. J.; Orvig, C. *Can. J. Chem.* **1988**, *66*, 123.
1274. Jakopčić, K.; Tamhina, B.; Zorko, F.; Herak, M. J. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1201; and references therein.
1275. Fischer, B. E.; Hodge, J. E. *J. Org. Chem.* **1964**, *29*, 776.
1276. Tamhina, B.; Herak, M. J. *Croat. Chem. Acta* **1973**, *45*, 603.
1277. Herak, M. J.; Tamhina, B. *Croat. Chem. Acta* **1973**, *45*, 237.
1278. Herak, M. J.; Janko, M.; Tamhina, B. *Mikrochim. Acta* **1973**, 783.
1279. Harris, R. L. N. *Aust. J. Chem.* **1976**, *29*, 1329.
1280. Kuhn, R.; Löw, I.; Trischmann, H. *Chem. Ber.* **1955**, *88*, 1492.
1281. Fisher, B. E.; Hodge, J. E. *J. Org. Chem.* **1964**, *29*, 776.
1282. Burgess, J.; de Castro, B.; Oliveira, C.; Rangel, M. *J. Chem. Res.* **1996**, *(S)* 234, *(M)*, 1338.
1283. Burgess, J.; Fawcett, J.; Russell, D. R.; Waltham, E. *Acta Crystallogr.* **1998**, *C54*, 2011.
1284. Zhang, Z.; Rettig, S. J.; Orvig, C. *Can. J. Chem.* **1992**, *70*, 763.
1285. Kleipool, R. J. C.; Weibaut, J. P. *Rec. Trav. Chim.* **1950**, *69*, 1041.
1286. Hider, R. C.; Huehns, E. R.; Porter, J. B. U. K Pat. Appl. GB2,242,191A, 1991..
1287. Burgess, J.; Patel, M. S.; Waltham, E. unpublished observations..
1288. Zhang, Z.; Hui, T. L. T.; Orvig, C. *Can. J. Chem.* **1989**, *67*, 1708.
1289. Xiao, G.; van der Helm, D.; Hider, R. C.; Rai, B. L. *J. Phys. Chem.* **1996**, *100*, 2345.
1290. Hou, Z.; Stack, T. D. P.; Sunderland, C. J.; Raymond, K. N. *Inorg. Chim. Acta* **1997**, *263*, 341.
1291. Liu, Z. D.; Liu, D. Y.; Lu, S. L.; Hider, R. C. *J. Pharm. Pharmacol.* **1999**, *51*, 555.
1292. Rai, B. L.; Liu, D. Y.; Lu, S. L.; Hider, R. C. *Eur. J. Med. Chem.* **1999**, *34*, 475.
1293. Liu, Z. D.; Khodr, H. H.; Liu, D. Y.; Lu, S. L.; Hider, R. C. *J. Med. Chem.* **1999**, *42*, 4814.
1294. Liu, Z. D.; Piyamongkol, S.; Liu, D. Y.; Khodr, H. H.; Lu, S. L.; Hider, R. C. *Bioorg. Med. Chem.* **2001**, *9*, 563.
1295. Piyamongkol, S.; Liu, Z. D.; Hider, R. C. *Tetrahedron* **2001**, *57*, 3479.
1296. Sheppard, L. N.; Kontoghiorghes, G. J. *Inorg. Chim. Acta* **1991**, *188*, 177.
1297. Streater, M.; Taylor, P. D.; Hider, R. C.; Porter, J. *J. Med. Chem.* **1990**, *33*, 1749.
1298. Yokel, R. A.; Fredenberg, A. M.; Durbin, P. W.; Xu, J.; Rayens, M. K.; Raymond, K. N. *J. Pharm. Sci.* **2000**, *89*, 545.
1299. Griffith, W. P.; Mostafa, S. I. *Polyhedron* **1992**, *11*, 2997.
1300. Scarrow, R. C.; Raymond, K. N. *Inorg. Chem.* **1988**, *27*, 4140.
1301. Charalambous, J.; Dodd, A.; McPartlin, M.; Matondo, S. O. C.; Pathirana, N. D.; Powell, H. R. *Polyhedron* **1988**, *7*, 2235.
1302. Clarke, E. T.; Martell, A. E.; Reibenspies, J. *Inorg. Chim. Acta* **1992**, *196*, 177.
1303. Xiao, G.; van der Helm, D.; Hider, R. C.; Dobbin, P. S. *J. Chem. Soc., Dalton Trans.* **1992**, 3265.
1304. Dobbin, P. S.; Hider, R. C.; Hall, A. D.; Taylor, P. D.; Sarpong, P.; Porter, J. B.; Xiao, G.; van der Helm, D. *J. Med. Chem.* **1993**, *36*, 2448.
1305. Lu, Z.-S.; Niu, D.-Z.; Sun, B.-W. *Chinese J. Struct. Chem.* **2001**, *20*, 466.
1306. Xiao, G.; van der Helm, D.; Hider, R. C.; Dobbin, P. S. *Inorg. Chem.* **1995**, *34*, 1268.
1307. Schlindwein, W.; Rangel, M.; Burgess, J. *J. Synchrotron. Rad.* **1999**, *6*, 579.
1308. Burgess, J.; Patel, M. S. *Inorg. Chim. Acta* **1990**, *170*, 241.
1309. Alshehri, S.; Burgess, J.; Darcey, K. A.; Patel, M. S. *Transition Met. Chem.* **1994**, *19*, 119.
1310. Lu, Z.-S.; Burgess, J.; Lane, R. *Transition Met. Chem.* **2002**, *27*, 239.
1311. Feng, M.-H.; van der Does, L.; Bantjes, A. *J. Med. Chem.* **1993**, *36*, 2822.
1312. Motekaitis, R. J.; Martell, A. E. *Inorg. Chim. Acta* **1991**, *183*, 71.
1313. Clarke, E. T.; Martell, A. E. *Inorg. Chim. Acta* **1992**, *191*, 57.
1314. Ma, R.; Reibenspies, J. J.; Martell, A. E. *Inorg. Chim. Acta* **1994**, *223*, 21.
1315. Clarke, E. T.; Martell, A. E. *Inorg. Chim. Acta* **1992**, *196*, 185.
1316. Abeysinghe, R. D.; Roberts, P. J.; Cooper, C. E.; MacLean, K. H.; Hider, R. C.; Porter, J. B. *J. Biol. Chem.* **1996**, *271*, 7965.
1317. Porter, J. B.; Gyparaki, M.; Burke, L. C.; Huehns, E. R.; Sarpong, P.; Saez, V.; Hider, R. C. *Blood* **1988**, *72*, 1497.

1318. Kontoghiorghes, G. J. *Inorg. Chim. Acta* **1987**, *135*, 145.
1319. Tsai, W.-C.; Ling, K.-H. *J. Chinese Biochem. Soc.* **1973**, *2*, 70.
1320. Nelson, W. O.; Karpishin, T. B.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1988**, *27*, 1045.
1321. Rai, B. L.; Khodr, H.; Hider, R. C. *Tetrahedron* **1999**, 1129.
1322. Santos, M. A. *Coord. Chem. Rev.* **2002**, *228*, 187.
1323. Taylor, P. D.; Morrison, I. E. G.; Hider, R. C. *Talanta* **1988**, *35*, 507.
1324. Ohkanda, J.; Katoh, A.; In *Reviews on Heteroatom Chemistry*; Oae, S.; Ohno, A.; Okuyama, T., Eds. MY: Tokyo, 1998, p 87.
1325. Kontoghiorghes, G. J.; Sheppard, L. *Inorg. Chim. Acta* **1987**, *136*, L11.
1326. Kontoghiorghes, G. J.; Sheppard, L.; Barr, J. *Inorg. Chim. Acta* **1988**, *152*, 195.
1327. Porter, J. B.; Morgan, J.; Hoyes, K. P.; Burke, L. C.; Huehns, E. R.; Hider, R. C. *Blood* **1990**, *76*, 2389.
1328. Rai, B. L.; Dekhordi, L. S.; Khodr, H.; Jin, Y.; Liu, Z.; Hider, R. C. *J. Med. Chem.* **1998**, *41*, 3347.
1329. Ellis, B. L.; Duhme, A. K.; Hider, R. C.; Hossain, M. B.; Rizvi, S.; van der Helm, D. *J. Med. Chem.* **1996**, *39*, 3659.
1330. El-Jammal, A.; Templeton, D. G. *Electrochim. Acta* **1993**, *38*, 2223.
1331. Barnabé, N.; Zastre, J. A.; Venkataram, S.; Hasinoff, B. B. *Free Radic. Biol. Med.* **2002**, *33*, 266.
1332. Kontoghiorghes, G. J. *Lancet* **1985**, 817.
1333. Kontoghiorghes, G. J. *Biochim. Biophys. Acta* **1986**, *869*, 141.
1334. Kontoghiorghes, G. J.; Evans, R. W. *FEBS Lett.* **1985**, *189*, 141.
1335. de Jong, G.; van Dijk, J. P.; van Eijk, E. G. *Clin. Chim. Acta* **1990**, *90*, 17.
1336. Evans, R. W.; Williams, J. *Biochem. J.* **1978**, *173*, 543.
1337. Aisen, P.; Listowsky, I. *Ann. Rev. Biochem.* **1980**, *49*, 357.
1338. Kontoghiorghes, G. J. *Biochim. Biophys. Acta* **1987**, *924*, 13.
1339. Kontoghiorghes, G. J. *Clin. Chim. Acta* **1987**, *163*, 137.
1340. Harris, W. R. *J. Inorg. Biochem.* **1984**, *21*, 263.
1341. Brady, M. C.; Lilley, K. S.; Treffry, A.; Harrison, P. M.; Hider, R. C.; Taylor, P. D. *J. Inorg. Biochem.* **1989**, *35*, 9.
1342. Kostar, J. F.; Voogd, A.; Ruigrok, T. J. C.; Sluiter, W. *Ann. N. Y. Acad. Sci.* **1996**, *793*, 74; and references therein.
1343. Ivsic, A.; Gojmerac, A.; Tamhina, B. *Talanta* **1991**, *38*, 1403.
1344. Vojković, V.; Juranović, I.; Tamhina, B. *Croat. Chem. Acta* **2001**, *74*, 467.
1345. Tamhina, B.; Brajenovic, N. *Process Metall.* **1992**, *7A*, 1027.
1346. Vojković, V.; Ivsic, A. G.; Tamhina, B. *Solvent Extr. Ion Exch.* **1996**, *14*, 479.
1347. Vojković, V.; Gojmerac, A.; Tamhina, B. *Croat. Chem. Acta* **1997**, *70*, 667.
1348. Hou, Z.; Whisenhunt, D. W.; Xu, J.; Raymond, K. N. *J. Am. Chem. Soc.* **1994**, *116*, 840.
1349. Imbert, D.; Thomas, F.; Baret, P.; Serratrice, G.; Gaude, D.; Pierre, J.-L.; Laulhère, J.-P. *New J. Chem.* **2000**, *24*, 281.
1350. Santos, M. A.; Gaspar, M.; Simões Gonçalves, M. L. S.; Amorin, M. T. *Inorg. Chim. Acta* **1998**, *278*, 51.
1351. Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 302.
1352. Trzaska, S. M.; Kim, M.; Bartsch, R. A.; Crumbliss, A. L. *Inorg. Chem.* **2001**, *40*, 5823.
1353. Karpishin, T. B.; Stack, T. D. P.; Raymond, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 6115.
1354. El Hage Chahine, J.-M.; Bauer, A.-M.; Baraldo, K.; Lion, C.; Ramiandrasoa, F.; Kunesch, G. *Eur. J. Inorg. Chem.* **2001**, 2287.
1355. Terpin, A. J.; Ziegler, M.; Johnson, D. W.; Raymond, K. N. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 157.
1356. Taylor, S. W.; Luther, G. W.; Waite, J. H. *Inorg. Chem.* **1994**, *33*, 5819.
1357. Loomis, L. D.; Raymond, K. N. *Inorg. Chem.* **1991**, *30*, 906.
1358. Scarrow, R. C.; Ecker, D. J.; Ng, C.; Liu, S.; Raymond, K. N. *Inorg. Chem.* **1991**, *30*, 900.
1359. Rodgers, S. J.; Lee, C.-W.; Ng, C. Y.; Raymond, K. N. *Inorg. Chem.* **1987**, *26*, 1622.
1360. McMurry, T. J.; Rodgers, S. J.; Raymond, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 3451.
1361. McMurry, T. J.; Hosseini, M. W.; Garrett, T. M.; Hahn, F. E.; Reyes, Z. E.; Raymond, K. N. *J. Am. Chem. Soc.* **1987**, *109*, 7196.
1362. Garrett, T. M.; McMurry, T. J.; Hosseini, M. W.; Reyes, Z. E.; Hahn, F. E.; Raymond, K. N. *J. Am. Chem. Soc.* **1991**, *113*, 2965.
1363. Mitchell, M. S.; Walker, D.-L.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1987**, *26*, 396.
1364. Tor, Y.; Libman, J.; Shanzer, A.; Lifson, S. *J. Am. Chem. Soc.* **1987**, *109*, 6517.
1365. Hisaeda, Y.; Ihara, T.; Ohno, T.; Murakami, Y. *Chem. Lett.* **1991**, 2139.
1366. Tse, B.; Kishi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 7892.
1367. Kiggen, W.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 714.
1368. Stutte, P.; Kiggen, W.; Vögtle, F. *Tetrahedron* **1987**, *43*, 2065.
1369. Kiggen, W.; Vögtle, F.; Franken, S.; Puff, H. *Tetrahedron* **1986**, *42*, 1859.
1370. Suh, J.; Lee, S. H.; Paik, H.-J. *Inorg. Chem.* **1994**, *33*, 3.
1371. Kretchmar, S. A.; Raymond, K. N. *J. Am. Chem. Soc.* **1986**, *108*, 6212.
1372. Richardson, D. R.; Baker, E. *J. Biol. Chem.* **1992**, *267*, 13972.
1373. Pierre, J. L.; Baret, P.; Gellon, G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 85.
1374. Baret, P.; Beaujolais, V.; Gaude, D.; Coulombeau, C.; Pierre, J.-L. *Chem. Eur. J.* **1997**, *3*, 969.
1375. Rodgers, S. J.; Ng, C. Y.; Raymond, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 4094.
1376. Albrecht-Gary, A. M.; Libman, J.; Shanzer, A. *Pure Appl. Chem.* **1996**, *68*, 1243.
1377. Failes, T. W.; Hambly, T. W. *Aust. J. Chem.* **2000**, *53*, 879.
1378. Marmion, C. J.; Murphy, T.; Starikova, Z.; Nolan, K. B. *Acta Crystallogr.* **2000**, *56C*, 491.
1379. Das, M. K.; Chaudhury, K.; Roy, N.; Sarkar, P. *Transition Met. Chem.* **1990**, *15*, 468.
1380. Burgess, J.; Patel, M. S. *J. Coord. Chem.* **1993**, *29*, 65.
1381. Fish, L. L.; Crumbliss, A. L. *Inorg. Chem.* **1985**, *24*, 2198.
1382. Wirgau, J. I.; Spasojević, I.; Boukhalfa, H.; Batinić-Haberle, I.; Crumbliss, A. L. *Inorg. Chem.* **2002**, *41*, 1464.
1383. Ng, C. Y.; Rodgers, S. J.; Raymond, K. N. *Inorg. Chem.* **1989**, *28*, 2062.
1384. Matsumoto, K.; Ozawa, T.; Jitsukawa, K.; Einaga, H.; Masuda, H. *Inorg. Chem.* **2001**, *40*, 190.
1385. Matsumoto, K.; Suzuki, N.; Ozawa, T.; Jitsukawa, K.; Masuda, H. *Eur. J. Inorg. Chem.* **2001**, 2481.

1386. Yoshida, I.; Murase, I.; Motekaitis, R. J.; Martell, A. E. *Can. J. Chem.* **1983**, *61*, 2740.
1387. Hara, Y.; Akiyama, M. *J. Am. Chem. Soc.* **2001**, *123*, 7247.
1388. Boukhalfa, H.; Crumbliss, A. L. *Inorg. Chem.* **2001**, *40*, 4183.
1389. Dhungana, S.; Heggemann, S.; Gebhardt, P.; Möllmann, U.; Crumbliss, A. L. *Inorg. Chem.* **2003**, *42*, 42.
1390. Jalal, M. A. F.; Hossain, M. B.; van der Helm, D.; Barnes, C. L. *Biol. Met.* **1988**, *1*, 77.
1391. Libman, J.; Tor, Y.; Shanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 5880.
1392. Tor, Y.; Libman, J.; Shanzer, A. *J. Am. Chem. Soc.* **1987**, *109*, 6518.
1393. Lesuisse, E.; Crichton, R. R.; Labbe, P. *Biochim. Biophys. Acta* **1990**, *1038*, 253 .
1394. Sun, Y.; Martell, A. E. *J. Am. Chem. Soc.* **1989**, *111*, 8023.
1395. Anderegg, G.; L'Eplattenier, F.; Schwarzenbach, G. *Helv. Chim. Acta* **1963**, *46*, 1409.
1396. Pidacks, C.; Whitehill, A. R.; Preuss, L. M.; Hesseltine, C. W.; Hutchings, B. L.; Bohonos, N.; Williams, J. H. *J. Am. Chem. Soc.* **1953**, *75*, 6064.
1397. Hossain, M. B.; Jalal, M. A. F.; Benson, B. A.; Barnes, C. L.; van der Helm, D. *J. Am. Chem. Soc.* **1987**, *109*, 4948.
1398. Jalal, M. A. F.; Love, S. K.; van der Helm, D. *Biol. Met.* **1988**, *1*, 4.
1399. Jalal, M. A. F.; van der Helm, D. *Biol. Met.* **1989**, *2*, 11.
1400. Keller-Schierlein, W.; Diekmann, H. *Helv. Chim. Acta* **1970**, *53*, 2035.
1401. Caudle, M. T.; Stevens, R. O.; Crumbliss, A. L. *Inorg. Chem.* **1994**, *33*, 843.
1402. Nishio, T.; Tanaka, N.; Hiratake, J.; Katsuba, Y.; Ishida, Y.; Oda, J. *J. Am. Chem. Soc.* **1988**, *110*, 8733.
1403. Hou, Z.; Sunderland, C. J.; Nishio, T.; Raymond, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 5148.
1404. Boukhalfa, H.; Brickman, T. J.; Armstrong, S. K.; Crumbliss, A. L. *Inorg. Chem.* **2000**, *39*, 5591.
1405. Jalal, M. A. F.; Love, S. K.; van der Helm, D. *J. Inorg. Biochem.* **1986**, *28*, 417.
1406. Jalal, M. A. F.; Love, S. K.; van der Helm, D. *J. Inorg. Biochem.* **1987**, *29*, 259.
1407. Nguyen-van-Duong, M. K.; Guillot, V.; Nicolas, L.; Gaudemer, A.; Lowry, L.; Spasojević, I.; Crumbliss, A. L. *Inorg. Chem.* **2001**, *40*, 5948.
1408. Boukhalfa, H.; Crumbliss, A. L. *Inorg. Chem.* **2000**, *39*, 4318.
1409. Tsubouchi, A.; Shen, L.; Hara, Y.; Akiyama, M. *New J. Chem.* **2001**, *25*, 275.
1410. Sun, Y.; Motekaitis, R. J.; Martell, A. E. *Inorg. Chim. Acta* **1998**, *281*, 60.
1411. Serratrice, G.; Boukhalfa, H.; Béguin, C.; Baret, P.; Caris, C.; Pierre, J.-L. *Inorg. Chem.* **1997**, *36*, 3898.
1412. Baret, P.; Béguin, C.; Gellon, G.; Pierre, J.-L.; Serratrice, G.; Thomas, F.; Laulhère, J.-P.; Saint-Aman, E. *Eur. J. Inorg. Chem.* **2000**, 1219.
1413. Santos, M. A.; Rodrigues, E.; Gaspar, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4398.
1414. Meyer, M.; Telford, J. R.; Cohen, S. M.; White, D. J.; Xu, J.; Raymond, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 10093.
1415. Baret, P.; Béguin, C.; Gellon, G.; Dhungana, S.; Heggemann, S.; Gebhardt, P.; Möllmann, U.; Crumbliss, A. L. *Inorg. Chem.* **2003**, *42*, 42.
1416. Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 4844; and references therein.
1417. Willems, J. B.; Köckerling, M. *Chem. Commun.* **2001**, 1380.
1418. Hider, R. C.; Liu, Z. D.; Khodr, H. H. *Methods Enzymol.* **2001**, *335*, 190.
1419. Koch, W. O.; Schünemann, V.; Gerdan, M.; Trautwein, A. X.; Krüger, H.-J. *Chem. Eur. J.* **1998**, *4*, 1255.
1420. Chun, H.; Weyhermuller, T.; Bill, E.; Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 2489.
1421. Turel, I.; Bukovec, N.; Farkas, E. *Polyhedron* **1996**, *15*, 269.
1422. Djurdjević, P.; Stankow, M. J.; Odović, J. *Polyhedron* **2000**, *19*, 1085.
1423. Werth, M. T.; Kurtz, D. M.; Howes, B. D.; Huynh, B. H. *Inorg. Chem.* **1989**, *28*, 1357.
1424. Critchley, J. K.; Hunter, C. J. *Trans.-Inst. Min. Metall.* **1986**, *95*, C173.
1425. Critchley, J. K.; Hunter, C. J. *Trans.-Inst. Min. Metall.* **1987**, *96*, C53.
1426. Reddy, G. S. *Trans.-Inst. Min. Metall.* **1987**, *96*, C53 (*Chem. Abs.* **1987**, *106*, 36393b; *Chem. Abs.* **1987**, *107*, 81470f).
1427. Hao, Q.; Yang, X.; Jian, F.; Lu, L.; Wang, X.; Razak, I. A.; Chantapromma, S.; Fun, H.-K. *Acta Crystallogr.* **2001**, *C57*, 42.
1428. Sangari, H. S.; Sodhi, G. S.; Kaur, J. *Indian J. Chem.* **1993**, *32A*, 730.
1429. Lanjewar, R. B.; Garg, A. N. *Polyhedron* **1993**, *12*, 2619.
1430. Singhal, S.; Sharma, C. L.; Garg, A. N.; Chandra, K. *Transition Met. Chem.* **2001**, *26*, 81.
1431. Singhal, S.; Sharma, C. L.; Garg, A. N.; Chandra, K. *Polyhedron* **2002**, *21*, 2489.
1432. Pandeya, K. B.; Singh, R. *Inorg. Chim. Acta* **1988**, *147*, 5.
1433. Pandeya, K. B.; Singh, R.; Prakash, C.; Baijal, J. S. *Inorg. Chem.* **1987**, *26*, 3216.
1434. Breviglieri, S. T.; Cavalheiro, E. T. G.; Chierice, G. O. *Polyhedron* **1996**, *15*, 839.
1435. Hughes, J. G.; Lawson, P. J. *J. Chem. Educ.* **1987**, *64*, 973.
1436. Manhas, B. N. S.; Kaur, K.; Kalia, S. B. *Synth. React. Inorg. Met.-Org. Chem.* **2000**, *30*, 609.
1437. Butler, A. R.; Elkins-Daukes, S.; Parkin, D.; Williams, D. L. H. *Chem. Commun.* **2001**, 1732.
1438. Sun, H.; Tian, M. *Huaxue Yu Nianhe* **1998**, 30 (*Chem. Abs.* **1998**, *128*, 200094g).
1439. Kimblin, C.; Churchill, D. G.; Bridgewater, B. M.; Girard, J. N.; Quarless, D. A.; Parkin, G. *Polyhedron* **2001**, *20*, 1891.
1440. Wieghardt, K.; Küppers, H.-J.; Weiss, J. *Inorg. Chem.* **1985**, *24*, 3067.
1441. Küppers, H.-J.; Wieghardt, K.; Nuber, B.; Weiss, J.; Bill, E.; Trautwein, A. X. *Inorg. Chem.* **1987**, *26*, 3762.
1442. Ballester, J.; Parker, O. J.; Breneman, G. L. *Acta Crystallogr.* **1994**, *C50*, 712.
1443. Lewis, G. R.; Dance, I. *J. Chem. Soc., Dalton Trans.* **2000**, 3176.
1444. Möller, E.; Sieler, J.; Kirmse, R. *Z. Naturforsch.* **1997**, *52B*, 919.
1445. Best, S. P.; Clark, R. J. H.; McQueen, R. C. S.; Walton, J. R. *Inorg. Chem.* **1988**, *27*, 884.
1446. Ogino, H.; Inomata, S.; Tobita, H. *Chem. Rev.* **1998**, *98*, 2093.
1447. Le Cloiret, A.; Best, S. P.; Borg, S.; Davies, S. C.; Evans, D. J.; Hughes, D. L.; Pickett, C. J. *Chem. Commun.* **1999**, 2285.
1448. Siebenlist, R.; Frühauf, H.-W.; Kooijman, H.; Veldman, N.; Spek, A. L.; Goubitz, K.; Fraanje, J. *Inorg. Chim. Acta* **2002**, *327*, 66.
1449. Bourassa, J.; DeGraff, W.; Kudo, S.; Wink, D. A.; Mitchell, J. B.; Ford, P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2853.
1450. Bourassa, J.; Lee, B.; Bernard, S.; Schoonover, J.; Ford, P. C. *Inorg. Chem.* **1999**, *38*, 2947.

1451. Bourassa, J. L.; Ford, P. C. *Coord. Chem. Rev.* **2000**, *200-202*, 887.
1452. Butler, A. R.; Glidewell, C.; Li, M.-H. *Adv. Inorg. Chem.* **1989**, *32*, 335.
1453. Lewin, M.; Fisher, K.; Dance, I. *Chem. Commun.* **2000**, 947.
1454. Rutchik, S.; Kim, S.; Walters, M. A. *Inorg. Chem.* **1988**, *27*, 1513.
1455. Stack, T. D. P.; Carney, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 1670.
1456. Challen, P. R.; Koo, S.-M.; Dunham, W. R.; Coucouvanis, D. *J. Am. Chem. Soc.* **1990**, *112*, 2455.
1457. Snyder, B. S.; Reynolds, M. S.; Noda, I.; Holm, R. H. *Inorg. Chem.* **1988**, *27*, 597 .
1458. Henderson, R. A.; Oglieve, K. E. *J. Chem. Soc., Dalton Trans.* **1999**, 3927.
1459. Dunford, A. J.; Henderson, R. A. *Chem. Commun.* **2002**, 360.
1460. Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1999**, 119.
1461. Gronberg, K. L. C.; Henderson, R. A. *J. Chem. Soc., Dalton Trans.* **1996**, 3667.
1462. Almeida, V. R.; Gormal, C. A.; Gronberg, K. L. C.; Henderson, R. A.; Oglieve, K. E.; Smith, B. E. *Inorg. Chim. Acta* **1999**, *291*, 212.
1463. Davies, S. C.; Evans, D. J.; Henderson, R. A.; Hughes, D. L.; Longhurst, S. *J. Chem. Soc., Dalton Trans.* **2001**, 3470.
1464. Daley, C. J. A.; Holm, R. H. *Inorg. Chem.* **2001**, *40*, 2785.
1465. Cui, Z.; Henderson, R. A. *Inorg. Chem.* **2002**, *41*, 4158.
1466. Hernandez-Molina, R.; Sokolov, M. N.; Sykes, A. G. *Acc. Chem. Res.* **2001**, *34*, 223.
1467. Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342.
1468. Dimmock, P. W.; Dickson, D. P. E.; Sykes, A. G. *Inorg. Chem.* **1990**, *29*, 5920.
1469. Shibahara, T.; Asano, T.; Sakane, G. *Polyhedron* **1991**, *10*, 2351.
1470. Lenormand, A. P.; Iveson, J.; Jordanov G. *Inorg. Chim. Acta* **1996**, *251*, 119.
1471. Ueyama, N.; Yamada, Y.; Okamura, T.-A.; Kimura, S.; Nakamura, A. *Inorg. Chem.* **1996**, *35*, 6473.
1472. Okuno, Y.; Uoto, K.; Yonemitsu, O.; Tomohiro, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1018.
1473. Burdett, J. K.; Miller, G. J. *J. Am. Chem. Soc.* **1987**, *109*, 4081.
1474. Ciurli, S.; Holm, R. H. *Inorg. Chem.* **1991**, *30*, 743.
1475. Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2354.
1476. Kovacs, J.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 702, 711 .
1477. Hauser, C.; Bill, E.; Holm, R. H. *Inorg. Chem.* **2002**, *41*, 1615.
1478. Ciurli, S.; Yu, S.-B.; Holm, R. H.; Srivastava, K. K. P.; Münck, E. J. *J. Am. Chem. Soc.* **1990**, *112*, 8169.
1479. Zhou, J.; Scott, M. J.; Hu, Z.; Peng, G.; Münck, E.; Holm, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 10843.
1480. Snyder, B. S.; Reynolds, M. S.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *Polyhedron* **1991**, *10*, 203.
1481. Kanatzidis, M. G.; Salifoglou, A.; Coucouvanis, D. *Inorg. Chem.* **1986**, *25*, 2460.
1482. Goh, C.; Segal, B. M.; Huang, J.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 11844.
1483. Nordlander, E.; Lee, S. C.; Cen, W.; Wu, Z. Y.; Natoli, C. R.; Cicco, D.; Filipponi, A.; Hedman, B.; Hodgson, K. O.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 5549.
1484. Cen, W.; MacDonnell, F. M.; Scott, M. J.; Holm, R. H. *Inorg. Chem.* **1994**, *33*, 5809.
1485. Chen, C.; Wen, T.; Li, W.; Zhu, H.; Chen, Y.; Liu, Q.; Lu, J. *Inorg. Chem.* **1999**, *38*, 2375.
1486. Demadis, K. D.; Campana, C. F.; Coucouvanis, D. *J. Am. Chem. Soc.* **1995**, *117*, 7832.
1487. Han, J.; Koutmos, M.; Al Ahmad, S.; Coucouvanis, D. *Inorg. Chem.* **2001**, *40*, 5985.
1488. You, J.-F.; Papaefthymiou, G. C.; Holm, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 2697.
1489. Xu, F. H.; Sun, W.; Yang, S. Y.; Yin, Y. Q. *Polyhedron* **1996**, *15*, 4169.
1490. Barbaro, P.; Bencini, A.; Bertini, I.; Briganti, F.; Midollini, S. *J. Am. Chem. Soc.* **1990**, *112*, 7238.
1491. Serezhkin, V. N.; Serezhkina, L. B.; Sidorina, N. E. *Russ. J. Coord. Chem.* **2000**, *26*, 500.
1492. Weerasooriya, R.; Aluthpatabendi, D. *Toxicol. Environ. Chem.* **1999**, *69*, 1.
1493. Lee, S. C.; Holm, R. H. *Inorg. Chem.* **1993**, *32*, 4745.
1494. Sitze, M. S.; Schreiter, E. R.; Patterson, E. V.; Freeman, R. G. *Inorg. Chem.* **2001**, *40*, 2298.
1495. Troyanov, S. I.; Feist, M.; Kemnitz, E. *Z. Anorg. Allg. Chem.* **1999**, *625*, 806.
1496. Figgis, B. N.; Solbolov, A. N.; Kucharsk, E. S.; Broughton, V. *Acta. Crystallogr.* **2000**, *56C*, e228.
1497. Morón, M. C.; Palacio, F.; Pons, J.; Casabó, J.; Solans, X.; Merabet, K. E.; Huang, D.; Shi, X.; Teo, B. K.; Carlin, R. L. *Inorg. Chem.* **1994**, *33*, 746.
1498. Beattie, J. K.; Moore, C. J. *Inorg. Chem.* **1982**, *21*, 1292.
1499. Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F.; Quadrelli, E. G. F. *Gazz. Chim. Ital.* **1997**, *127*, 103.
1500. Kobayashi, H.; Sato, A.; Tanaka, H.; Kobayashi, A.; Cassoux, P. *Coord. Chem. Rev.* **1999**, *190-192*, 921.
1501. Schröder, D.; Loos, J.; Schwartz, H.; Thissen, R.; Dutuit, O. *Inorg. Chem.* **2001**, *40*, 3161.
1502. Murata, K.; Irish, D. E. *Spectrochim. Acta* **1988**, *44A*, 739.
1503. James, B. D.; Bakalova, M.; Liesegang, J.; Reiff, W. M.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **2001**, *40*, 4617.
1504. Healy, P. C.; Patrick, J. M.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 2031.
1505. Reiff, W. M.; Whitten, E. H.; Mottle, K.; Brennan, T. F.; Garafolo, A. R. *Inorg. Chim. Acta* **1983**, *77*, L27.
1506. Köhn, R. D.; Kociok-Köhn, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1877.
1507. Renz, M.; Hemmert, C.; Gornitzka, H.; Meunier, B. *New J. Chem.* **1999**, *23*, 773.
1508. Viswanathan, R.; Palaniavar, M.; Balasubramanian, T.; Muthiah, P. T. *J. Chem. Soc., Dalton Trans.* **1996**, 2519.
1509. Rodriguez, M.-C.; Lambert, F.; Morgenstern-Badarau, I.; Cesario, M.; Guilhem, J.; Keita, B.; Nadjo, L. *Inorg. Chem.* **1997**, *36*, 3525.
1510. Millington, K. R.; Wade, S. R.; Willey, G. R.; Drew, M. G. B. *Inorg. Chim. Acta* **1984**, *89*, 185.
1511. Daran, J.-C.; Jeannin, Y.; Martin, L. M. *Inorg. Chem.* **1980**, *19*, 2935.
1512. Bjerrum, J.; Lukeš, I. *Acta Chem Scand.* **1986**, *40A*, 31.
1513. Brubaker, G. R.; Peterson, R. A. *Inorg. Chim. Acta* **1989**, *155*, 139.
1514. Haberecht, J.; Borrmann, H.; Kneip, R. *Z. Kristallogr. New Cryst. Struct.* **2001**, *216*, 510.
1515. Armbruster, M.; Rotter, H. W.; Thiele, G. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1681.
1516. Armbruster, M.; Ludwig, T.; Rotter, H. W.; Thiele, G.; Oppermann, H. *Z. Anorg. Allg. Chem.* **2000**, *626*, 187.
1517. Šima, J.; Brezová, V. *Coord. Chem. Rev.* **2002**, *229*, 27.
1518. Mucklejohn, S. A.; O'Brien, N. W.; Brumleve, T. R. *J. Phys. Chem.* **1985**, *89*, 2409.

1519. Yoon, K. B.; Kochi, J. K. *Z. Anorg. Allg. Chem.* **1988**, *561*, 174.
1520. Pohl, S.; Sark, W. *Z. Naturforsch.* **1984**, *39B*, 1236.
1521. Moyer, R. O.; Lindsay, R.; Suib, S.; Zerger, R. P.; Tanaka, J.; Gibbins, S. G. *Inorg. Chem.* **1985**, *24*, 3890.
1522. Linn, D. E.; Gibbins, S. G. *Inorg. Chem.* **1997**, *36*, 3461.
1523. Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546.
1524. Bautista, M. T.; Earl, K. A.; Morris, R. H. *Inorg. Chem.* **1988**, *27*, 1124.

Comprehensive Coordination Chemistry II
ISBN (set): 0-08-0437486

Volume 5, (ISBN 0-08-0443273); pp 403–553

5.5
Ruthenium and Osmium: Low Oxidation States

C. E. HOUSECROFT
University of Basel, Switzerland

5.5.1 INTRODUCTION

Like most fields of coordination chemistry, that of low-oxidation-state ruthenium and osmium has grown enormously since the review in *Comprehensive Coordination Chemistry* (*CCC*), published in 1987,[1,2] and there has been a huge growth in the area of $[Ru(bpy)_3]^{2+}$ and related polypyridine chemistry. This review covers the coordination chemistry of M^{II} and M^{II} (M = Ru and Os). The page limitation of this review is such that a fully comprehensive coverage of the literature from the mid-1980s to mid-2002 is impossible, and only a terse discussion of each topic has been possible. While this is regrettable, it is unavoidable. Organometallic complexes (defined as those with M—C bonds) are excluded except for orthometallated complexes, e.g., cyclometallated polypyridine ligands. Emphasis is placed on articles published in widely accessible journals. Where practical, the chapter is subdivided into sections by (i) oxidation state of the group 8 metal, and (ii) by ligand donor atom. In the case of hydrides and dihydrogen complexes, ambiguity in oxidation state arising from H^- or H_2 ligand coordination means that all such complexes are treated in one section with no specification of metal oxidation state.

A number of reviews have been published that survey the general coordination chemistry of ruthenium and osmium.[3–15] The chemistry and thermodynamics of ruthenium and its inorganic compounds and aqueous species have also been reviewed.[16]

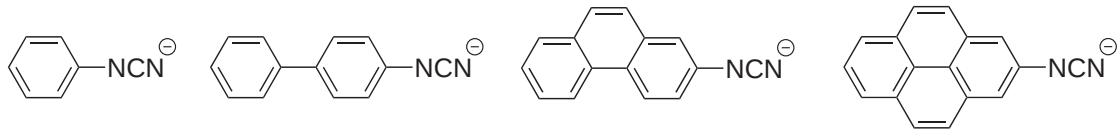
5.5.2 RUTHENIUM(III) AND OSMIUM(III)

5.5.2.1 Nitrogen-donor Ligands

5.5.2.1.1 Monodentate ligands

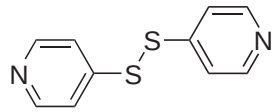
The water exchange in $[Ru(NH_3)_5(H_2O)]^{3+}$ has been studied using quantum chemical methods, with both free and hydrated ions being investigated.[17] EPR spectroscopic data have been reported for $[M(NH_3)_5(H_2O)][CF_3SO_3]_3$ (M = Ru, Os) over a range of temperatures for solid powders and frozen solutions; variable-temperature ^1H NMR spectra of $[M(NH_3)_5(H_2O)][CF_3SO_3]_3$ in propane-1,2-diol carbonate, and resonances for the axial and equatorial NH_3 ligands and for the H_2O ligand have been assigned.[18] Syntheses of *cis*- and *trans*-$[RuCl_2(NH_3)_4]Cl$ have been reported; the complexes are useful precursors to a variety of disubstituted Ru^{III} and Ru^{II} complexes.[19]

Reactions of $[Ru^{III}Cl(NH_3)_5]Cl_2$ with appropriate *o*-substituted pyridines are efficient methods of preparing $[Ru^{II}(NH_3)_4L]^{2+}$ where L = 2-acetylpyridine or 2-benzoylpyridine and for which an *N,O* chelating mode is confirmed from NMR spectroscopic data.[20] The complexes $[Ru(NH_3)_5L][PF_6]_n$ ($n = 3$ or 2; $L = CH_2{=}CHCN$, HO_2CCH_2CN, EtCN) have been prepared and characterized; hydrolysis of the Ru^{III}-coordinated RCN ligand gives rise to a coordinated amide.[21,22] Ammine complexes $[Ru(NH_3)_5L]^{2+}$ containing cyanamide ligands (e.g., $L^- = (1)$–(4)) have been prepared and characterized by electronic absorption spectroscopy and cyclic voltammetry; the Ru^{3+}/Ru^{2+} couple shifts to more positive potential with increasing conjugation of the R group in $[RNCN]^-$. Adduct formation between 18-crown-6 and the ammine complexes $[Ru(NH_3)_5L]^{3+}$ (L = 4-aminopyridine or dimethylaminopyridine) leads to a blue shift of the LMCT band, and a negative shift of the Ru^{3+}/Ru^{2+} potential, leading to the conclusion that it is possible to tune the redox potential by second-sphere coordination to 18-crown-6.[23–25] Related Ru^{II} and mixed valence complexes have also been studied (see Section 5.5.3.1.1).



(1) (2) (3) (4)

The EPR powder spectra of the low-spin complexes $[Os(NH_3)_5L][CF_3SO_3]_3$ ($L = H_2O$ or (**5**)) have been analyzed; the negative sign obtained for the axial splitting when L = (**5**) has been rationalized in terms of $Os^{III} \rightarrow L$ backbonding. Crystal field parameters have also been derived.[26] The spectral and electrochemical properties of $[Ru(NH_3)_5L]^{n+}$ (Ru^{III} or Ru^{II}; $L^- = RCO_2^-$; R = 4-py-*N*-Me^+ or $L = RCONH^-$; R = Ph, 4-py-*N*-Me^+, 4-py-*N*-H^+) have been studied in detail as a function of pH; the carboxamido Ru^{III} complexes are weak bases and are deprotonated only in strongly acidic solution.[27]



(5)

The complex *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{3+}$ has been synthesized by oxidation of the corresponding Ru^{II} species; electrochemical oxidation is quantitative and reversible. In aqueous solution, the Ru^{III} species decays at a rate that is inversely proportional to $[H^+]$; aged solutions contain mainly *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$.[28,29]

Ruthenium(III) complexes involving heterocyclic ligands include *trans*-$[RuCl_4(im)_2]^-$ (im = imidazole). In D_2O, Cl^- displacement occurs to give, first, $[RuCl_3(D_2O)(im)_2]$ and, after longer periods, $[RuCl_2(D_2O)_2(im)_2]^+$ and then $[RuCl(D_2O)_3(im)_2]^{2+}$. ^1H NMR spectroscopy has been used to monitor these changes, despite the paramagnetic nature of the complex. Similar reactions occur with 4-methylimidazole complexes, and the steps can be reversed (although not quantitatively) by addition of KCl. The effects of changing the solvent to CD_3OD and dmso-d^6 have been studied and the structure of $[RuCl_2(dmso\text{-}d^6)_2(im)_2]$ (formed by reductive decay of the corresponding Ru^{III} species) has been determined.[30] The kinetics of aquation of *trans*-$[RuCl_4(im)_2]^-$ to $[RuCl_3(H_2O)(im)_2]$ have been reported.[31] In related work, the aquation of $[Him]_2[RuCl_5(im)]$[32] and *trans*-$[RuCl_4(5\text{-}NO_2im)_2]$ (5-NO_2im = 5-nitroimidazole) were reported.[33] The potential tumor-inhibiting properties of *trans*-$[Him][RuCl_4(im)_2]$ have been investigated[31] and it has been found that $[Him][RuCl_4(im)_2]$ and $[Hind][RuCl_4(ind)_2]$ (ind = indazole) bind at a higher rate to poly(dG)·poly(dC) than to poly(dA)·poly(dT); aquation of the complexes is a prerequisite to binding.[34] *trans*-$[RuCl_4(ind)_2]^-$ exhibits tumor inhibition;[35,36] various salts have been prepared with the aim of optimizing water solubility for clinical trials. The structure of $[PPh_4][RuCl_4(ind)_2]$ has been determined.[35] In, for example, THF, $[Hind][trans\text{-}RuCl_4(ind)_2]$ is converted to *mer*-$[RuCl_3(ind)_3]$, the structure of which has been confirmed.[36] NMR and EPR spectroscopic studies of *trans*-$[Ru(NH_3)_4(im)L]^{n+}$ (Ru^{III} with L = isonicotinamide, pyridine,

imidazole, NH_3, Cl^-, SO_4^{2-}) reveal that π-bonding by the *trans* ligand has a marked effect on the d(π)–im(π) orbital mixing. From the EPR data, a description of the frontier d(π) orbitals involved in electron transfer is given. The reduction potentials and energies of the im $\rightarrow Ru^{III}$ CT transitions show a linear correlation with the π-donor/acceptor ability of L. The crystal structure of *trans*-$[Ru(NH_3)_4(im)_2]Cl_3$ has been determined.[37]

By using $[RuCl_2(PPh_3)_2(bpy)]Cl$ as a precursor, the complexes $[RuCl_3(PPh_3)L_2]\cdot 4H_2O$ (L = im, Meim) have been prepared; crystallographic data for $[RuCl_3(PPh_3)(Meim)_2]\cdot 4H_2O$ confirm *mer*-Cl and *cis*-imidazole ligands.[38]

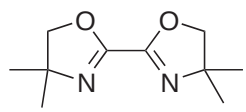
Section 5.5.3.1.1 should be consulted for NO complexes of Ru^{II} or Ru^{III}.

5.5.2.1.2 Didentate ligands

The reaction of $[NH_4]_2[OsBr_6]$ with 1,2-ethanediamine (en) gives the Os^{IV} complex *cis*-$[Os(enH)_2(en)]Br_2$; the Os^{III} complex $[Os(en)_3]Br_3\cdot 2H_2O$ is isolated from the filtrate. The redox chemistry of these complexes has been studied.[39] Oxidative addition of *N,N′*-diphenylamidines to $[MCl_2(PPh_3)_3]$ (M = Ru, Os) first gives $[M^{III}Cl_2(PhNCRNPh)(PPh_3)_2]$ (M = Ru, R = H, Ph; M = Os, R = H, Me, Ph). Longer reaction times yield $[Ru^{III}Cl(PhNCRNPh)_2(PPh_3)]$ or Os^{IV} species.[40]

A few reports focus on tris(2,2′-bipyridine)ruthenium(III) chemistry; the bulk of the bpy discussions comes in Section 5.5.3.1.2. $[Ru(bpy)_3]^{3+}$ is a powerful oxidant and oxidizes cobalt(II) macrocyclic complexes; laser flash photolysis has been used to follow the kinetics of the electron transfer reactions between $[Ru(bpy)_3]^{3+}$ and $[CoL]^{2+}$ (L = [14]aneN$_4$, *C-meso*-Me$_6$[14]aneN$_4$, [14]tetraeneN$_4$, [15]aneN$_4$ and 1,4,8,11-tetramethylcyclam) and the results considered in terms of Marcus theory.[41] The complexes $[Ru(bpy)_n(4,4'\text{-}X_2bpy)_{3-n}]^{3+}$ (X = Me, OMe, NH_2, NMe_2) show quite intense LMCT absorptions in the red/near IR region. The intensity of the LMCT absorption increases as the donor strength of X increases, and the results are analyzed in terms of donor strength and Hammett substituent parameters.[42] Polymeric, water-soluble oxides that act as chloride oxidation catalysts are produced by hydrolyzing $[Ru(4,4'\text{-}Me_2bpy)Cl_3(H_2O)]$ and $[Ru(tpy)Cl_3]$ (tpy = 2,2′:6′,2″-terpyridine). The polymer formed from $[Ru(4,4'\text{-}Me_2bpy)Cl_3(H_2O)]$ exhibits high turnovers for electro- and chemical catalysis and is proposed as a potential component of photoconversion systems.[43] Reactions of $RuCl_3\cdot xH_2O$ with bpy or phen (phen = 1, 10-phenanthroline) in methanoic acid yield $[RuCl_3(bpy)(CO)]$ or $[RuCl_3(phen)(CO)]$, both of which contain CO *trans* to an *N*-donor atom.[44]

The complex *mer*-$[RuCl_3$(**6**)(dmf)] has been prepared and structurally characterized; it is a useful precursor to a range of mixed ligand complexes of Ru^{III}.[45]



(**6**)

5.5.2.1.3 Macrocyclic ligands

Reaction of the Ru^{III} macrocyclic complex $[RuLCl_2]^+$ (L = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) with NO_2^- results in a disproportionation of the initial $[Ru^{III}LCl(NO_2)]^+$, the final products being *trans*-$[Ru^{IV}L(O)Cl]^+$ and $[Ru^{II}L(OH)(NO)]^{2+}$.[46] The reaction between [Ru(OEP)Me] (H_2OEP = octaethylporphyrin) and 2,2,6,6,-tetramethylpiperidine-1-oxyl (TEMPO) produces [Ru(OEP)CO]. There is clear evidence that the CO ligand is derived from the axially bound CH_3 group, making this reaction an important example of CH_3 to CO transformation.[47]

A number of Ru^{III} and Os^{III} complexes of 1,4,7-triazacyclononane (tacn) are covered with related M^{II} complexes in Section 5.5.3.1.20.

5.5.2.1.4 Di- and trinuclear complexes

The dinuclear complexes $[\{Cl_4(dmso\text{-}S)Ru\}_2(\mu\text{-}L)]^{2-}$ and $[\{Cl_3(dmso\text{-}S)(dmso\text{-}O)Ru\}_2(\mu\text{-}L)]$ (e.g., L = pyrazine, pyrimidine, 4,4′-bipyridine) have been studied with the aim of probing their antineoplastic properties. At 298 K and pH 7.4, $[\{Cl_4(dmso\text{-}S)Ru\}_2(\mu\text{-}L)]^{2-}$ retains a dinuclear core

but hydrolysis results in the formation of $[\{Cl_3(H_2O)(dmso\text{-}S)Ru\}_2(\mu\text{-}L)]^{2-}$. Reduction to mixed valence dinuclear species occurs readily at physiological pH.[48]

The Ru^{III} complex $[\{(NH_3)_5Ru\}_2(\mu\text{-}L)]^{4+}$ where L^{2-} is 1,4-dicyanamido-2,3,5,6-tetramethylbenzene(2−) has been studied with emphasis on its temperature-dependent magnetic properties and long-range antiferromagnetic coupling between the metal centers.[49] A related complex, $[\{(NH_3)_5Ru\}_2(\mu\text{-}L)]^{4+}$, in which L^{2-} is 4,4′-dicyanamidobiphenyl has also been prepared and characterized.[50]

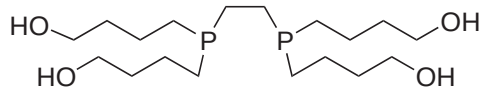
A significant number of studies involve dinuclear species of the type $[\{(bpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ ("blue ruthenium dimer") and its role as a water oxidation catalyst. Water oxidation is a complex stepwise process, with a redox system cycling between five different oxidation states of the catalyst.[51] There is evidence for a mechanism in which activation of solvent water by hydrogen bonding to the μ-O atom plays a key role.[52] Further mechanistic studies have involved EPR and Raman spectroscopic studies.[53,54] Oxidation of water to O_2 by the mixed valence species $[\{5,5'\text{-}(HO_2C)_2bpy\}_2(H_2O)Ru^{III}(\mu\text{-}O)Ru^{IV}\{5,5'\text{-}(HO_2C)_2bpy\}_2(OH)]^{4+}$ has also been reported.[55] The oxidation of $[\{(bpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ by bromate in aqueous $HClO_4$ occurs by parallel acid-independent and acid-dependent pathways.[56] The complexes $[\{(4,4'\text{-}Cl_2bpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ and $[\{(5,5'\text{-}Cl_2bpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ undergo reversible one-electron oxidations to the Ru^{III}/Ru^{IV} species followed by a reversible step to Ru^{IV}/Ru^{V}. The latter is an active catalyst for oxidation of H_2O to O_2. Reduction of $[\{(4,4'\text{-}Cl_2bpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ or $[\{(5,5'\text{-}Cl_2bpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ produces $[RuL_2(H_2O)_2]^{2+}$ (L = 4,4′-Cl_2bpy or 5,5′-Cl_2bpy).[57] Immobilization of the water oxidation catalysts on electrode surfaces has been explored. Electropolymerization studies of a series of complexes $[\{(Xbpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ (Xbpy is a functionalized bpy ligand) in noncoordinating CH_2Cl_2 electrolyte have been carried out. In related work, $[\{L_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ where L = 4-(4-pyrrol-1-ylbutyl)-4-methyl-2,2′-bipyridine or 4,4′-di-*tert*-butyl-2,2′-bipyridine have been synthesized and their electropolymerization carried out to give functionalized polypyrrole-modified electrodes.[58,59]

The electrochemical oxidation of $[\{(bpy)_2(NH_3)Ru\}_2(\mu\text{-}O)]^{4+}$ releases N_2. Oxidation of the ruthenium species initially gives $[\{(bpy)_2(NH_3)Ru\}_2(\mu\text{-}O)]^{5+}$ followed by irreversible five-electron oxidation and H^+ loss.[60] The Ru^{III} complexes $[\{(bpy)_2LRu\}_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2]^{2+}$ have been prepared as perchlorate salts for L = im, 1- and 4-Meim. Structural data for L = 1-Meim confirm a *trans* arrangement of imidazole and oxo ligands. The complexes exhibit reversible one-electron oxidation and reduction processes.[61] The interaction of $[\{(bpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$ with DNA results in reductive cleavage of the complex to form $[Ru(bpy)_2(H_2O)_2]^{2+}$ and the rate of reaction increases in the presence of Mg^{2+}. $[Ru(bpy)_2(H_2O)_2]^{2+}$ has the ability to oxidize DNA with strand scission.[62]

The $Ru^{III}Ru^{III}$ complex $[\{(tpy)(C_2O_4)Ru\}_2(\mu\text{-}O)]\cdot 8H_2O$ has been prepared and structurally, spectroscopically, and electrochemically characterized; the Ru–O–Ru bridge angle is 148.5°. In strong acid, $[\{(tpy)(C_2O_4)Ru\}_2(\mu\text{-}O)]$ converts to $[\{(tpy)(H_2O)_2Ru\}_2(\mu\text{-}O)]^{4+}$. Electrochemical studies include the observation of pH-dependent cyclic voltammograms; in contrast to the redox activity of $[\{(bpy)_2(H_2O)Ru\}_2(\mu\text{-}O)]^{4+}$, that of $[\{(tpy)(H_2O)_2Ru\}_2(\mu\text{-}O)]^{4+}$ does not seem to show a stable $Ru^{IV}Ru^{IV}$ species.[63] For the trinuclear $[(bpy)_2(H_2O)Ru(\mu\text{-}O)Ru(bpy)_2(\mu\text{-}O)Ru(bpy)_2(H_2O)]^{6+}$, the isolated complex is a $Ru^{III}Ru^{IV}Ru^{III}$ species, but electrochemical studies in aqueous solution over a pH range −0.16 to 13.9 show that seven valence-state combinations from $Ru^{II}Ru^{II}Ru^{II}$ to $Ru^{IV}Ru^{V}Ru^{IV}$ can be accessed.[64]

5.5.2.2 Phosphorus-, Arsenic-, and Antimony-donor Ligands

The predominant coordination chemistry of group 15 donors with Ru and Os concerns metal oxidation states of ≤2. For the +3 oxidation state, limited examples have been reported in recent years. $[PMePh_3][trans\text{-}RuCl_4(PPh_3)_2]$[65], *mer*-$[OsBr_3(SbPh_3)_3]$[66] and $[OsBr_2(PPh_3)_2(MeCO_2)]$[67] have been prepared and structurally characterized. Oxidation in dilute HNO_3 of the corresponding Os^{II} complexes gives $[trans\text{-}OsL_2X_2][BF_4]$ (X = Cl, Br; L = 1,2-$(PMe_2)_2$ C_6H_4, 1,2-$(PPh_2)_2$ C_6H_4, 1,2-$(PPh_2)_2C_6F_4$, 1,2-$(AsMe_2)_2C_6H_4$, 1,2-$(PMe_2)(AsMe_2)C_6H_4$, 1,2-$(AsMe_2)$ C_6F_4, $Ph_2PCH_2CH_2PPh_2$, $Me_2PCH_2CH_2PMe_2$ and $Ph_2AsCH{=}CHAsPh_2$; Os^{IV} species result if concentrated HNO_3 medium is used.[68] A related series of Ru^{III} complexes has been reported,[69] as have $[trans\text{-}OsL_2I_2][BF_4]$ and $[trans\text{-}OsL'_4I_2][BF_4]$ compounds for L = didentate *P,P*- or *As,As*-donor and L′ = PMe_3, $AsMe_3$ or $SbMe_3$; the crystal structures of $[trans\text{-}Ru\{1,2\text{-}(AsMe_2)_2C_6F_4\}_2Br_2][BF_4]$[69] and $[trans\text{-}Os(AsMe_3)_4I_2][I_3]$[70] have been determined. Complexation of the water-soluble bisphosphine (**7**) with Ru^{III} gives $[Ru(\mathbf{7})_2Cl_2]Cl$ which is also water soluble.[71]



(7)

5.5.2.3 Oxygen-donor Ligands

5.5.2.3.1 Monodentate ligands

Spectrophotometric methods have been used to follow the kinetics of aquation and anation of $[RuCl_4(H_2O)_2]^-$, $[RuCl_3(H_2O)_3]$, $[RuCl_2(H_2O)_4]^+$ and $[RuCl(H_2O)_5]^{2+}$ over a temperature range 288–318 K.[72] The aqua-ammine complex $[Ru(H_2O)_3(NH_3)_3]^{3+}$ has been prepared and isolated as the trifluoromethanesulfonate salt.[73]

During attempts to prepare *fac*-$[OsCl_3(PPh_3)_3]$, recrystallization from methanol resulted in the isolation of $[OsCl_3(PPh_3)_2(MeOH)]$. The MeOH ligand is labile and the latter complex is a useful precursor to a range of $[OsCl_2(PPh_3)_2L]$ complexes where L^- is an *O,O′*-donor ligand.[74]

Interest in ruthenium halo-sulfoxide complexes has increased with the discovery of their potential for anti-tumor activity. The dmso ligand and its derivatives can be *O*- or *S*-bonded and coordination to Ru^{III} and Os^{III} is covered here and in Section 5.5.2.4.1. A simple route to $[Ru(dmso\text{-}O)_6]^{3+}$ starting from $RuCl_3 \cdot xH_2O$ has been described; *O*-coordination is confirmed by a crystal structure determination of the $CF_3SO_3^-$ salt.[75] The complexes *mer,cis*-$[RuCl_3(dmso\text{-}S)(R_2SO\text{-}O)L]$ (L = NH_3, imidazole, pyrazole, indazole, pyridine or isoquinoline) have been prepared by treating $[RuCl_3(dmso\text{-}S)_3]$ with L in CH_2Cl_2. The crystal structure of *mer,cis*-$[RuCl_3(dmso\text{-}S)(dmso\text{-}O)(NH_3)]$ confirms the ligand arrangement and the linkage isomerism that accompanies the substitution reaction. Treatment of the Na^+ salt of *trans*-$[RuCl_4(dmso\text{-}S)_2]^-$ with the same ligands L yields *trans*-$[RuCl_4(dmso\text{-}S)L]^-$ with retention of the *S*-coordination mode.[76]

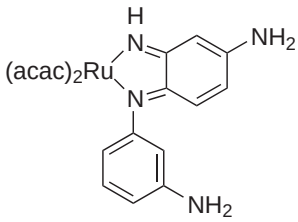
5.5.2.3.2 Didentate ligands

Reaction between $[Ru(PPh_3)_3Cl_2]$ and 3-chloroperbenzoic acid yields $[Ru(PPh_3)_2Cl_2(O_2CC_6H_4\text{-}3\text{-}Cl)]$; the carboxylate ligand is *O,O′*-bonded with each *O*-donor *trans* to a Cl atom.[77] Again starting from $[Ru(PPh_3)_3Cl_2]$, the complexes $[Ru(PPh_3)_2Cl_2L]$ have been prepared where HL is salicylaldehyde, 2-hydroxyacetophenone or 2-hydroxynaphthylaldehyde; each L^- ligand acts as an *O,O′*-chelate. If HL is used in a twofold excess, Ru^{II} products are obtained.[78] Although $K_3[Ru(ox)_3] \cdot 5.5H_2O$ has been known since 1931, studies on the pure compound have been few. The solid-state structure has now been determined and confirms $K_3[Ru(ox)_3] \cdot 5.5H_2O$ to be isomorphous with its Rh^{III} and Ir^{III} analogs.[79]

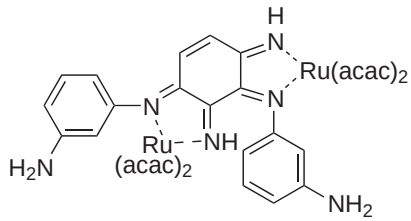
β-Ketonate complexes of Ru^{III} are reported in a number of papers. The parent complex $[Ru(acac)_3]$ has been subject to a polarized neutron diffraction study at 4.18 K, to powder neutron diffraction studies and to single-crystal structure determinations at 293 K, 92 K, and 10.5 K. The structure is disordered at all temperatures.[80] Measurements of the magnetic susceptibilities (at 2.5 K and 300 K) have been made along different crystal axis directions, and the results analyzed.[81] An investigation of the relationships between ionization potentials and half-wave potentials of a series of tris(*β*-ketonate)Ru^{III} complexes has been reported,[82] and the electrochemical properties of $[Ru(acac)_3]$ in chloroaluminate molten salt media have been reported. The reduced species $[Ru(acac)_3]^-$ can react with $AlCl_4^-$; reduction by bulk electrolysis of a small amount of $[Ru(acac)_3]$ in the melt yields $[RuCl_6]^{3-}$.[83]

Treatment of $RuCl_3 \cdot xH_2O$ with Hacac gives *trans*-$[Ru(acac)_2Cl_2]^-$ (the first *trans*-bis(acac) complex to have been made). The complex anion is a precursor to a range of Ru^{IV}, Ru^{III}, and Ru^{II} *trans*-bis(acac) complexes including *trans*-$[Ru^{II}(acac)_2L_2]$ where L = MeCN or pyrazine (pyz); the *cis* analogs result from direct reaction between $[Ru(acac)_3]$ and MeCN or pyz (see also Section 5.5.3.4.1).[84] The reaction of $[Ru(acac)_3]$ with molten 1,3-diaminobenzene yields complexes (**8**)–(**10**). Their formation involves Ru-mediated oxidative di- and trimerization of 1,3-diaminobenzene.[85] Structural data for $[Ru(acac)_3]$ and $[Ru(3\text{-}Bracac)_3]$ (H-3-Bracac = 3-bromopentane-2,4-dione)

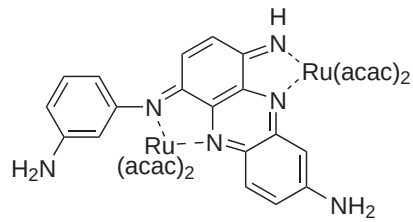
have been reported.[86] Protonation of $[RuL_3]$ (L = acac$^-$ and derivatives) in MeCN leads to $[RuL_2(MeCN)_2]^+$.[87] The Ru^{II} complexes $[RuL_2(MeCN)_2]$ (L = acac$^-$ and derivatives) have been used as precursors to mixed β-diketonate Ru^{III} complexes.[88] The mechanisms of the interconversions between the three isomers of $[Ru(acac)(tfpb)_2]$ (Htfpb = 4,4,4-trifluoro-1-phenyl-1,3-butanedione) have been studied in dmf at 363 K, 383 K, and 403 K. The data are consistent with a bond-rupture mechanism through trigonal–bipyramidal intermediates.[89] Starting from $[Ru(3\text{-}Iacac)_3]$ (H-3-Iacac = 3-iodopentane-2, 4-dione), the alkyne-functionalized complexes $[Ru(3\text{-}Me_3SiC{\equiv}Cacac)_3]$ and $[Ru(3\text{-}HC{\equiv}Cacac)_3]$ may be prepared. The latter has been polymerized; ^{1}H NMR spectroscopic data are consistent with a chain-like polymer and electrochemical data indicate that there is only short-range Ru—Ru communication.[90] Peroxide oxidation of $Na[Ru(hfac)_3]$ (Hhfac = 1,1,1,5,5,5-hexafluoroacetylacetone) yields $[Ru(hfac)_3]$; from either the Ru^{II} or Ru^{III} complex, *cis*-$[Ru(hfac)_2\ (MeCN)_2]$ can be prepared. Treatment of *cis*-$[Ru(acac)_2(MeCN)_2]^+$ with hfac$^-$ gives $[Ru(acac)_2(hfac)]$, from which the Ru^{II} complex *cis*-$[Ru(acac)(hfac)(MeCN)_2]$ has been prepared.[91] Measurements of the rates of electron transfer cross-reactions between $[Ru(CF_3COCHCOCR)_3]$ and $[Ru(CF_3COCHCOCR)_3]^-$ (R = CF_3, Me, ^{t}Bu, Ph, furyl, thienyl) have been made in MeCN using stopped-flow methods.[92]



(**8**)



(**9**)



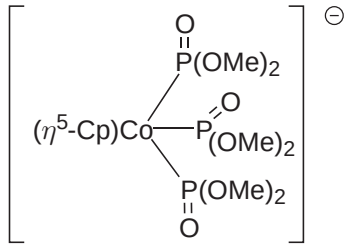
(**10**)

Assignment of oxidation states in quinone (Q)/semiquinone (SQ) complexes is not straightforward. The structural and spectroscopic characteristics of $[Ru(bpy)_2(DBSQ)]^+$ and $[Os(bpy)_2(DBCat)]^+$ (DBCat = 3,5,-di-*tert*-butylcatechol; SQ = semiquinone) reveal a difference in charge distribution between the complexes on going from Ru to Os. For Os, C—O bond lengths of the quinone ligand are consistent with a reduced catecholate and, in line with this, near-IR transitions and EPR spectroscopic data are consistent with an oxidation state of +3. In contrast, the Ru complex appears to be somewhere between Ru^{II}-DBSQ and Ru^{III}-DBCat.[93] The same mid-picture is concluded from structural data for *trans*-$[Ru(4\text{-}^tBu\text{-}py)_2(DBSQ)_2]$, although it is pointed out that the result may arise from a crystallographic disorder of a localized $Ru^{III}(SQ)$ (Cat) species. Related systems have also been analyzed.[94] In $[Ru(PPh_3)_2(DBSQ)Cl_2]$, the structural properties of the *O,O′*-donor ligand are consistent with a semiquinone formulation and, therefore, Ru^{III}. Complexes containing both 3,5,-di-*tert*-butylcatechol and tetrachlorocatechol (Cl_4SQ = semiquinone form) have also been studied, and the structure of $[Ru(PPh_3)_2(Cl_4SQ)_2]$ has been determined; the structural parameters are consistent with a semiquinone form of the ligand.[95] Treatment of $[Ru(PPh_3)_3Cl_2]$ with 1-hydroxy-2,4,6,8-tetra-*tert*-butylphenoxazinyl radical (HphenoxSQ) gives $[Ru(PPh_3)_2Cl_2(phenoxSQ)]$ or $[Ru(PPh_3)Cl(phenoxSQ)_2]$ depending on the reactant stoichiometry. Coupling between the radical and the $S = 1/2$ Ru center in $[Ru(PPh_3)_2Cl_2(phenoxSQ)]$ renders the complex diamagnetic; $[Ru(PPh_3)Cl(phenoxSQ)_2]$ is paramagnetic. The work has been extended to a number of related complexes.[96] Reaction of $[Ru(NH_3)_5Cl]Cl_2$ and 3,4-dihydroxybenzoic acid in NH_4OH solution yields $[Ru(NH_3)_4$ (diox-COO)] where diox-COO = 3,4-diolatobenzoate. $[Ru(NH_3)_4(diox\text{-}COO)]$ could be formulated as $[Ru^{III}(NH_3)_4(cat\text{-}COO)]$ or $[Ru^{II}(NH_3)_4(SQ\text{-}COO)]$.[97] Further complexes with catecholate, semiquinone or quinone ligands are described under Ru^{II} in Section 5.5.3.3.

5.5.2.3.3 *Tripodal ligands and polyoxometallates*

Several Ru^V, Ru^{IV}, and Ru^{III} complexes containing the tripodal ligand (**11**) have been prepared; among these are $[(\mathbf{11})(MeCN)Ru^{III}(\mu\text{-}OH)_2Ru^{III}(NCMe)(\mathbf{11})]^{2+}$ and $[(\mathbf{11})Ru^{III}(\mu\text{-}OH)_2(\mu\text{-}O_2CH)Ru^{III})(\mathbf{11})]^+$ for which structural data have been reported. Application of the dimers

as electrocatalysts for the oxidation of formaldehyde is described.[98] Two reports of the substituted Keggin ion $[SiW_{11}O_{39}Ru^{III}(H_2O)]^{5-}$ have appeared.[99,100] The potassium salt has been characterized by spectroscopic and electrochemical methods. The H_2O ligand can be replaced by NO, and the latter reduced to coordinated N_2.[99]



(**11**)

5.5.2.4 Sulfur- and Selenium-donor Ligands

5.5.2.4.1 Monodentate ligands

Ruthenium(III) and osmium(III) *O*-bonded dmso ligands were described in Section 5.5.2.3.1. Synthetic and structural studies of *S*-bonded dmso and tetrahydrothiophene *S*-oxide (ttso) ligands include those of *trans*-$[RuCl_4(dmso\text{-}S)_2]^-$[101–103] *trans*-$[RuCl_4(ttso\text{-}S)_2]^-$,[104] *mer*-$[RuCl_3(ttso\text{-}S)_3]$,[104] *mer*-$[RuCl_3(dmso\text{-}S)_2(dmso\text{-}O)]$,[103] *trans*-$[RuCl_4(dmso\text{-}S)L]^-$ (L = nitrogen donor ligand, e.g., imidazole, NH_3, pyrazole),[76] *mer,cis*-$[RuCl_3(dmso\text{-}S)(dmso\text{-}O)L]^-$ (L = nitrogen donor ligand, e.g., NH_3, pyridine, pyrazole),[76] (see also discussion in Section 5.5.2.3.1), *mer*-$[RuCl_3(dmso\text{-}S)(Me_2NCH_2CH_2NMe_2)]$,[105] *mer,cis*-$[RuCl_3(1\text{-}Meim)_2(dmso\text{-}S)]$,[106] and *trans*-$[RuCl_4$ $(dmso\text{-}S)(4\text{-}Etpy)]^-$.[106] Linkage isomerism $Ru^{III}S \rightarrow O$ and $Ru^{II}O \rightarrow S$ is discussed in Section 5.5.3.4.1.

The Ru^{III} complex *mer*-$[RuCl_3(tht)_3]$ has been prepared and structurally characterized.[107] Thiourea (tu) coordinates through the *S*-donor atom in $[Ru(NH_3)_5(tu)]^{3+}$ and does not show a tendency to isomerize to the *N*-bonded form in the presence of aqueous base (contrast *O*- to *N*-isomerization for urea); instead, the dinuclear complex $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ forms. Structural data for $[Ru(NH_3)_5(tu)]^{3+}$ are consistent with significant LMCT from the filled pπ *S*-orbital to a vacant *d*-orbital on Ru^{III}.[108] The synthesis and properties of $[Os(SC_6F_5)_3(PR_3)_2]$ have been described.[109] Reactions of $[Os(SR)_3(PMe_2Ph)_2]$ (R = C_6F_5, C_6F_4H) with $PhCO_2H$ or HCl yield $[Os^{III}(SR)_2(O_2CPh\text{-}O,O')(PMe_2Ph)_2]$ or $[Os^{IV}(SR)_3Cl(PMe_2Ph)]$; the former contains *trans*-thiolate ligands.[110] With MeCOSH or PhCOSH, $[Os(SR)_3(PMe_2Ph)_2]$ (R = C_6F_5, C_6F_4H) reacts to give octahedral $[Os(SR)_2(SOCR'\text{-}O,S)(PMe_2Ph)_2]$ (R′ = Me, Ph); the RS^- ligands are mutually *trans*.[111] The complex $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ exhibits an Os—F interaction involving an *ortho*-F substituent of one thiolate ligand. On heating (toluene, reflux), C—F cleavage and C—S bond formation occur to give $[Os(C_6F_5)_2(1,2\text{-}S_2C_6F_4)(PMe_2Ph)_2]$ and $[Os(SC_6F_5)_2(1,2\text{-}S_2C_6F_4)$-$(PMe_2Ph)]$.[112] A series of complexes $[Os(SC_6F_5)_2(O_2CR\text{-}O,O')(PMe_2Ph)_2]$ (R = Me, CF_3, and fluorinated Ph derivatives) has been made starting from $[Os(SC_6F_5)_3(PMe_2Ph)_2]$; electrochemical data are reported.[113]

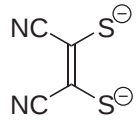
The oxidation by HSO_5^- of a number of thiolate complexes of Ru^{III} occurs by a two-step process. The first (but not the second) oxidation step is sensitive to the thiolate R group. Synthetic and spectroscopic details are given for the complexes $[Ru(NH_3)_4(H_2O)(SR)]^{2+}$ ($RS^- = C_6F_5$, 4-MeC_6H_4, Ph, 4-$MeOC_6H_4$, 4-$NO_2C_6H_4$) and $[Ru(NH_3)_4(H_2O)(S(O)_2R)]^{2+}$ (R = Ph, 4-ClC_6H_4, 4-$NO_2C_6H_4$).[114]

5.5.2.4.2 Didentate ligands

Nitric acid oxidation of *trans*-$[RuL_2X_2]$ (L = $MeSCH_2CH_2SMe$, $PhSCH_2CH_2SPh$, $PhSeCH_2CH_2$-SePh; X = Cl, Br) yields the corresponding Ru^{III} complexes, isolated as the BF_4^- salts.[69] Thermolysis of $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ results in C—F cleavage and C—S bond formation and the

production of $[Os(C_6F_5)_2(1,2\text{-}S_2C_6F_4\text{-}S,S')(PMe_2Ph)_2]$ and $[Os(SC_6F_5)_2(1,2\text{-}S_2C_6F_4\text{-}S,S')(PMe_2Ph)]$.[112] Starting from $RuCl_3{\cdot}xH_2O$, $Na_2(1,2\text{-}S_2C_6H_4)$ and PMe_3, $[Ru^{III}(1,2\text{-}S_2C_6H_4)_2(PMe_3)_2]^-$ and its Ru^{IV} analog have been prepared. Structural data support extended π-electron delocalization over the planar $Ru(S_2')_2$-units; comparisons are made with analogous Fe complexes and bonding, spectroscopic and reactivity differences are discussed.[115]

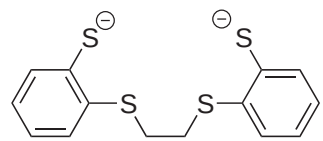
Complex formation between Ru^{III} and ligand (**12**) has been investigated; $[Ru(\mathbf{12})_3]^{3-}$ is easily prepared and can be oxidized to the corresponding Ru^{IV} complex. Substitution by PPh_3, py, or im (L) occurs very slowly, and in $[Ru^{IV}(\mathbf{12})_3]^{2-}$, it occurs with concomitant reduction to yield *trans*-$[Ru(\mathbf{12})_2L_2]^-$.[116]



(**12**)

5.5.2.4.3 *Dinuclear complexes with bridging S_2^{2-} ligands*

The reaction of alkaline aqueous $[RuL(acac)(OH)][PF_6]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) with $Na_2S{\cdot}xH_2O$ or H_2Se yields the dinuclear complexes $[\{L(acac)Ru\}_2(\mu\text{-}S_2)][PF_6]_2$ or $[\{L(acac)Ru\}_2(\mu\text{-}Se_2)][PF_6]_2$. Structural parameters for $[\{L(acac)Ru\}_2(\mu\text{-}S_2)]^{2+}$, the electronic spectrum, electrochemical data and the diamagnetism of the complex all support an exchange-coupled Ru^{III} complex containing S_2^{2-}. The diselenide complex is considered to have an analogous bonding picture.[117] These conclusions are important in view of the differing bonding models proposed for similar types of complex.[118] In the complex $[\{(\mathbf{13}\text{-}S,S',S'',S''')(PCy_3)Ru\}_2(\mu\text{-}S_2)]$, the S_2^{2-} bridge connects two homochiral $Ru(\mathbf{13})(PCy_3)$ units. A formal oxidation state of +3 can be assigned to each Ru center, although the RuS_2Ru unit is described as a delocalized four-center six-electron π-system.[119] The S_2^{2-} bridging unit is also present in the dinuclear Ru^{III} complex $[\{(P(OMe)_3)_2ClRu\}_2(\mu\text{-}S_2)(\mu\text{-}Cl)_2]$,[120] further chemistry of which is described in Section 5.5.3.4.2.



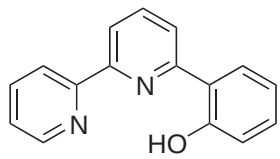
(**13**)

5.5.2.5 Mixed-donor Atom Ligands

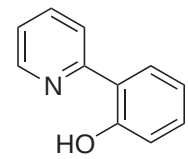
5.5.2.5.1 *N,O-donors*

The tris chelate $[Ru(pic)_3]$ (Hpic = picolinic acid) can be prepared from $RuCl_3{\cdot}xH_2O$ in the presence of base. Electronic and EPR spectroscopic data are reported; reduction (electrochemical and chemical) gives $[Ru(pic)_3]^-$ which, in air, reverts to the Ru^{III} complex. The pic^- ligands can be displaced by quinolate ligands.[121] Treatment of $RuCl_3{\cdot}xH_2O$ with (**14**) (HL) yields $[RuL_2]^+$, isolated as the PF_6^- salt. The presence of the two *N,N,O*-donors stabilizes the Ru^{III} oxidation state, and cyclic voltammetry shows that the Ru^{III}/Ru^{IV} couple is accessible.[122] Ligand (**15**) (HL) forms the complexes $[RuL_3]$, $[RuL_2(acac)]$ and $[RuL_2(bpy)]^+$; their electrochemical properties (compared with those of related species) indicate that there is a decrease of 0.75 V in the Ru^{II}/Ru^{III} couple as an extra *N,O*-donor replaces an *N,N*-donor.[123] A series of complexes $[RuLX_2(AsPh_3)_2]$ (HL = 8-hydroxyquinoline, 2-aminophenol, 2-amino-3-hydroxypyridine; X = Cl, Br) has been reported, and their ability to act as catalysts for alcohol oxidations has been tested.[124] The compounds $[RuLCl_2(PPh_3)_2]$ in which HL is an imine of salicylaldehyde, 2-hydroxyacetophenone and 2-hydroxynaphthylaldehyde (prepared by reduction of the corresponding oxime

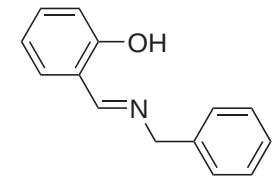
in situ) have been prepared and characterized; structural data confirm a *trans*-arrangement of phosphines.[125] Treatment of $[RuX_2(PPh_3)_3]$ (X = Cl, Br) with (**16**) (HL) gives $[Ru^{II}L_2(PPh_3)_2]$ and the cyclometallated product $[Ru^{III}LL'(PPh_3)]$; in both complexes, L^- acts as an *N,O*-chelate, whereas $[L']^{2-}$ is a *C,N,O*-donor. The Ru^{II} complexes are unstable in solution with respect to conversion to the cyclometallated species.[126] In the complexes $[RuL_2Cl(PPh_3)]$ where HL = (**17**), the L^- ligand is an *N,O*-chelate with the two *N*-donors mutually *cis*, and the two *O*-donors *trans* to each other; EPR spectroscopic and electrochemical data have been reported for the complexes.[127] The series of Os^{II} and Os^{III} complexes $[OsL(L'_2)]^{n+}$ (HL = 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline; L′ = bpy or 2-(3-tolylazo) pyridine) has been reported; The redox stability of the metal center in the new complexes and in $[OsL_3]$ is discussed in terms of the π-acceptor properties of the ligands.[128]



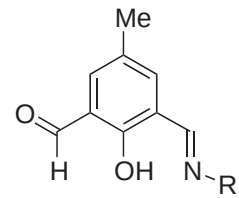
(**14**)



(**15**)



(**16**)

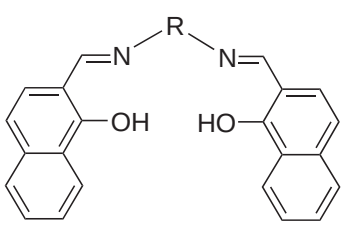


R = Me, Et

(**17**)

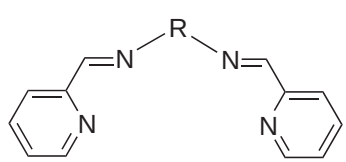
Benzamide and $[RuH_2(CO)(PPh_3)_2]$ or $[RuHCl(PPh_3)_3]$ react to form dinuclear amidato complexes featuring bridging $[PhC(O)NH]^-$ ligands; in one product, cyclometallation of the benzene ring occurs. Related reactions have been carried out using toluamides.[129]

Schiff base Ru^{III} complexes include $[RuLXCl]^{n+}$ and $[RuLX(CO)]^{n+}$ where H_2L = (**18**) and X = Cl^-, im, 2-Meim or the *N*-donor of the N-containing R group in (**18**). The complexes are low-spin d^5, and EPR spectroscopic data are reported.[130] Work from the same researchers has focused on the O_2 affinities of Ru^{III} Schiff base complexes (H_2L is related to (**18**) or L is (**19**)); the O_2 adducts were characterized by electrochemical and spectroscopic methods and are described as Ru^{IV} superoxo complexes.[131] A comparison of the reactivity of $[Ru^{III}LCl(PPh_3)]$ for H_2L = (**20**) and $[Ru^{II}Cl_2L]$ where L is an *S,N,N″,S′* or *P,N,N″,P′* Schiff base ligand related to (**20**), shows that with soft donor atoms and Ru^{II}, the complex is susceptible to photosubstitution of the axial ligands; this reaction does not occur in $[Ru^{III}LCl(PPh_3)]$ (H_2L = (**20**)).[132]



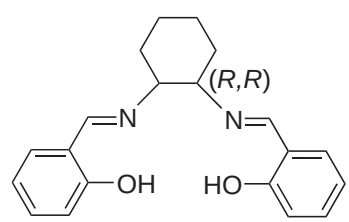
R = C_6H_4, $(CH_2)_2$, $CHMeCH_2$, $CH_2CH_2NHCH_2CH_2$

(**18**)



R = various spacers

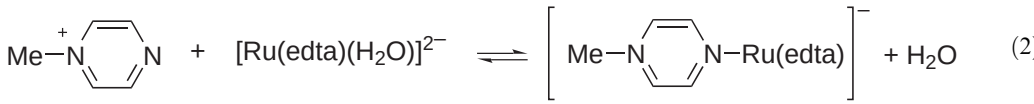
(**19**)



(**20**)

Ruthenium(III) complexes with *N*- and *O*-donor atom ligands are dominated by those containing $edta^{4-}$ and related ligands, and the area has been reviewed.[133] The structure of [Ru(Hedta)(H_2O)] has been determined; there is one pendent CO_2H group and the aqua ligand is *trans* to an *N*-donor.[134] The H_2O ligand in $[Ru(edta)(H_2O)]^-$ is labile and readily displaced by a variety of ligands. The reaction of $[Ru(edta)(H_2O)]^-$ with isonicotinamide (isna) has been investigated by spectrophotometric methods over the pH range 6–10. At pH 6, isna coordinates through the pyridine *N*-atom but as the pH (and protonation state) changes, isomerization occurs and at pH 9, the isna ligand is bound through the amido-*N* atom. The process is reversible.[135] The reaction of $[Ru(edta)(H_2O)]^-$ with 4-sulfanylpyridine leads to substitution, with *N*-coordination of the incoming ligand being kinetically favored over the *S* mode, while *S*-coordination is thermodynamically favored. The *N*-bound ligand isomerizes to the *S*-bound form by a dissociative pathway.[136] The kinetics of the substitutions in $[Ru(edta)(H_2O)]^-$ with adenine, adenosine, AMP, ADP, and ATP have been studied; it is proposed that the 5′-nucleo--nucleotides bind in a rapid nucleophilic concentration-dependent step, followed by a concentration-independent ring-closure.[137] Stopped-flow methods have been used to investigate the kinetics of the reaction between [Ru(Hedta)(H_2O)] and thiourea. Over the pH range 1.5–8.5, the reaction follows first-order kinetics with respect to each reactant.[138] Mixed ligand complexes have been prepared by treating $[Ru(Hedta)Cl]^-$ with adenine, guanine, hypoxanthine, 2,6-diaminopurine and 2-thioxanthine. Characterization data are consistent with adenine, 2,6-diaminopurine and 2-thioxanthine coordinating through N(3) and N(9), C_6NH_2 and N(7), and C_6O and N(7) respectively; complexes with an M_2L_2 stoichiometry are proposed. Guanine and hypoxanthine appear to form 1:1 complexes with ligand coordination through N(7).[139] Complex formation with adenosine, guanine, xanthosine, inosine, cytidine, and uridine has also been studied.[140] The reaction between [Ru(Hedta)(H_2O)] and 2-mercaptonicotinic acid, HL, initially yields a product in which L^- is *S*-bonded to the Ru(edta)-unit. Deprotonation of this compound results in a change to *N,S*-coordination. If the Ru^{III}-edta precursor is in a twofold excess, a dinuclear product is obtained.[141] Reaction between $[Ru(edta)(H_2O)]^-$ and guanosine-5′-monophosphate (5′-GMP) has been monitored by spectrophotometric and kinetic measurements. Stopped-flow studies carried out at pH 8 have illustrated that the reaction between $[Ru(edta)(OH)]^{2-}$ and 5′-GMP exhibits second order kinetics. Related Ru^{II} chemistry is also reported; coordination of 5′-GMP to the Ru^{II}(edta)-unit occurs through N(7) or N(3), i.e., two isomers are formed.[142] The kinetics of the reduction of $[Ru(edta)(pyz)]^-$ by L-ascorbic acid and catechol is first order with respect to both $[Ru(edta)(pyz)]^-$ and reducing agent. Mechanistic proposals involve outer-sphere electron transfer.[143] There is a large difference between the affinities of *N*-methylpyrazinium ion for Ru^{II}(edta) and Ru^{III}(edta) (Equations (1) and (2)) and this results in the irreversibility in the electrochemical responses exhibited by the complexes:[144]

(1)



(2)

Treatment of $[Ru(Hedta)Cl]^-$ with CO at pH 1 yields [Ru(Hedta)(H_2O)(CO)]; the complexes K[Ru(edta)(CO)(H_2O)] and $K_3[\{Ru(edta)\}_2(\mu\text{-}CO)(\mu\text{-}OH)]$ have also been isolated. For the dinuclear species, EPR spectroscopic results are consistent with $Ru^{III}Ru^{III}$ coupling.[145] A rapid reaction occurs between $[Ru^{III}(edta)(H_2O)]^-$ and NO at pH 5; stopped-flow kinetics have been used to follow the process in which tightly bound Ru^{II} nitrosyl complexes are formed.[146,147]

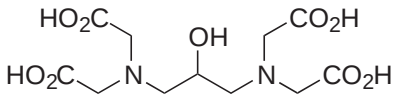
When K[Ru(Hedta)Cl] and [Ru(Hedta)(H_2O)] are treated with dppm, the products are [Ru(Hedta)(dppm)] and [Ru(H_2edta)(dppm)]. The structure of [Ru(H_2edta)(dppm)]·dmso·H_2O has been determined and confirms a chelating dppm ligand with each *P*-donor *trans* to an *N*-donor of the H_2edta^{2-} ligand; the latter has two pendent CO_2H groups. Reactions with related

ligands, e.g., dppe and $Ph_2AsCH_2CH_2AsPh_2$, result in analogous complexes to those found for dppm.[148] Two pendant CO_2H groups are also confirmed for $[Ru(H_2edta)Cl_2]^-$.[149,150] By reacting $RuCl_3 \cdot xH_2O$ with edta-diamide in acidic solution, the salt $[NH_4][Ru(Hedta)Cl] \cdot 2H_2O$ is obtained; the ammonium ion results from hydrolysis of the amide groups. Structural data confirm $Hedta^{3-}$ is a pentadentate *N,N′,O,O′,O″*-donor.[151]

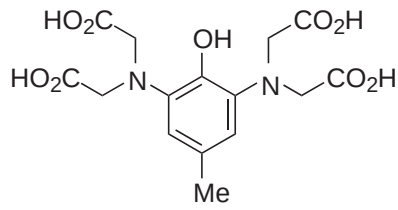
Dinuclear complexes $[(edta)Ru(\mu\text{-}L)Ru(edta)]^{n-}$ (L = benzotriazolate, benzimidazolate; $n = 3, 4, 5$) have been synthesized and characterized by electrochemical and spectroelectrochemical measurements. The benzimidazolate-bridged complex behaves as a valence-trapped system, whereas the benzotriazolate-bridged species possesses significant electronic delocalization. ZINDO MO methods have been used to probe the bonding in these systems.[152] The mixed-valence complex $[(NC)_5M^{II}(\mu\text{-}CN)Ru^{III}(edta)]^{5-}$ (M = Fe, Ru, Os) is produced when $[M(CN)_6]^{4-}$ is added to $[Ru(edta)(H_2O)]^-$. In the electronic spectra of the complexes, an intense absorption appears between 600 nm and 1,000 nm depending on M, and is assigned to an intervalence transition from M^{II} to Ru^{III}. Increasing the concentration of $[Ru(edta)(H_2O)]^-$ in the reaction facilitates the formation of higher nuclearity products.[153] In related work, the reaction of $[Ru(CN)_6]^{4-}$ and $[Ru(Hedta)(H_2O)]$ is shown to yield the mixed-valence complex $[(Hedta)Ru(\mu\text{-}CN)Ru(CN)_5]^{4-}$; the mechanism for its formation is associative. The thermochromism of the MMCT band is investigated.[154] The kinetics of the reduction of $[(edta)Ru^{III}(\mu\text{-}CN)Fe^{III}(CN)_5]^{4-}$ by L-ascorbic acid have been followed spectrophotometrically, as has the oxidation of $[(edta)Ru^{III}(\mu\text{-}CN)Fe^{II}(CN)_5]^{5-}$ by $S_2O_8^{2-}$. It is concluded that an Fe-centered outer-sphere electron transfer mechanism operates in both processes.[155] The kinetics of substitution in $[(NH_3)_5Ru^{III}(edta)Ru^{III}(H_2O)]^{2+}$ by thiourea have also been investigated.[156]

The ligand H_4pdta (propylenediaminetetraacetic acid) is a close relation of H_4edta. The crystal structure of $[Ru(Hpdta)(H_2O)] \cdot H_2O$ shows that the $Hpdta^{3-}$ ligand is pentadentate with a pendent CO_2H group. The kinetics of the substitution of H_2O by thiourea and SCN^- have been investigated over the pH range 2–9 and as a function of temperature.[157]

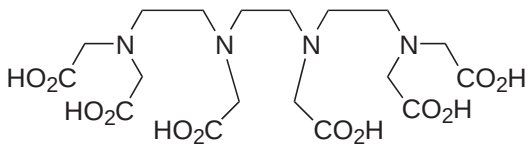
The reactions between (**21**) (H_5L), $[RuCl_2(dmso)_4]$ and RCO_2^- (R = Ph, Me, 4-HOC_6H_4, 4-$NH_2C_6H_4$) lead to $[Ru_2(\mu\text{-}L)(\mu\text{-}O_2CR)_2]^-$. The bridging L^{5-} ligand is symmetrically disposed between the two Ru^{III} centers. Magnetic measurements for the complexes reveal a strong antiferromagnetic interaction between the metal centers. Electrochemical data indicate that the mixed valence $Ru^{III}Ru^{II}$ species is quite stable.[158] Ligand (**22**) (H_5L) behaves in a similar manner to (**21**), forming $[Ru_2(\mu\text{-}L)(\mu\text{-}O_2CR)_2]^-$. Magnetic and electrochemical properties of the complexes have been studied; large antiferromagnetic coupling constants are observed.[159] The ligand L^{6-} where H_6L = (**23**) has been incorporated into the complexes $[Ru^{II}{}_2L(H_2O)_2]^{2-}$, $[Ru^{III}{}_2L(H_2O)_2]$, $[Ru^{III}Ru^{II}L(OH)]^{2-}$, and $[Ru^{IV}Ru^{III}L(O)]^-$. The $Ru^{II}{}_2$ and $Ru^{III}{}_2$ complexes possess structures in which each Ru center is in an edta-like coordination environment. The effects of pH on the complexes has been discussed, and electrochemical methods have been used to measure a comproportionation constant for the $Ru^{II}Ru^{III}$ complex. Oxidation of $[Ru^{III}Ru^{II}L(OH)]^{2-}$ gives a metastable oxo-bridged $Ru^{III}{}_2$ species which aquates to give $[Ru^{III}{}_2L\ (H_2O)_2]$.[160]



(**21**)



(**22**)



(**23**)

5.5.2.5.2 *N,S- and S,O-donors*

The conjugate base of pyridine-2-thiol (HL) is a potential *N,S*-donor. Oxidation of $[OsL_2(PPh_3)_2]$ gives two isomers of $[OsL_2(PPh_3)_2]^+$; in $[OsL_2(PPh_3)_2][PF_6]\cdot nH_2O$ ($n = 1$ or 0), the $N_2S_2P_2$ donors are in *cis,cis,trans* and *trans,trans,trans*-arrangements respectively.[161] The Os^{III} complex $[Os(SR)_3(PMe_2Ph)_2]$ ($R = C_6F_5$, C_6F_4H) reacts with R′COSH (R′ = Me, Ph) to give $[Os(SR)_2(SOCR'\text{-}O,S)(PMe_2Ph)_2]$. The crystal structure of $[Os(SR)_2(SOCMe\text{-}O,S)(PMe_2Ph)_2]$ has been determined.[111]

5.5.2.6 Halide and Cyanide Ligands

Diffuse reflectance UV–vis spectra have been reported for RuF_3 (and other *d*-block trifluorides), and the spectra have been assigned.[162] The chloro complexes $[Ru(MeCN)_nCl_{6-n}]$ for $n = 2$, 3, or 4 have been prepared and isolated; the structure of $Ru(MeCN)_3Cl_3$ has been determined. The latter complex acts as a mediator for the oxidation of cyclohexene, methylcyclohexene, 1-tetralol and tetralin.[163] The Ru^{III} complexes $[RuX_4(CN^tBu)_2]^-$ (X = Cl, Br) are produced in the reaction of CN^tBu with $[RuCl_6]^{2-}$ or $K_3[Ru_2Br_9]$. Electronic spectroscopic and electrochemical data are reported for the complexes.[164,165] The results of Raman, resonance Raman and electronic spectroscopic investigations of *trans*-$[RuBr_4(MeCN)_2]^-$ have been described, and a comparison with *trans*-$[RuCl_4(MeCN)_2]^-$ made.[166] Electrochemical and spectroelectrochemical studies have shown that oxidation of *trans*-$[RuBr_4(CN^tBu)_2]^-$ in MeCN results in the formation of *mer, trans*-$[RuBr_3(CN^tBu)_2(MeCN)]$. Reduction of $[RuBr_4(CN^tBu)_2]^-$ in MeCN produces *mer,trans*-$[RuBr_3(CN^tBu)_2(MeCN)]^-$.[167]

The salt $Rb_3[Os_2Br_9]$ was the first structurally confirmed example of a diosmium confacial nonahalide. SCF-Xα–SW calculations on $[Os_2Br_9]^{3-}$ and $[Ru_2Br_9]^{3-}$ support increased M—M interaction for the third (cf. earlier) row metals; comparisons have been made between the electronic spectra of $[Os_2Br_9]^{3-}$ and $[Ru_2Br_9]^{3-}$.[168] Starting from $[RuCl_3(dppb)L]$ (L = py, 4-Mepy, dmso), electrosynthesis is a successful method of preparing $[L(dppb)Ru(\mu\text{-}Cl)_3RuCl(dppb)]$. It is proposed that the reaction proceeds by reaction of $[RuCl_3(dppb)L]$ with its reduced form generated at the electrode surface, and this mechanism is supported by the presence of $[Ru_2Cl_5(dppb)_2]$ in the electrolysis cell.[169] The structure of *mer*-$[RuCl_3(dppb)(4\text{-}Mepy)]$ has been determined.[169]

From the results of a study of the electronic and magnetic circular dichroism (MCD) spectroscopic properties of the d^5 complexes $[M(CN)_6]^{3-}$ (M = Ru, Os), LMCT assignments have been confirmed and earlier *d–d* assignments for $[M(CN)_6]^{3-}$ (M = Fe, Os) have been questioned. Attempts to measure the intraconfigurational *d–d* splitting of the T_{2g} ground state of $[Bu_4N]_3[Ru(CN)_6]$ were not successful.[170] The kinetics of electron self-exchange in $[Os(CN)_6]^{4-/3-}$ have been studied in aqueous solution using ^{13}C NMR line-broadening methods, and a rate constant of $(8.9 \pm 0.5) \times 10^4$ dm^3 mol^{-1} s^{-1} (298 K, 1 mol dm^{-3} Na^+) has been determined. The rate constant shows a dependence on $[Na^+]$ and on the cation present in the electrolyte. The data are discussed within the context of inner-sphere and solvent reorganization barriers.[171]

5.5.3 RUTHENIUM(II) AND OSMIUM(II)

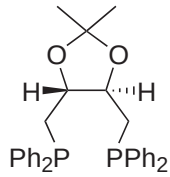
5.5.3.1 Nitrogen-donor Ligands

5.5.3.1.1 *Mononuclear complexes with simple ligands*

N-donor ligands that are covered in this section are RCN, $RNCN^-$, NH_3, N_2H_4, NO_2^-, NO, NS, N_2, and pyridine.

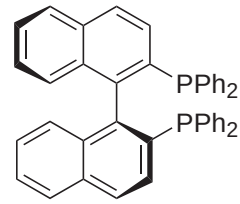
The complex $[Ru^{II}Br(PhCN)_5]^+[trans\text{-}Ru^{III}Br_4(PhCN)_2]^-$ results when $RuBr_3\cdot xH_2O$ reacts with benzaldehyde oxime in aqueous HBr (6 M) in a Ru-mediated dehydration of the oxime.[172] The cation $[Ru(dppb)(RCN)_4]^{2+}$ (R = Me, Ph) can be prepared from $[Ru_2Cl_4(dppb)_2]$ or $[RuCl_2(PPh_3)(dppb)]$. Structural data for $[Ru(dppb)(MeCN)_4][PF_6]_2$ have been reported.[173] The products of the reactions of $[Ru_2Cl_4L_2]$ or $[RuCl_2(PPh_3)L]$ (L = dppb, diop (**24**) or binap (**25**)) with RCN (Me, Ph) depend on the reaction conditions. When RCN is present in high concentrations, the main product is $[RuClL(RCN)_3]^+$ isolated as $[RuClL(RCN)_3][PF_6]$ although if sufficient

PF_6^- is present, abstraction of a second Cl^- occurs to give $[RuL(RCN)_4][PF_6]_2$. When no chloride abstractor is present, $[RuCl_2L(RCN)_2]$ can be isolated. When the latter is dissolved in benzene, $[Ru_2Cl_4L_2(RCN)]$ is produced, while in chlorocarbon solvents, the product is $[Ru_2Cl_3L_2(RCN)_2]^+$.[174]



(*R,R*)-diop

(**24**)



(*S*)-binap

(**25**)

A series of complexes *cis*-$[Ru(RNCN)_2(bpy)_2]$ (R = Ph, 2-ClC_6H_4, 2,3-$Cl_2C_6H_3$, 2,4,5-$Cl_3C_6H_2$, 2,3,4,5-Cl_4C_6H, or C_6Cl_5) has been prepared and characterized. Their oxidation by controlled-potential electrolysis gives the corresponding Ru^{III} species which exhibit low-energy LMCT bands arising from the $Ru^{III}(NCN)$ chromophore.[175] This chromophore has also been generated by oxidation of $[Ru(RNCN)(bpy)(tpy)]^+$.[176] The crystal structure of $[Ru(2,4\text{-}Cl_2C_6H_3NCN)(bpy)(tpy)][PF_6]\cdot$dmf has been determined; the cyanamide ligand resides *trans* to one of the bpy *N*-donor atoms.[176]

The complex $[Ru(NH_3)_5(EtCN)][PF_6]_2$ and its Ru^{III} analog have been synthesized and characterized. Aquation of $[Ru(NH_3)_5(EtCN)]^{2+}$ yields *trans*-$[Ru(NH_3)_4(H_2O)(EtCN)]^{2+}$. The kinetics of this process and of the reaction of $[Ru(NH_3)_4(H_2O)(EtCN)]^{2+}$ with pyrazine have been investigated.[21,22] The photolysis of $[Ru(NH_3)_5L]^{2+}$ (L = 2-cyanopyridine, 3-cyanopyridine, 4-cyanopyridine) at 365 nm, 404 nm and 436 nm in aqueous solution results in NH_3 and cyanopyridine photoaquation. Coordination of L is through the CN group and no linkage isomerization is observed.[177] Related Ru^{II} complexes in which L is *N*-methyl-2-cyanopyridinium, *N*-methyl-3-cyanopyridinium, *N*-methyl-4-cyanopyridinium, *N*-decyl-4-cyanopyridinium, *N*-dodecyl-4-cyanopyridinium, or *N*-benzyl-4-cyanopyridinium have also been described.[178] A review of the photochemical reactions of complexes of the type $[Ru(NH_3)_5L]^{2+}$ has appeared.[179] The photosensitized aquation of $[Ru(NH_3)_5(py)]^{2+}$ by several dyes has been investigated under conditions where the sensitizers absorb light. The results indicate that the excited state precursor for the photosubstitution is in the energy range 17,000–17,700 cm^{-1}.[180]

Tetracyano ligands have been used to bridge between four $Ru(NH_3)_5$ moieties. The complexes $[\{Ru(NH_3)_5\}_4(\mu\text{-}L)]^{8+}$ (L = tetracyanoethene, tetracyano-*p*-quinodimethane, 1,2,4,5-tetracyanobenzene, 2,3,5,6-tetracyanopyrazine) exhibit intense, long-wavelength electronic absorptions. Oxidation to $[\{Ru(NH_3)_5\}_4(\mu\text{-}L)]^{10+}$ and reduction to $[\{Ru(NH_3)_5\}_4(\mu\text{-}L)]^{7+}$ and $[\{Ru(NH_3)_5\}_4(\mu\text{-}L)]^{6+}$ can readily be achieved. The species are fully delocalized with partially reduced ligands or partially oxidized Ru centers.[181] Treatment of [5,10,15,20-tetrakis(4-cyanophenyl)porphyrinato] cobalt(II) or [5,10,15,20-tetrakis(4-cyano-2,6,-dimethylphenyl)porphyrinato]cobalt(II) with $[Ru(NH_3)_5(OSO_2CF_3)]^{2+}$ introduces cyano-bound pendant $Ru^{II}(NH_3)_5$ groups to the porphyrinato complexes.[182]

For the complexes $[Ru(NH_3)_5(py)]^{2+}$, $[Ru(NH_3)_5(pyz)]^{2+}$, and $[Ru(NH_3)_5(Hpyz)]^{3+}$, MLCT and oxidation processes have been the subject of a theoretical study at the ZINDO-95 level, and transition operator calculations have been applied to $[Ru(NH_3)_5(pyz)]^{2+}$.[183,184] Structural parameters for the Ru^{II} complexes $[Ru(NH_3)_5(py)][SO_3CF_3]_2$ and $[Ru(NH_3)_5(PhCN)][SO_3CF_3]_2$ and the Ru^{III} complex $[Ru(NH_3)_5(PhCN)][S_2O_6]_{3/2}$ have provided valuable input data for molecular modeling and calculations relating to electron-transfer processes and metal–ligand coupling.[185] By combining $[Ru(NH_3)_5L]^{2+}$ (L = py, pyz, 4,4′-bpy) with polyether-tailed sulfonate counterions, highly viscous, room-temperature ionic liquids have been produced. Electron self-exchange rate constants have been obtained for the $Ru^{3+/2+}$ couples; data for the pyrazine-bridged dinuclear melt have also been reported.[186]

The rate law for the oxidation of $[Ru(NH_3)_5(HL)]^{2+}$ (HL = isonicotinamide) by I_2 in acidic solution contains two terms, one depending on $[I_2]$ and one depending on $[I_3^-]$ and [Ru^{II} complex]. An outer-sphere electron-transfer mechanism is proposed for each term.[187] Reduction of $[Ru^{III}(NH_3)_5L]^{2+}$ (HL = nicotinamide or isonicotinamide) to $[Ru^{II}(NH_3)_5L]^+$ is accompanied by an isomerization from the amide-bonded L^- to pyridine-bonded HL.[188] Bromine oxidation of

$[Ru(NH_3)_5L]^{2+}$ (L = py, pyz), $[Ru(NH_3)_4(bpy)]^{2+}$, $[(NH_3)_5Ru\ (\mu\text{-pyz})Ru(NH_3)_5]^{5+}$, and $[(NH_3)_5Ru(\mu\text{-pyz})Rh(NH_3)_5]^{5+}$ is first-order in both Br_2 and Ru. It is proposed that the mechanism is outer-sphere electron transfer from Ru^{2+} to Br_2 and that $[Br_2]^-$ is formed as a reactive intermediate. The influence of $[H^+]$ has been investigated.[189] The rates of bimolecular electron-transfer self-exchange reactions for $[Ru(NH_3)_5(py\text{-}d^5)]^{2+}$ and *trans*-$[Ru(NH_3)_4(4\text{-Mepy-}d^3)(3\text{-Fpy})]^{2+}$ (4-Mepy = 4-methylpyridine, 3-Fpy = 3-fluoropyridine) have been studied by using deuterium NMR line-broadening measurements. The rates of reaction decrease dramatically in solvents that are strong Lewis bases, indicating that specific solvent–solute interactions are involved in defining the energetics of reactant-pair association.[190] The kinetics of the reaction of $[Ru(NH_3)_5(H_2O)]^{2+}$ with a mixture of valine and tyrosine tRNAs have been studied. There is a first-order dependence on each component, and a strong dependence on the ionic strength is consistent with ion pairing during binding. For the binding of $[Ru(NH_3)_5(H_2O)]^{2+}$ to guanine sites on RNA, the equilibrium association constant is 2.9×10^3. Aerial oxidation results in the coordination of $Ru(NH_3)_5^{3+}$. Electronic spectroscopic and electrochemical data for the system are discussed.[191]

Dibenzo-42-crown-14 forms an adduct with $[Ru(NH_3)_4(phen)]^{2+}$. The cation is positioned within a cavity formed by the macrocycle and a hydrogen-bonded network exists involving the crown O atoms and NH_3 H atoms; there is also weak π-stacking between the phen rings and benzene rings of the crown ether.[192] Adduct formation between $[Ru(NH_3)_5(pyz)]^{2+}$ and 18-crown-6 involves hydrogen bonding between the *trans*-ammine and the cyclic ether (see also Section 5.5.3.2.1).[25] Related studies have looked at the adducts formed between mono-, di-, tri-, and tetraammine Ru^{II} complexes and 18-crown-6,[193] and the effects of going from Ru^{II} to Ru^{III} on adduct formation between ammine complexes and 18-crown-6.[23,24,194] The interactions between $[Ru(NH_3)_5L]^{2+}$ (L = pyz or 4,4′-bpy) and α-cyclodextrin, β-cyclodextrin and dimethyl-β-cyclodextrin have also been investigated; equilibrium constants lie in the range 20–100. Encapsulation of the ammine complex affects the rate of electron transfer for Ru^{II} oxidation, there being a decrease in the observed rate constants. Steric arguments are used to account for these observations.[195]

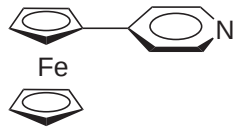
An efficient method of preparing $[Ru(NH_3)_4(L)][BF_4]_2$ where L = 2-acetylpyridine or 2-benzoyl pyridine starting from $[Ru(NH_3)_5Cl]^{2+}$ has been reported; spectroscopic and electrochemical data are discussed.[20]

Ruthenium(II) and osmium(II) ammine complexes incorporating π-bonded alkene ligands include $[M(NH_3)_5L]^{2+}$ where M = Ru, Os and L = styrene, 4-vinylbenzoic acid, dimethyl acetylene carboxylate, 1,3-cyclohexadiene and 3-cyclohexene-1,1-dimethanol. The complexes have been investigated by NMR spectroscopic and electrochemical techniques; there is preferential coordination of the vinyl C=C rather than an η^2-ring mode.[196] In the η^2-alkene complex $[Ru(NH_3)_5(H_2C{=}CHCONH_2)]^{2+}$, linkage isomerization for the acrylamide ligand accompanies oxidation of the metal center.[197]

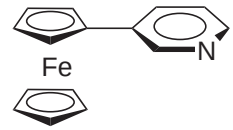
Ruthenium ammine complexes that also contain *P*-donor ligands have been reviewed, and this covers details of synthesis, characterization and reactivity.[198] The photolysis ($\lambda = 313$ nm) of *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(H_2O)]^{2+}$, *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}_2]^{2+}$, and *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}(CO)]^{2+}$ leads to photoaquation of NH_3 in each complex. At pH 4, exclusive NH_3 photoaquation occurs in *trans*-$[Ru(NH_3)_4\{P(OEt)_3\}_2]^{2+}$, but at pH 2, photoaquation of $P(OEt)_3$ is observed. Both NH_3 and CO photoaquation occur at pH 4 in $[Ru(NH_3)_4\{P(OEt)_3\}(CO)]^{2+}$.[199] For related complexes in which the phosphite ligand is $P(OMe)_3$ or $P(OC_2H_4Cl)_3$, photolabilization of both NH_3 and the *P*-donor ligand occurs in *trans*-$[Ru(NH_3)_4(P\text{-donor})_2]^{2+}$, and of NH_3 is observed in *trans*-$[Ru(NH_3)_4(P\text{-donor})(H_2O)]^{2+}$. The ammine ligand in each complex is selectively photolabilized when the samples are irradiated with light of energy corresponding to the $^1A_{1g} \rightarrow {}^1A_{2g}$ or $^1A_1 \rightarrow {}^1A_2$ transitions respectively.[200] The UV–visible absorption and emission spectra of *trans*-$[Ru(NH_3)_4(P\text{-donor})(H_2O)]^{2+}$ (*P*-donor = PR_3 or $P(OR)_3$) have been investigated. The complexes are luminescent at 298 K with emission quantum yields in the range 1.0×10^{-3} (for $P(O^iPr)_3$) and 8.4×10^{-2} (for $P(OBu)_3$); λ_{max}(emission) is close to 408 nm for each complex.[201]

The complexes $[Ru(NH_3)_5(\mathbf{26})]^{2+}$ and $[Ru(NH_3)_5(\mathbf{27})]^{2+}$ have been prepared and isolated as PF_6^- salts. Oxidation by ferrocenium ion occurs with the redox change being centered on Ru. The solvent has a significant effect on the difference between $E_{1/2}^{o}(Fe^{3+}/Fe^{2+})$ and $E_{1/2}^{o}(Ru^{3+}/Ru^{2+})$ and there is a linear relationship between this ΔE^o and the Gutmann solvent donor number.[202]

A review that surveys the preparation and spectroscopic and structural properties of hydrazine and substituted hydrazine complexes of *d*-block metals has appeared.[203] The syntheses of $[M(NH_2OH)(CO)_2(PPh_3)_2X][SO_3CF_3]$ and $[M(NH_2NH_2)(CO)_2(PPh_3)_2X][SO_3CF_3]$ (M = Ru, Os; X = Cl, Br) have been detailed. Treatment of $[M(NH_2NH_2)(CO)_2(PPh_3)_2X]^+$ with $Pb(OAc)_4$



(26)



(27)

yields $[M(NH{=}NH)(CO)_2(PPh_3)_2X]^+$.[204] The reactions between $[RuH_2L_4]$ ($L = P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$) and the bis(diazonium) salts $[N_2ArArN_2][BF_4]_2$ (ArAr = 4,4′-$C_6H_4C_6H_4$, 4,4′-(2-$MeC_6H_3C_6H_3$-2-Me), 4,4′-$C_6H_4CH_2C_6H_4$) yield $[HL_4Ru(\mu\text{-}HN{=}NArArN{=}NH)RuL_4H][BF_4]_2$. Spectroscopic data for the complexes are presented and the crystal structure of the analogous Fe complex $[H\{P(OEt)_3\}_4Fe(\mu\text{-}HN{=}NArArN{=}NH)Fe\{P(OEt)_3\}_4H][BF_4]_2$ has been determined, showing that the H and diazene ligands are mutually *cis*. The diruthenium cations react with $[RN_2]^+$ to produce $[(RN_2)L_4Ru(\mu\text{-}HN{=}NArArN{=}NH)RuL_4H]^{4+}$.[205] Treating $[OsH_2L_4]$ ($L = P(OEt)_3$, $PPh(OEt)_2$, $PPh_2(OEt)$ with methyl triflate and $RNHNH_2$ (R = H, Me, Ph, 4-$NO_2C_6H_4$) gives $[OsH(RNHNH_2)L_4]^+$. In contrast, if triflic acid is added after the methyl triflate, the complexes $[Os(RNHNH_2)_2L_4]^{2+}$ (R = H, Me, Ph) are isolated. Spectroscopic data are reported, and the crystal structure of $[Os(NH_2NH_2)_2\{P(OEt)_3\}_4][BF_4]_2$ has been determined; the hydrazine ligands are mutually *cis*. Related complexes including $[Os(MeN{=}NH)_2\{P(OEt)_3\}_4][BF_4]_2$ and $[Os(NH_2NH_2)\{P(OEt)_3\}_5][BF_4]_2$ have also been described.[206] Reaction of triflic acid with $[RuH_2L_4]$ ($L = P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$) followed by treatment with excess $RNHNH_2$ (R = H, Me, Ph, 4-MeC_6H_4, 4-$NO_2C_6H_4$) leads to the formation of $[RuH(RNHNH_2)L_4]^+$ and $[Ru(RNHNH_2)_2L_4]^{2+}$. Reactions of $[Ru(RCN)_2L_4]^{2+}$ (R = Me, C_6H_4-Me; $L = P(OEt)_3$, $PPh(OEt)_2$) with hydrazines have also been investigated and the products found to depend on L, the hydrazine and the reaction conditions.[207]

The electrochemical oxidation of $[Os(bpy)(tpy)(NH_3)]^{2+}$ in the presence of secondary amines in aqueous solution (pH 7) leads to $[Os(bpy)(tpy)(NNR_2)]^{3+}$ which can be reduced to $[Os(bpy)(tpy)(NNR_2)]^{2+}$. Structural data have been obtained for representative complexes. The redox chemistry of the new compounds has been described.[208]

The synthesis and structure of the mixed-valence, hydrazine-bridged complex $[\{P(OEt)_3\}_2ClRu(\mu\text{-}N_2H_4)(\mu\text{-}Cl)(\mu\text{-}S_2)RuCl\{P(OEt)_3\}]$ has been reported.[209]

Azido complexes of Ru^{II} include $[RuH(N_3)(dmpe)_2]$, formed by reacting NaN_3 with $[RuH_2(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphino)ethane). The reaction of NaN_3 with $[RuCl_2(depe)_2]$ yields *trans*-$[Ru(N_3)_2(depe)_2]$ (depe = 1,2-bis(diethylphosphino)ethane).[210] A related complex is *trans*-$[Ru(N_3)_2(PMe_3)_4]$; conversion to the *cis*-isomer occurs and has been followed by ^{31}P NMR spectroscopy and cyclic voltammetry.[211]

A series of complexes of type $[Ru(NO_2)(PR_3)_2(tpy)]^+$ has been prepared starting from $RuCl_3{\cdot}xH_2O$. Changing the PR_3 ligands causes the CV responses to vary from reversible to irreversible. Electrochemically generated $[Ru(NO_2)(PR_3)_2(tpy)]^{2+}$ is unstable with respect to $[Ru(NO)(PR_3)_2(tpy)]^{3+}$, perchlorate salts of which have been characterized.[212] The nitrite complex $[Ru(bpy)(NO_2)_4]^{2-}$ can be prepared conveniently from $[(\eta^6\text{-}C_6H_6)Ru(bpy)Cl]Cl$ and NO_2^- in MeOH, and the K^+ salt has been fully characterized; all nitrite ligands are *N*-coordinated. The reaction of $K_2[Ru(bpy)(NO_2)_4]$ with pyridine results in *fac*-$K[Ru(bpy)(NO_2)_3(py)]$ and *cis*-$[Ru(bpy)(NO_2)_2(py)_2]$.[213] Linkage isomerism for the NO_2^- ligand is exemplified in the three pairs of complexes $[Ru(NO)(NO_2\text{-}N)(bpy)_2]^{2+}$ and $[Ru(NO)(NO_2\text{-}O)(bpy)_2]^{2+}$, $[Ru(NO)(NO_2\text{-}N)L_2]$ and $[Ru(NO)(NO_2\text{-}O)L_2]$ (L = pyridine-2-carboxylate), and $[Ru(NO)(NO_2\text{-}N)(bpy)(py)_2]^{2+}$ and $[Ru(NO)(NO_2\text{-}O)(bpy)(py)_2]^{2+}$, and equilibria involving the isomer pairs have been studied. ^{15}N-labelling has been used to aid the investigation of the mechanisms of isomerization; no oxygen exchange between the NO and NO_2^- ligands was observed.[214]

Ambiguities often arise in assigning the oxidation state to the metal center when NO is involved as a ligand. In this review, the ligand is treated as NO^+ in the majority of cases, consistent with the description of a number of bonding analyses. The complexes below are, as a consequence, covered under "ruthenium(II)." The crystal structure of $Na_2[Ru(NO_2)_4(NO)(OH)]{\cdot}2H_2O$ has been determined.[215] The complex is photochromic and is excited with blue–green light. Synchrotron X-ray single crystal diffraction and FT-IR spectroscopic data for the ground and excited states of the low-temperature phase of $Na_2[Ru(NO_2)_4(NO)(OH)]{\cdot}2H_2O$ have been reported.[216] In the complex $[Ru(NO)(NO_2)_2(OEt)(Me_2NCH_2CH_2NMe_2)]$, the NO and ethoxy ligands are mutually *trans*.[217]

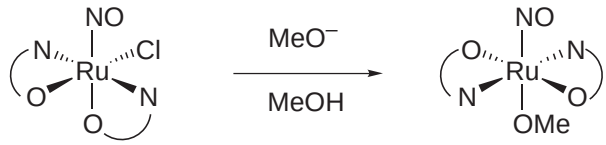
Starting from $[Ru(NO)Cl_5]^{2-}$, it is possible to obtain *cis*-$[Ru(NO)Cl_4(MeCN)]^-$ at 278 K in the absence of light. Structural characterization of this complex reveals a short N—O bond (99.8 pm) and an Ru—N—O bond angle of 175.1°. In the light, *cis*-$[Ru(NO)Cl_4(MeCN)]^-$ eliminates NO to yield *trans*-$[RuCl_4(MeCN)_2]^-$.[218] The electrochemical behavior of *mer*-$[Ru(NO)Cl_3(acac)]^-$, *cis*-$[Ru(NO)Cl(acac)_2]$, *mer*-$[Os(NO)Cl_3(acac)]^-$ and *cis*-$[Os(NO)Cl(acac)_2]$ has been investigated, and each complex was shown to undergo a one-electron oxidation. Structural data confirm the ligand dispositions.[219] The low-temperature IR vibrational spectra of the light-induced metastable states of $K_2[Ru(NO)Cl_5]$ have been recorded and analyzed and the results compared with those of $Na_2[M(NO)(CN)_5]\cdot 2H_2O$ (M = Fe, Ru, Os); there is evidence for NO linkage photoisomerization.[220] The ^{99}Ru Mössbauer effect (at 4.2 K) has been measured in several ruthenium NO complexes. The isomer shifts are similar for most of the complexes, but for $K_2[Ru^{II}(NO)Cl_5]$, it is significantly more negative, implying a strong ligand field in this complex.[221]

Decomposition of $[(NH_3)_4(NO)Ru(\mu\text{-}S_2)Ru(NO)(NH_3)_4]^{6+}$ gives *trans*-$[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ as one of the products. Spectroscopic and structural data support an NO^+ formulation. The substitution by Cl^- of the aqua ligand in $[Ru(NH_3)_4(NO)(H_2O)]^{3+}$ proceeds much more slowly than in $[Ru(NH_3)_5(H_2O)]^{3+}$. Theoretical (DFT) studies have probed the extent of O(aqua) π-donation.[222] New synthetic routes to the complexes *trans*-$[Ru(NH_3)_4(NO)L]^{3+}$ (L = imidazole, histidine, pyridine, nicotinamide, isonicotinamide or pyrazine) have been described; in each complex, IR spectroscopic data are consistent with a significant positive charge residing on the NO ligand.[223,224] The reduction of *trans*-$[Ru(NH_3)_4(NO)L]^{3+}$(L = isonicotinamide or pyrazine) with Eu^{II} result in the formation of NO and *trans*-$[Ru(NH_3)_4(H_2O)L]^{2+}$.[224] It has been found that in the series of complexes $[Ru(NH_3)_4(NO)L]^{n+}$ where L = nicotinamide, isonicotinamide, pyrazine, pyridine, imidazole, histidine, NH_3, $P(OMe)_3$, $P(OEt)_3$, there are correlations between the Lever parameter and (i) the potential for the reduction of $Ru(NO)^+$ to Ru(NO) and (ii) ν(NO). The gradient and intercept from the former linear correlation are related to interligand coupling through the Ru center and to the amount of Ru → NO backbonding.[225]

The preparation and properties of *cis* and *trans*-$[RuCl(NO)(bpy)_2]^{2+}$ and the crystal structure of the *trans*-isomer have been reported.[226] Flash-photolysis (λ = 355 nm) of aqueous *cis*-$[RuCl(NO)(bpy)_2]^{2+}$ releases NO and results in the formation of *cis*-$[Ru^{III}Cl(OH)(bpy)_2]^+$.[227] $[RuCl(NO)(bpy)_2]^{2+}$ undergoes electron transfer when it reacts with 2,2,2-trifluoroethylamine to form $[RuCl(NO)(bpy)_2]^+$. The organic products are a result of nucleophilic substitution on the intermediate 2,2,2-trifluoroethyldiazonium ion, the latter being stabilized by complexation.[228] The reaction of *cis*-$[Ru(NO)(H_2O)(bpy)_2]^{3+}$ with HCO_2H yields $[(bpy)_2Ru(\mu\text{-}NO)_2Ru(bpy)_2]^{2+}$ as well as *cis*-$[Ru(NO)(OCHO)(bpy)_2]^{2+}$ and *cis*-$[Ru(OCHO)(H_2O)(bpy)_2]^+$. In $[(bpy)_2Ru(\mu\text{-}NO)_2Ru(bpy)_2]^{2+}$, the bridging nitrosyl ligands are assigned an NO^- formulation. This dinuclear complex exhibits two successive one-electron oxidations to give $[(bpy)_2Ru(\mu\text{-}NO)_2Ru(bpy)_2]^{4+}$; the redox chemistry is discussed in detail.[229] The reaction of NO_2^- with *cis*-$[Ru(NO)(MeCN)(bpy)_2]^{3+}$ produces *cis*-$[Ru(NO_2)(MeCN)(bpy)_2]^+$ and *cis*-$[Ru(NO)(MeCONH)(bpy)_2]^+$. It is proposed that oxide abstraction from NO_2^- to the NO ligand is a key step in the pathway from $[Ru(NO)(MeCN)(bpy)_2]^{3+}$ to $[Ru(NO_2)(MeCN)(bpy)_2]^+$.[230] The synthesis and spectroscopic and structural characterization of *trans*-$[Ru(NO)(OH)(bpy)_2]^{2+}$ have been reported.[231] The related complex *trans*-$[Ru(NO)(OH)(en)_2]^{2+}$ has also been prepared, as well as *cis*- and *trans*-$[Ru(NO)X(en)_2]^{n+}$ (X = Cl, Br, I, OAc and NCS and n = 2; X = H_2O and n = 3). For the *trans* isomers, there is a decrease in the value of (NO) as the π-donor ability of X^- increases; a similar trend is not observed for the *cis* isomers.[232]

The nitrosyl complex *trans*-$[Ru(NO)Cl(py)_4]^{2+}$ reacts with acetone in the presence of NH_3 or RNH_2 to give α-imino oxime adducts. These data are consistent with a novel mechanism involving nucleophilic attack by enamines on the bound NO^+ ligand.[233] The complex *cis*-$[Ru(NO)(NO_2\text{-}O)(bpy)_2]^{2+}$ undergoes a redox-induced linkage-isomerization of the NO_2^- ligand. At 298 K, the product of the one-electron reduction of *cis*-$[Ru(NO)(NO_2\text{-}O)(bpy)_2]^{2+}$ converts rapidly to *cis*-$[Ru(NO)(NO_2\text{-}N)(bpy)_2]^+$, one-electron oxidation of which yields *cis*-$[Ru(NO)(NO_2\text{-}N)(bpy)_2]^{2+}$. Comparisons are made between this and related thermally induced processes.[234] The crystal structure of $[Ru(NO)X(OH)(bpy)(py)_2]^{2+}$ has been determined, and the results of chemical oxidation and electrochemical reduction of *cis*-$[Ru(NO)X(bpy)(py)_2]^{n+}$ (X = OH, Cl, NO_2 and n = 2; X = py and n = 3) have been discussed.[235]

Nucleophiles (e.g., OH^- and N_3^-) react with *cis*-$[Ru(NO)ClL_2]$ (HL = 2-pyridinecarboxylic acid) to produce $[L_2(NO)Ru(\mu\text{-}H_3O_2)Ru(NO)L_2]^+$, the bridging unit in which is formally $\{(H_2O)(OH^-)\}$. Treatment of *cis*-$[Ru(NO)ClL_2]$ with MeO^- in MeOH leads to *trans*-$[Ru(NO)(OMe)L_2]$. Isomerizations involving the *N,O*-donor sets that accompany this reaction are shown in Equation (3).[236]



cis-[Ru(NO)ClL$_2$] *trans*-[Ru(NO)(OMe)L$_2$] (3)

In the complexes [H_2L][$RuCl_3$(NO)L] and [$RuCl_2$(NO)L(HL)] (HL = 2-pyridine methanol), L^- acts as an *N,O*-chelate with the *O*-donor *trans* to the nitrosyl ligand, while HL is monodentate and an *N*-donor. By heating [$RuCl_2$(NO)L(HL)], [RuCl(NO)L_2] is obtained, while a geometrical isomer of this complex is produced from the reaction of hydrous nitrosylruthenium trichloride with an excess of HL in boiling water.[237] The same ruthenium(III) precursor has been used to prepare [$RuCl_3$(NO)L]$^-$ where HL = 8-quinolinol or one of its derivatives; the bromo analogs have also been made. A structural determination of [Me_4N][$RuBr_3$(NO)L] shows that the Br^- ligands are in a *mer* arrangement, each Br^- is *cis* to the nitrosyl group, and the *O*-donor of the chelating quinolinato ligand is *trans* to the NO. The observed structural preferences are consistent with the strong π-acceptor ability of the NO ligand.[238] Three geometrical isomers of [Ru(NO)(OAc)L_2] in which HL = 2-methyl-8-quinolinol have been structurally characterized,[239] and in related work, isomers of [Ru(NO)ClL_2] where HL = 2-methyl-8-quinolinol, 2,4-dimethyl-8-quinolinol, 2-ethyl-8-quinolinol and 5-chloro-8-quinolinol have been prepared and characterized.[240]

The osmium(II) complexes [Os(NO)Br_3(Et_2S)(Et_2SO-*O*)] and [Os(NO)Cl_2(PEt_2Ph)$_2$($MeOCH_2$-CH_2O)] have been prepared and crystallographically characterized. In both complexes, the NO ligand is bound in a linear mode.[241] [Ru$(NO)_2(PPh_3)_3$] can be prepared conveniently from $Ru(OH)_3$ (prepared *in situ* from $RuCl_3 \cdot xH_2O$), concentrated HNO_3 and PPh_3, or by treating an ethanolic solution of $HRu(SO_4)_2 \cdot 6H_2O$ with concentrated HNO_3 followed by PPh_3. A third method is the reaction of $AgNO_3$ with $RuCl_3 \cdot xH_2O$ in ethanol, followed by removal of AgCl and treatment with PPh_3. The reactions of [$Ru(NO)_2(PPh_3)_3$] with HX (X = Cl, Br, I) result in the formation of [$Ru(NO)X_3(PPh_3)_2$].[242] Reactions of [M(NO){$P(OEt)_2Ph$}$_4$]$^+$ (M = Ru, Os) (formed by deprotonating [M(NO)H{$P(OEt)_2Ph$}$_4$]$^{2+}$) with Br_2, isocyanides and CO have been investigated. Bromine oxidation leads to [Ru(NO)Br_2{$P(OEt)_2Ph$}$_3$]$^+$ or [Os(NO)Br{$P(OEt)_2Ph$}$_4$]$^{2+}$. With RNC or CO, the products are [M(RNC)$_4${$P(OEt)_2Ph$}$_2$]$^{2+}$ (M = Ru, Os) or [Ru(NO)$(CO)_2${$P(OEt)_2Ph$}$_2$]$^+$, respectively.[243] The synthesis and spectroscopic and structural characterization of *trans*-[Ru(NO)Cl(depe)$_2$]$^{2+}$ have been described; the nitrosyl ligand is bound in a linear mode and spectroscopic properties are consistent with NO^+ character. A reversible one-electron process at $E_{1/2} = 0.040$ V (vs. SHE) is assigned to the NO^+/NO redox couple.[244] The structure of [Ru(NO)Cl_3($AsPh_3$)$_2$] has been determined.[245]

The reaction of OsO_4 with $NH_2OH \cdot HCl$ in the presence of ox^{2-} produces [Os(NO)$(ox)_2$]$^-$, isolated as the K^+, PPh_4^+ or $AsPh_4^+$ salts. It is proposed that the anion possesses a square-based pyramidal structure. Treatment of [Os(NO)$(ox)_2$]$^-$ with HX (X = Cl, Br, I) produces [Os(NO)(ox)Cl_3]$^{2-}$, [Os(NO)$Br_4(H_2O)$]$^-$, [Os(NO)Br_4]$^-$, and [Os(NO)X_5]$^{2-}$ (X = Cl, Br, I). The ligand phen reacts with [Os(NO)X_5]$^{2-}$ (X = Cl, I) to give [Os(NO)X_3(phen)] or with [Os(NO)Br_5]$^{2-}$ to yield [Hphen]$_2$[Os(NO)Br_5]$\cdot 2H_2O$.[246]

The dinuclear complex *trans*-[(NO)(py)$_4$Ru(μ-CN)Ru(py)$_4$(CN)]$^{3+}$ has been prepared and spectroscopically characterized. Photoinduced extrusion of NO occurs when the complex is irradiated at the donor–acceptor CT band. Electronic coupling in the complex is discussed, as well as the results of controlled potential reduction (of NO) and oxidation (of Ru^{II} in the dicyano chromophore).[247] Bridging NO ligands are observed in [(acac)$_2$Ru(μ-NO)$_2$Ru(acac)$_2$] which formally possesses a $\{Ru_2(NO)_2\}^{4+}$ core. The complex exhibits two one-electron reductions (one reversible and the other irreversible) and an irreversible two-electron oxidation in which decomposition to *cis*-[Ru(NO)(MeCN)(acac)$_2$]$^+$ occurs.[248]

Treatment of [$Ru^{III}LCl_2$]$^+$ (L = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) with NO_2^- results in disproportionation of the initial [Ru^{III}LCl(NO$_2$)]$^+$, and the ultimate products are [Ru^{II}L(OH)(NO)]$^{2+}$ and *trans*-[Ru^{IV}L(O)Cl]$^+$.[46]

The thionitrosyl ligand features in [Os(NS)Cl_3(PPh_3)$_2$], the crystal structure of which has been determined. The phosphine ligands are mutually *trans*.[249]

Several papers have reported N_2 bound to Ru^{II} or Os^{II}. Aqueous solution studies with the aim of preparing [$Ru(H_2O)_5(N_2)$]$^{2+}$ by reaction between [$Ru(H_2O)_6$]$^{2+}$ and N_2 (^{15}N labeled) have been described. The reaction was monitored by use of ^{17}O and ^{15}N NMR spectroscopies and evidence

is presented for the first observation of the formation of the fully aquated N_2 complex of Ru^{II}.[250] *trans*-$[RuCl_2L]$ in which L is the macrocyclic ligand 2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane, reacts with Mg under an atmosphere of N_2 in aqueous solution and at ≈298 K to give *trans*-$[RuCl(N_2)L]^+$. This is the first complex of its type, and is subsequently converted into *trans*-$[Ru(OH)(N_2)L]^+$ and *trans*-$[Ru(H_2O)(N_2)L]^{2+}$.[251] The complex $[RuH_2(N_2)_2(PCy_3)_2]$ is formed by the reversible reaction of N_2 with $[RuH_2(H_2)_2(PCy_3)_2]$. The latter reacts with Ph_3SiH or Ph_3GeH to yield $[RuH_2(H_2)(Ph_3SiH)(PCy_3)_2]$ or $[RuH_2(H_2)(Ph_3GeH)(PCy_3)_2]$ which react immediately with N_2 to produce $[RuH_2(N_2)_2(PCy_3)_2]$. In the case of the Ge-containing complex, a second product is $[RuH_2(N_2)(Ph_3GeH)(PCy_3)_2]$.[252] By treating $[OsH_2L_4]$ (L = PPh_2OMe, PPh_2OEt, $PPh(OEt)_2$) with CF_3SO_3Me in Et_2O under N_2, the complexes $[OsH(N_2)L_4][CF_3SO_3]$ are obtained with concomitant evolution of CH_4. Substitution reactions with H_2, CO, and RNC have been investigated.[253]

The next subsection deals with Ru^{II} and Os^{II} complexes in which pyridine and derivative ligands are of interest. DFT calculations have been used to probe the bonding in $[Ru(CN)_5L]^{n-}$ where L = py, pyz, *N*-Mepyz$^+$. The Ru–L dissociation energies follow the order py < pyz < *N*-Mepyz$^+$, and this is consistent with the predicted σ-donating and π*-accepting abilities of the heterocyclic ligands.[254] Structural data for *trans*-$[RuCl_2(py)_4]$ reveal that the compound exhibits shorter M—N and M—Cl bond lengths than the corresponding Fe^{II}, Co^{II}, and Ni^{II} complexes.[255] The reaction of *trans*-$[RuCl_2(py)_4]$ with TlL (HL = 2-ClC_6H_4NCNH, 2,3-$Cl_2C_6H_3NCNH$, 2,4,5-$Cl_3C_6H_2NCNH$, 2,3,4,5-Cl_4C_6HNCNH, and C_6Cl_5NCNH) in dmf yields *trans*-$[RuL_2(py)_4]$. The *trans* arrangement has been crystallographically confirmed, and spectroelectrochemical studies have accessed the corresponding Ru^{III} complexes.[256] The syntheses of *trans*-$[RuCl_2(Hnic)_4]$ and *trans*-$[RuCl_2(Hinic)_4]$ (Hnic and Hinic = 3- and 4-pyridinecarboxylic acid)[257] and *trans*-$[RuCl_2(dinic)_4]$ (H_2dinic = 3,5-pyridinedicarboxylic acid)[258] from a "ruthenium blue" have been described. The complexes have been characterized[257,258] and there is a pH dependence on the MLCT absorptions in the electronic spectra for the Hnic and Hinic complexes; a blue shift is observed as the pH increases.[257] The reaction of *trans*-$[RuCl_2(py)_4]$ with an excess of NO_2^- or CN^- in refluxing pyridine leads to *trans*-$[Ru(NO_2)_2(py)_4]$ or *trans*-$[Ru(CN)_2(py)_4]$ respectively. If *trans*-$[Ru(NO_2)_2(py)_4]$ is treated with concentrated HCl at reflux, the product is *trans*-$[Ru(NO)Cl(py)_4]^{2+}$. This can be converted to *trans*-$[RuCl(py)_4(Me_2CO)]^+$, a labile complex that is used as a precursor to *trans*-$[RuCl(py)_4L]^+$ where L is an *N*-donor ligand. The reaction of *trans*-$[Ru(NO)Cl(py)_4]^{2+}$ with *trans*-$[RuCl(py)_4(pyz)]^+$ or pyrazine leads to the formation of $[Cl(py)_4Ru(\mu\text{-pyz})Ru(py)_4Cl]^{2+}$.[259]

Photolysis using near UV-vis irradiation of *cis*-$[Ru(NH_3)_4(py)_2]^{2+}$, related complexes in which the heterocyclic ligand is 4-methylpyridine, 4-acetylpyridine or isonicotinamide (isn), and *cis*-$[Ru(NH_3)_4(isn)L]^{2+}$ (L = py, 4-methylpyridine, 4-acetylpyridine), results in NH_3, isn and L aquation. Detailed analysis of the observations is given.[260] The photochemical behavior of *cis*,*cis*,*trans*-$[RuCl_2(dmso)_2(4\text{-}^tBupy)_2]$ has been studied; excitation at the CT and ligand-field absorptions results in labilization of the dmso ligand; the corresponding MeCN complexes are produced with complete retention of configuration.[261]

The syntheses of $[Ru(NCX)Y(bpy)(py)_2]^{n+}$ (X = O, Y = NO_2 and $n = 0$; X = O, Y = py and $n = 1$; X = S, Y = NO_2 and $n = 0$; X = S, Y = NO and $n = 2$; X = S, Y = py and $n = 1$) have been reported, and the structures of representative complexes have been determined.[262]

A family of compounds of the general formula $[RuCl_2(CO)L(PPh_3)_2]$ where L is an *N*-heterocyclic ligand (e.g., py, 2-CNpy, 3-CNpy, 4-CNpy, 2-Mepy, 3-Mepy, 4-Mepy, 1-Meim, 2-Meim) has been synthesized and spectroscopically and electrochemically characterized, and a number of physicochemical parameter correlations are explored. The structure of $[RuCl_2(CO)(4\text{-Mepy})(PPh_3)_2]$ has been elucidated.[263] Reaction of $[RuH_2(CO)(PPh_3)_3]$ with $[C_7H_7][BF_4]$ in the presence of excess py, 4-Mepy or bpy leads to the formation of $[RuH(CO)(PPh_3)_2L_2]$ where L = py or 4-Mepy, or L_2 = bpy. Characterization of the products includes the X-ray structure of $[RuH\text{-}(CO)(PPh_3)_2(4\text{-Mepy})_2]$; the two *N*-donors are mutually *cis* with the two PPh_3 ligands mutually *trans*.[264] The reaction of $[MHCl(CO)(PPh_3)_3]$ (M = Ru, Os) with HgL_2 (L^- = 2-(2′-pyridyl)phenyl) results in the formation of $[MCl(CO)(PPh_3)_2L]$ in which L^- acts as an *N*,*C*-donor. An additional ligand can be introduced by first abstracting Cl^-; this method gives routes to $[MI(CO)(PPh_3)_2L]$, $[M(CO)_2(PPh_3)_2L]^+$ and $[M(CO)(PPh_3)L(S_2CNMe_2)]$.[265] The use of HgL_2 precursors has been extended to the transformations of $[MHCl(CO)(PPh_3)_3]$ (M = Ru, Os) to $[MCl(CO)(PPh_3)_2L]$ in which HL = 2-(1′-naphthyl)-pyridine, 2-phenylquinoline and 2,3-diphenylquinoxaline. Chloride substitution by $Me_2NCS_2^-$ in $[MCl(CO)(PPh_3)_2L]$ proceeds with loss of one PPh_3 ligand to give $[M(CO)(PPh_3)L(S_2CNMe_2)]$.[266] Coordination of each L^- to Ru^{II} or Os^{II} activates it towards electrophilic substitution, and nitration and bromination reactions are described.[265,266]

Resonance Raman spectra have been reported and assigned for the ground and excited states of $[Ru(NH_3)_5(4,4'\text{-bpy})]^{2+}$ and $[Ru(NH_3)_5(4,4'\text{-bpyH})]^{3+}$.[267] There has been considerable interest in Ru^{II} complexes containing the *N*-methyl-4,4′-bipyridinium and related ligands, and in the potential applications of some of these complexes in nonlinear optical (NLO) materials. The electronic spectrum of the *N*-methyl-4,4′-bipyridinium radical ($MQ^{\cdot}$) exhibits broad absorptions at 360 nm and 600 nm assigned, respectively, to $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ ligand radical transitions. Resonance Raman spectroscopic data for $MQ^{\cdot}$, $[Ru(bpy)_2(MQ^{\cdot})_2]^{2+}$ and $[Os(bpy)_2(MQ^{\cdot})(CO)]^{2+}$ have been reported, and band assignments include that for the $M^{II}(d\pi) \rightarrow MQ^{\cdot}(\pi^*)$ MLCT transition.[268] The complexes $[Ru(NH_3)_5L]^{3+}$ ($L^+ = N$-R-4,4′-bipyridinium; R = Me, Ph, 2,4-$(NO_2)_2C_6H_3$), $[Ru(NH_3)_4(1\text{-Meim})L]^{3+}$ ($L^+ = N$-R-4,4′-bipyridinium; R = Me, Ph) and $[Ru(NH_3)_4(4\text{-}NMe_2py)L]^{3+}$ ($L^+ = N$-R-4,4′-bipyridinium; R = Me, Ph) have been prepared and characterized. The complexes all possess donor–acceptor groups that are mutually *trans*, and they exhibit large, tunable static first hyperpolarizabilities, β_0, that are associated with intense, low-energy MLCT excitations.[269] The series of compounds has been extended and further explored, and *trans*-$[Ru(NH_3)_4(4\text{-}NMe_2py)L]^{3+}$ where $L^+ = N$-(4-acetylphenyl)-4,4′-bipyridinium is found to have a particularly large β_0 value.[270] The complexes in these series exhibit completely reversible switching of large molecular quadratic NLO responses.[271] More recently, the range of complexes has included the acceptors *N*-methyl-2,7-diazapyrenium and *N*-(2-pyrimidyl)-4,4′-bipyridinium. Among the general trends that have become apparent, it is observed that for a given acceptor ligand, the MLCT energy decreases as the donor strength of the donor ligand increases, and follows the order py < NH_3 < 1-Meim. The complex exhibiting the largest β_0 value is *trans*-$[Ru(NH_3)_4(1\text{-Meim})L]$ where $L^+ = N$-methyl-2,7-diazapyrenium.[272] Salts previously observed to exhibit large β_0 values have been studied by using electroabsorption spectroscopy in butronitrile glasses at 77 K.[273] The complexes *trans*-$[Ru\{1,2\text{-}(Me_2As)_2C_6H_4\}_2Cl]^{2+}$ ($L^+ = N$-R-4,4′-bipyridinium; R = Me, Ph, 4-AcC_6H_4, 2,4-$(NO_2)_2C_6H_3$, 2-pyrimidyl) have been synthesized and characterized, but show no evidence for ground state charge-transfer even though they are strongly dipolar and polarizable.[274]

The reader is also directed to Section 5.5.3.1.21 for a discussion of miscellaneous *N*-heterocyclic ligands.

5.5.3.1.2 *$[M(bpy)_3]^{2+}$ (M = Ru or Os; bpy = 2,2′-bipyridine) and related heteroleptic complexes containing 2,2′-bipyridine, 2,2′-bipyrimidine, and 2,2′-bipyrazine*

The widespread interest in $[Ru(bpy)_3]^{2+}$ chemistry necessarily leads to a substantial section devoted to this and related complexes. Two reviews cover general aspects of 2,2′-bipyridine coordination chemistry: $[M(bpy)_3]^{n+}$ (M = Ru, Os)[275] and complexes containing at least two bpy units.[276] Further reviews are given in Section 5.5.3.1.4. General methods of synthesis of $[Ru(bpy)_3]^{2+}$ include those of $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$,[277,278] $[Ru(bpy)_3][ClO_4]_2 \cdot H_2O$,[279] and $[Ru(bpy)_3][NO_3]_2 \cdot 6H_2O$,[279] and a one-pot synthesis of $[Ru(bpy)_3]^{2+}$ and related Ru^{III} complexes.[280] The application of microwave irradiation has been described for the preparation of a range of Ru^{II} polypyridine complexes including $[Ru(bpy)_3][ClO_4]_2 \cdot 3H_2O$, $[Ru(bpy)_3][PF_6]_2$, $[Ru(bpy)_3][SO_4]$. Salts of $[Os(bpy)_3]^{2+}$ can be synthesized by the same method although yields are lower than for the corresponding Ru^{II} complexes.[281] The advantage of the microwave irradiation over more traditional methods of synthesis is the reduction in reaction times from, typically, 4 h to 20 min. General procedures to tris(heteroleptic)ruthenium(II) and osmium(II) complexes where the ligands are didentate polypyridyl species have also been described.[282,283]

There have been several crystallographic studies involving the $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ ions: $[Os(bpy)_3][PF_6]_2$,[284] $[Ru(bpy)_3][PF_6]_2$,[285] $[Ru(bpy)_3][ClO_4]_2$,[286] and $[Ru(bpy)_3]_2[W_{10}O_{32}] \cdot 3dmso$.[287] In the latter, the cations occupy cavities in the polyoxometallate lattice and there are C—H—O hydrogen bonds between the cations and anions. A comparison has been made between the structures of $[Ru(bpy)_3][PF_6]_2$ and $[Ru(bpm)_3][PF_6]_2$ (bpm = 2,2′-bipyrimidine).[285] In the solid state, $Na[Ru(bpy)_3][Ru(ox)_3]$ has a 3D network structure that is chiral, the absolute configuration being Λ.[288] The results of X-ray diffraction studies of aqueous solutions of sulfates or chlorides of $[Ru(bpy)_3]^{2+}$ indicate that approximately two H_2O molecules are present at a distance of 350–360 pm from the Ru^{II} center, and that 10–11 H_2O molecules are in the range 530–630 pm. Further high-electron density peaks were observed in the region of 770–1,120 pm from the cation.[289] The $[RuL_3][PF_6]_2 \cdot Me_2CO$ has been determined; the cation has a similar structure to that of $[Ru(bpy)_3]^{2+}$ but the replacement of C by N atoms in the ligands has a significant effect on the crystal packing.[290]

X-ray structural data for $[Ru(bpy)_3]^{2+}$ and a wide range of other polypyridyl derivatives of Ru^{II} have been used to develop molecular mechanics parameters for these types of complex with the MM3* force field. Correlations between coordination geometry and emission properties of the Ru^{II} complexes have been examined.[291]

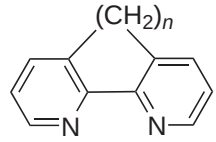
Spectroscopic studies of $[M(bpy)_3]^{2+}$ (M = Ru, Os) have included ^1H NMR spectroscopic investigations of the one- and three-electron reduced forms of these complexes. ^1H NMR contact shifts have been measured for $[M(bpy)_3]^{+}$ and $[M(bpy)_3]^{-}$ and the results used to estimate spin density distributions.[292] The ^{99}Ru NMR spectra of $[Ru(bpy)_3]^{2+}$ and other polypyridyl derivatives of Ru^{II} in MeCN have been recorded. The chemical shifts are sensitive to the coordination environment and have been correlated with the energies of the MLCT bands for the complexes.[293] NMR spectroscopy has been used to investigate the ground state interactions between $[Ru(bpy)_3]^{2+}$ and phenol or monochlorophenols in D_2O; analogous studies with $[Ru(bpz)_3]^{2+}$ (bpz = 2,2′-bipyrazine) have also been reported. There is evidence for offset face-to-face π-stacking interactions between PhOH and the ligands. The formation constants for the 1:1 $[Ru(bpy)_3]^{2+}$:ArOH complexes follow the order $C_6H_5OH < 4\text{-}ClC_6H_4OH < 3\text{-}ClC_6H_4OH < 4\text{-}ClC_6H_4OH$.[294]

Spectroscopic properties of $[Ru(bpy)_3]^{2+}$,[295] and the effects of varying the diimine ligands in $[Ru(bpy)_{3-n}L_n]^{2+}$ (L = diimine) on the electronic spectra and redox properties of these complexes have been reviewed.[296] The properties of the optical emission and excitation spectra of $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2(bpy\text{-}d^8)]^{2+}$ and $[Ru(bpy\text{-}d^8)_3]^{2+}$ and of related Os^{II}, Rh^{III}, and Pt^{II} and Os^{II} species have been analyzed and trends arising from changes in the metal d or MLCT character in the lowest triplet states have been discussed.[297] A study of the interligand electron transfer and transition state dynamics in $[Ru(bpy)_3]^{2+}$ has been carried out.[298] The results of X-ray excited optical luminescence and XANES studies on a fine powder film of $[Ru(bpy)_3][ClO_4]_2$ show that C and Ru localized excitation enhances the photoluminescence yield, but that of N does not.[299]

Comparisons between the electronic structures (using a ZINDO analysis) of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)(NH_3)_4]^{2+}$, and between related pairs of compounds where bpy is replaced by 2,2′-bipyrazine or 1,2-benzoquinonediimine, show that bpy is unable to accept extra electron density from the metal center whereas the opposite is true for 1,2-benzoquinonediimine. The acceptor properties of the 2,2′-bipyrazine ligand fall between those of bpy and 1,2-benzoquinonediimine.[300] Using the Fenske–Hall method, the electronic structures of $[Ru(bpy)_{3-n}(ppy)_n]^{(2-n)+}$ (Hppy = 2-phenylpyridine) have been investigated. The coordinated ppy^- is a *C,N*-donor. The electronic structures of the heteroleptic complexes exhibit a separation of the Ru—C and Ru—N σ-bonding character. It is proposed that the observed preference for *cis*- over *trans*- and for *fac*- over *mer*-isomers may arise from the enhanced σ-donating ability of the C atom when it is *trans* to an *N* rather than *C*-donor.[301]

A study of the vibrational spectra of $[Ru(bpy)_3]^{2+}$ has included normal coordinate analyses of both the ground and ^{3}MLCT excited states of the complex.[302,303] The results of normal-coordinate analysis calculations can be used to gain structural data for transient species; the method has been applied to calculate the ^{3}MLCT-state structure of $[Ru(bpy)_3]^{2+}$.[304] Resonance Raman and time-resolved Raman spectra of $[Ru(bpy)_2L]^{2+}$ and $[RuL_3]^{2+}$ (L = 4, 4′-bipyrimidine) have been recorded and analyzed. The time-resolved Raman studies using a 354.7 nm harmonic of a 10 ns Nd:YAG laser show that there is selective population of the bpm-localized excited state for $[Ru(bpy)_2L]^{2+}$.[305] A resonance Raman spectroscopic investigation of $[RuL_nL'_{3-n}]^{2+}$ where L, L′ = bpy, 4,4′-Me_2bpy, 4,4′-Br-2-bpy, and $n = 0$–3 shows that for the homoleptic complexes, the lowest excited state has the excited electron localized on one of the ligands, and for most of the heteroleptic complexes, the excited electron is localized on the more easily reduced ligand. For $[Ru(bpy)(4,4'\text{-}Me_2bpy)_2]^{2+}$ and $[Ru(bpy)(4,4'\text{-}Br_2bpy)_2]^{2+}$, however, the Raman data are consistent with a mixture of excited-state species.[306] A picosecond Raman-scattering study has been made of the electron localization in the CT excited state of $[Ru(bpy)_3]^{2+}$.[307] Resonance Raman and time-resolved Raman spectroscopy have been used to investigate the ^{3}MLCT populations of a series of Ru^{II} complexes containing bpy and tetramethylbipyridine ligands,[308] of complexes containing 2-(2-pyridyl)pyrazine,[309] and of Ru^{II} complexes with bpy and bpz ligands.[310] Resonance Raman spectra of $[Ru(bpz)_3]^{2+}$ in sulfuric acid solutions of various concentrations are consistent with protonation of all the non-coordinated N atoms; the first three protonation steps involve successive ligands to give $[Ru(Hbpz)_3]^{5+}$.[311] Resonance-enhanced Raman spectroscopy has been used to measure the lifetimes and emission spectra (at 298 and 77 K) of $[RuL_3]^{2+}$ where L is one of the polymethylene bridged ligands (**28**). The resonance Raman and emission spectra differ as a function of the length of the polymethylene bridge; as *n* varies from 1 to 4, there is

increased twisting about the 2,2′-bond in the bipyridine ligand and therefore an increased deviation from planarity.[312] Analysis of highly resolved emission spectra of $[RuL_nL'_{3-n}]^{2+}$ (L and L′ = bpy, bpy-d^8, bpz) doped into $[Zn(bpy)_3][ClO_4]_2$ shows that there is a distinction between the localized and delocalized MLCT transitions to the lowest excited states. For example, localized excitation in $[Ru(bpy)_2(bpz)]^{2+}$ means that only ligand-centered modes of bpz are observed in the emission spectrum. In $[Ru(bpy)_2(bpy\text{-}d^8)]^{2+}$, there is evidence for delocalization of the excited state electron as is observed in $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy\text{-}d^8)_3]^{2+}$.[313] Related studies at 1.3 K on $[Os(bpy)_n(bpy\text{-}d^8)_{3-n}]^{2+}$ ($n = 1, 2$) doped into $[Zn(bpy)_3][ClO_4]_2$ have been carried out, and the properties of the complexes are compared with those of $[Os(bpy)_3]^{2+}$ and $[Os(bpy\text{-}d^8)_3]^{2+}$. The emission lifetimes increase on deuteration, and it is concluded that, in contrast with previous models, the excited electronic state is delocalized over the three ligands.[314] Electronic absorption and ESR spectroscopic data for $[RuL_x(bpy)_{3-x}]^{2-n}$ (L = 2-(2′-pyridyl)quinoline; $x = 1$–3; $n = 0$–3) provide evidence that the electrochemically generated electrons are localized onto separate ligands. The compositions of the redox orbitals of the mixed-ligand systems have been analyzed.[315]



n = 1–4

(**28**)

Time-resolved IR difference spectra for the MLCT excited states in the range 1,400–1,625 cm^{-1} have been recorded for $[Ru(bpy)_3]^{2+}$. By comparisons with ground-state spectroscopic data and data for the electrochemically generated $[Ru(bpy)_3]^{3+}$ and $[Ru^{II}(bpy^{\cdot-})(bpy)_2]^{+}$, it has been possible to assign the new spectra; the results provide evidence for a localized $*[Ru^{III}(bpy^{\cdot-})(bpy)_2]^{2+}$ on a 100 ns timescale.[316]

The long lifetimes and high redox potentials of a range of ruthenium(II) complexes and in particular $[Ru(bpy)_3]^{2+}$ have important consequences for their use as photoactive redox catalysts. This area of research is extremely active and we now focus on the decay of the excited state of $[Ru(bpy)_3]^{2+}$ ($*[Ru(bpy)_3]^{2+}$) and its quenching. Braterman *et al.* have described the electronic absorption spectrum and structure of the emitting state of $[Ru(bpy_3]^{2+}$, and the effects of excited state asymmetry.[317,318] The effects of solvent on the absorption spectrum of $*[Ru(bpy)_3]^{2+}$ have been studied. In H_2O, MeCN and mixtures of these solvents, the value of ε(450 nm) remains the same ($(4.6 \pm 0.4) \times 10^3$ dm^3 mol^{-1} cm^{-1}). The ground state spectrum is essentially independent of solvent ($\varepsilon(452\,nm) = 1.46 \times 10^4\,dm^3\,mol^{-1}\,cm^{-1}$).[319] The studies have been extended to $*[Ru(phen)_3]^{2+}$. For both $*[Ru(bpy)_3]^{2+}$ and $*[Ru(phen)_3]^{2+}$, the decay parameters as a function of temperature in H_2O, MeCN and mixtures of these solvents are similar. The results suggest that the nature of the localization of the electron in the excited state has little effect on the photophysics and electron-transfer quenching in fluid solution at 298 K.[320] Studies have also been made of the ^{3}MLCT state of $[Os(bpy)_3]^{2+}$ in H_2O–MeOH (or in deuterated systems), and in H_2O–D_2O and H_2O–dioxane mixtures. An isotope effect on the rate-constant of the nonradiative decay of the excited state is observed in water, but the effect is only small in MeOH; the rate of decay in H_2O–D_2O shows a linear dependence on the mole fraction of D_2O, but there is no such dependence on the mole fraction of MeOH in the H_2O–MeOH mixtures.[321] The solvent effects of a series of linear alcohols on the nonradiative decay of $*[Ru(bpy)_3]^{2+}$ have also been investigated.[322] The decay of the ^{3}CT states of $[Ru(bpy)_2L][ClO_4]_2 \cdot 2H_2O$, $[Ru(bpy)_2L][PF_6]_2 \cdot 2H_2O$, $[Ru(biq)_3][ClO_4]_2$, $[Ru(tpy)_2][ClO_4]_2$ and $[Ru(tpy)_2][PF_6]_2$ has been studied for crystalline samples over the temperature range 77–480 K, and spectra compared with those of solution samples. For the salts of $[Ru(tpy)_2]^{2+}$, it is concluded that the rate-determining step of the ^{3}CT decay above 200 K is the exoergonic intersystem crossing of ^{3}(d–d) to the ground state.[323]

Time-resolved femtosecond (fs) absorption spectroscopy has been applied to investigate the earliest events of the decay of $*[Ru(bpy)_3]^{2+}$ and provides information relating to the dynamics associated with the evolution of the Franck–Condon state to the lowest-energy excited state of $[Ru(bpy)_3]^{2+}$. Within 300 fs of the initial excitation, the latter process is effectively complete. The conclusions of this work are of particular importance in terms of updating the views concerning the relaxation of $*[Ru(bpy)_3]^{2+}$.[324]

Many investigations of the quenching of $*[Ru(bpy)_3]^{2+}$ have been reported, a large proportion of which involve viologens as the electron-transfer agent. Applications to the photoreduction of water are a major driving force for research in this area. Scheme 1[325] shows the hydrogen-producing cycle with a general electron-transfer agent (ETA) and utilizing a colloidal platinum dispersion on polyvinyl alcohol (Pt(PVA)).

$$[Ru(bpy)_3]^{2+} \xrightarrow{h\nu} *[Ru(bpy)_3]^{2+}$$

$$*[Ru(bpy)_3]^{2+} \longrightarrow [Ru(bpy)_3]^{2+}$$

$$*[Ru(bpy)_3]^{2+} + ETA \longrightarrow [Ru(bpy)_3]^{3+} + ETA^{-}$$

$$*[Ru(bpy)_3]^{2+} + ETA \longrightarrow [Ru(bpy)_3]^{2+} + *ETA$$

$$[Ru(bpy)_3]^{3+} + ETA^{-} \longrightarrow [Ru(bpy)_3]^{2+} + ETA$$

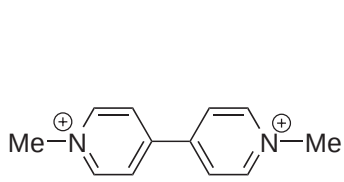
$$2ETA^{-} + 2H^{+} \xrightleftharpoons{Pt(PVA)} 2ETA + H_2$$

$$[Ru(bpy)_3]^{3+} + edta^{4-} \longrightarrow [Ru(bpy)_3]^{2+} + edta^{3\bullet-} \downarrow \text{products}$$

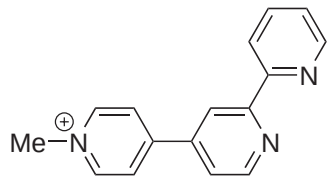
Scheme 1

A number of cobalt(III) encapsulated cage complexes have been used as electron-transfer agents; their advantage over viologens is their long-term stability in photochemical cycles. The most effective complex is $[CoL]^{3+}$ where L is 1-chloro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane; at a concentration of 4×10^{-3} mol dm^{-3}, this cage exhibits a similar ability to methylviologen to produce H_2.[325] Laser flash photolysis in sodium dodecyl sulfate and sodium laurate micelles has been used to investigate the kinetics of electron transfer between $*[Ru(bpy)_3]^{2+}$ and *N,N*′-dimethylviologen (MV^{2+}, (**29**)). The decay follows first-order kinetics ($k_{obs} \approx 10^6$–10^7 s^{-1}); dependences of k_{obs} on surfactant and quencher concentration, as well as detailed analysis of the data have been discussed.[326] The temperature dependences of the rate constant and product cage escape yields for the electron transfer from $*[Ru(bpy)_3]^{2+}$ to MV^{2+} in 1-butyl-3-methylimidazolium hexafluorophosphate have been investigated; under these conditions, photoelectron transfer occurs at a diffusion-controlled rate.[327] Photophysical properties of $[Ru(bpy)_2(MQ)_2]^{4+}$ ($MQ^+ = N$-methyl-4,4′-bipyridinium ion) and $[Ru(bpy)_2(\mathbf{30})]^{3+}$ have been compared, and the crystal structure of the PF_6^- salt of the latter determined. $[Ru(bpy)_2(MQ)_2]^{4+}$ exhibits strong luminescence from the Ru → bpy MLCT state (80 K in EtOH-MeOH glass) and this transition is quenched at the temperature of the solvent glass-to-fluid transition as a result of ligand-to-ligand CT. Over the range 80–300 K, the dominant feature of $[Ru(bpy)_2(\mathbf{30})]^{3+}$ is the low-lying Ru → (**30**) MLCT state.[328] Ligands (**31**) have been incorporated into a series of complexes $[Ru(bpy)_2(\mathbf{31})]^{4+}$ and $[Ru(4,4'\text{-}Me_2bpy)_2(\mathbf{31})]^{4+}$, and the effect of O_2 on the electrogenerated chemiluminescence of these species has been studied. The light emission occurs not from an MLCT excited state, but from decomposition products formed from the reaction of O_2 with the viologen units. This reaction prevents quenching of the excited state by the viologen.[329] The rates of electron transfer from the MLCT excited state to the viologen acceptors in the complexes $[Ru(bpy)_{3-n}(\mathbf{32})_n]^{(2+2n)+}$, $[Ru(4,4'\text{-}Me_2bpy)_{3-n}(\mathbf{32})_n]^{(2+2n)+}$, and $[4,4',5,5'\text{-}Me_4Ru(bpy)_{3-n}(\mathbf{32})_n]^{(2+2n)+}$ have been measured, and the results have been discussed in terms of a kinetic model involving rapid MLCT exciton hopping and rate-determining electron transfer to the viologen.[330] Ligands related to (**32**) but with a wider range of spacers between the donor and acceptor centers have also been investigated. For $(CH_2)_m$ spacers, the rate constant for electron transfer decreases significantly as the number of CH_2 groups increases.[331] The complexes $[Ru(bpy)_2(\mathbf{33})]^{6+}$ have been synthesized and characterized by spectroscopic and electrochemical methods. In the ground state, there is no interaction between the Ru^{II} center and the bisviologen

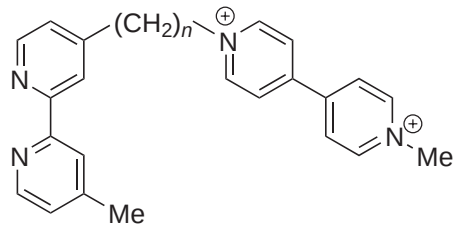
unit. Quenching of the photoexcited state has been examined, and electrochemical studies show that photoinduced two-step electron transfer from the Ru center to the bisviologen occurs to give long-lived, charge-separated states.[332] Related work reports the application of these systems to photoinduced H_2 evolution in a system containing the reduced form of NADPH.[333,334]



(**29**)

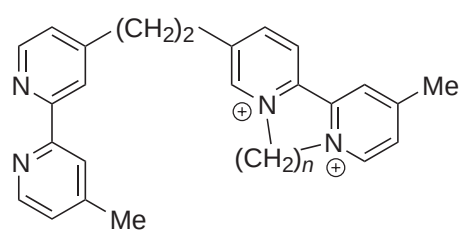


(**30**)



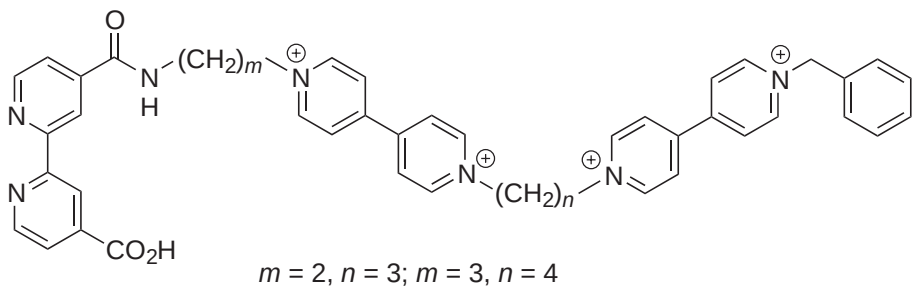
n = 1, 2, 3, 5, 8

(**31**)



n = 2, 3, or 4

(**32**)

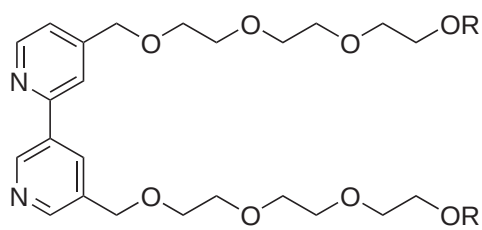


m = 2, *n* = 3; *m* = 3, *n* = 4

(**33**)

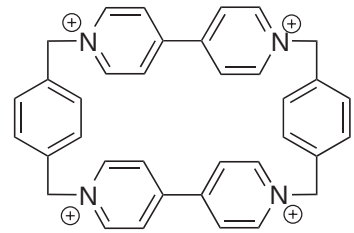
The interactions between the complexes $[Ru(\mathbf{34})_3]^{2+}$ and MV^{2+} (**29**) or the cyclic bis(bipyridinium) ion (**35**) have been studied. Supramolecular association can occur between the dialkoxybenzene units of (**34**) (R = 4-$MeOC_6H_4$) and MV^{2+} ($K = 28 \pm 1\,mol\,dm^{-3}$) or (**35**) ($K = 1{,}200 \pm 100\,mol\,dm^{-3}$), but this is not possible for $[Ru(\mathbf{34})_3]^{2+}$ when R = H in ligand (**34**). Electron transfer from $*[Ru(\mathbf{34})_3]^{2+}$ ((**34**) with R = 4-$MeOC_6H_4$) to the acceptors has been investigated by using time-resolved laser flash photolysis, and the results support the existence of the supramolecular assemblies.[335] Related work describes photoinduced electron transfer in supramolecular assemblies involving (**35**) and $[RuL_3]^{2+}$ in which the ligands are related to (**34**) or $L_3 = (\mathbf{36})$.[336]

Quenching of the excited state of $[Ru(bpy)_3]^{2+}$ occurs with a wide range of species which may or may not be covalently linked to the ruthenium(II) coordination sphere. Persulfate ion quenches $*[Ru(bpy)_3]^{2+}$ and the electron transfer process results in the formation of $SO_4^{\bullet -}$ which reacts with the acetate buffer and chloride ions present in solution. The net result is a reduction in the overall quantum yield of $[Ru(bpy)_3]^{3+}$ (see Scheme 1).[337] The quenching of both $*[Ru(bpy)_3]^{2+}$ and $*[Ru(bpz)_3]^{2+}$ by ferrocene, 1,1′-dimethylferrocene, 1,2,3,4,5-pentamethylferrocene, 1,1′,2,2′,3,3′,4,4′-octamethylferrocene and decamethylferrocene occurs competitively by energy and electron transfer.[338] Excited-state quenching in double-complex salts has covered a number of compounds: $[Ru(bpy)_3]_3[Co\{4,4'\text{-}(CO_2)_2bpy\}_3]_2$,[339] $[Ru(4,4'\text{-}Me_2bpy)_3]_3[Co\{4,4'\text{-}(CO_2)_2bpy\}_3]_2$,[339] $[Ru(bpz)_3]_3[Co\{4,4'\text{-}(CO_2)_2bpy\}_3]_2$,[339] $[M(bpy)_3]_2[Cr(CN)_6]Cl$ (M = Ru, Os),[340] $[Ru(bpy)_3]_2[Fe(CN)_6]Cl{\cdot}8H_2O$,[341] $[Ru(bpy)_3]_2\,[Co(CN)_6]Cl{\cdot}8H_2O$,[341] $[Ru(bpy)_3]_2[Co(CN)_6]_2SO_4$,[341] and $[Ru(bpz)_3][Fe(CN)_6]Cl{\cdot}14H_2O$,[341] as well as combinations of $[Ru(phen)_3]^{2+}/[Cr(CN)_6]^{3-}$,

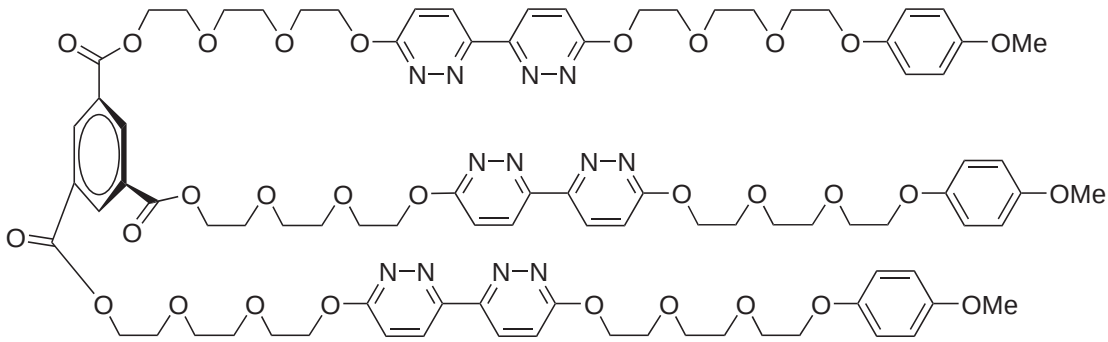


R = H, 4-MeOC$_6$H$_4$

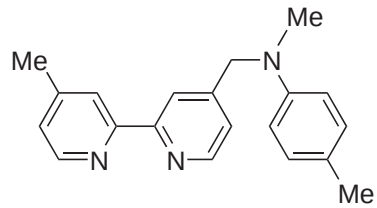
(**34**)



(**35**)



(**36**)



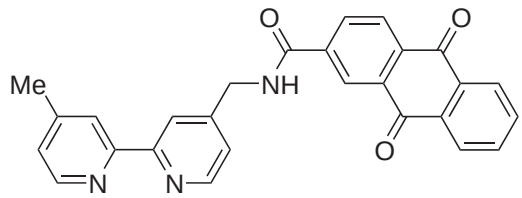
(**37**)

$[Ru(phen)_3]^{2+}/[Fe(CN)_6]^{3-}$, $[Ru(bpy)_3]^{2+}/[Cr(CN)_6]^{3-}$, $[Ru(bpy)_3]^{2+}/[Fe(CN)_6]^{3-}$ and $[Ru(bpy)_3]^{2+}/[Ni(CN)_4]^{2-}$ in the presence of LiCl, NaCl, KCl and CsCl.[342] The rate of energy transfer in $[Os(bpy)_3][Cr(CN)_6]Cl{\cdot}8H_2O$ is about eight times greater than in the Ru^{II} analog (4.8×10^7 s^{-1} vs. 6.0×10^6 s^{-1} at 77 K).[340]

By combining $[Ru(bpy)_3]^{2+}$ and metalloporphyrin domains, the aim is to couple the excited-state redox properties of the former with catalytic properties of the latter. Towards this end, the quenching of the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ by Fe^{III} *meso*-tetra(4-sulfanatophenyl)porphyrin has been studied in aqueous solution. The Fe^{III} porphyrin forms a 1:1 complex with $[Ru(bpy)_3]^{2+}$ under conditions of low ionic strength ($K = 1.5 \pm 0.01$) and the complex formation results in significant quenching. At higher ionic strengths or when bpy is replaced by $[4,4'\text{-}(CO_2)_2bpy]^{2-}$, no complex formation occurs and quenching of the excited state is diffusional.[343] Quenching of $*[Ru(bpy)_3]^{2+}$ by the conjugate bases of 2,4-$Cl_2C_6H_3OH$, 2,5-$Cl_2C_6H_3OH$, and 2,6-$Cl_2C_6H_3OH$ has been studied in MeOH and $MeOH/H_2O$ mixtures. In each solvent, the quenching constants, k_q, for 2,5-$Cl_2C_6H_3OH$ were smaller than for the 2,4- and 2,6-isomers. The production of $[Ru(bpy)_3]^{3+}$(Scheme 1) was observed by using laser-flash photolysis, and the effects of the solvent on quantum yields are discussed.[344] Values of k_q and cage escape yields of the redox products for electron transfer between $*[Ru(bpy)_3]^{2+}$ and a series of aromatic amines have been determined as a function of temperature in $MeCN/H_2O$ media. The solvent reorganization energies for electron-transfer quenching and back electron-transfer within the solvent cage have

been determined, and it is found that the highest reorganization energies are exhibited by primary amines; relationships between these energies and amine structure are discussed.[345]

Electron transfer from $[Ru(bpy)_3]^{2+}$ to C_{60} has been observed across a covalent link, and is supported by a photoinduced ESR signal showing characteristics of both $[Ru(bpy)_3]^{3+}$ and $C_{60}^{\bullet -}$. A rate constant for photoinduced electron transfer of 6.4×10^{-6} s^{-1} has been estimated.[346] When $[Ru(bpy)_3]^{2+}$ is covalently attached by a $(CH_2)_4$ chain to the electron-donating phenothiazine unit, and a covalently linked *N,N′*-diquaternary-2,2′-bipyridinium acceptor is employed, excitation to the ^{3}MLCT state results in a long-lived charge-separated state. A solvent dependence is observed.[347] The rate of electron transfer from the phenothiazine donor to the MLCT states has been discussed in terms of Marcus theory.[348] Effective quenching is also observed for the complex $[RuL_2L']^{2+}$ where L = 4,4′-$(CONEt_2)_2$bpy and L′ = 37. It is proposed that a rapid equilibrium is established between the initial MLCT excited state and the redox-separated state which lies at higher energy. Back electron transfer within the redox-separated state plays a dominant role in the decay to the ground state.[349] Partial quenching of the initial excited state of $[Ru(bpy)_2(\mathbf{38})]^{2+}$ in MeCN at 298 K occurs, and in $[Ru(4,5,4',5'\text{-}Me_4bpy)_2(\mathbf{38})]^{2+}$, electron transfer quenching is virtually complete. It is concluded from the data that the redox-separated states represented by $[Ru(bpy)_2(38^{\bullet -})]^{2+}$ undergo fast back electron transfer to return to the ground state.[350]



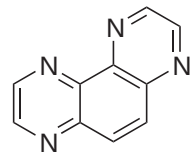
(**38**)

Laser flash photolysis has been used to investigate energy transfer from the ^{3}MLCT state of $[Ru(bpy)_3]^{2+}$ to acridine, acridine-9-carboxylate and phenazine, as well as electron transfer from substituted phenols to methyl viologen mediated by the triplet state of acridine-9-carboxylate.[351] Flash photolysis and pulse radiolysis methods have been applied to a study of the relaxation dynamics and product distribution in the decay of the high-lying excited states generated by two-photon capture by $[Ru(bpy)_3]^{2+}$ or electron capture by $[Ru(bpy_3]^{3+}$. High-power flash excitation produces the lowest lying MLCT states as well as a transient photoproduct which is formulated as $[Ru(bpy\text{-}N,N')_2(bpy\text{-}N)]^{2+}$.[352] For the photochemical reaction between $*[Ru(bpy)_3]^{2+}$ and Fe^{3+} in various concentrated electrolyte solutions, it has been found that there is a positive salt effect, the size of which depends on the salt. The effects that the electrolyte have on the activation and diffusion-controlled rate constants have been described.[353]

By using time-resolved IR luminescence and kinetic modeling, it has been shown that, contrary to previous proposals, singlet molecular O_2 ($^1\Delta_g$) is not formed during the electron-transfer reaction between $[Ru(bpy)_3]^{3+}$ and $O_2^{\bullet -}$ in aqueous solution. Results indicate that the only singlet O_2 formed photolytically in a system involving $[Ru(bpy)_3]^{2+}$, MV^{2+} and O_2 is produced by energy transfer between $*[Ru(bpy)_3]^{2+}$ and ground state O_2.[354] The rate constant for the quenching of $*[Ru(bpy)_3]^{2+}$ by $O_2^{\bullet -}$ in MeCN has been determined as $(1.3 \pm 0.3) \times 10^{10}$ dm^3 $mol^{-1}s^{-1}$. Again, there is no evidence for the formation of singlet molecular O_2 ($^1\Delta_g$).[355] Photo-excitation of the complex $[Ru(bpy)_2(4,4'\text{-}R_2bpy)]^{2+}$ where R = CONHCHMeCONMeOH yields a long-lived nitroxyl radical on one of the R groups, with singlet O_2 being responsible for this transformation.[356]

The emission from $*[Ru(bpz)_3]^{2+}$ is quenched by carboxylic acids; the observed rate constants for the process can be rationalized in terms of the protonation of the non-coordinated N atoms on the bpz ligands. The effects of concentration of carboxylate ion on the absorption and emission intensity of $[Ru(bpz)_3]^{2+}$ have been examined.[357] The absorption spectrum of $[Ru(bpz)(bpy)_2]^{2+}$ shows a strong dependence on $[H^+]$ because of protonation of the free N sites; the protonated species exhibits no emission. Phosphorescence is partly quenched by H_3O^+ even in solutions where $[H^+]$ is so low that protonation is not evidenced from the absorption spectrum.[358] The lifetime of the excited state of the nonemissive $[Ru(Hbpz)(bpy)_2]^{3+}$ is 1.1 ns, much shorter than that of $[Ru(bpz)(bpy)_2]^{2+}$ (88 nm).[359] The effects of complex formation between $[Ru(bpz)(bpy)_2]^{2+}$ and Ag^+ on electronic spectroscopic properties have also been studied.[358] Like bpz, coordinated 2,2′-bipyrimidine and 2-(2′-pyridyl)pyrimidine also have the

potential to be protonated with concomitant effects on the absorption spectra of the Ru^{II} complexes. The pK_a values for the monoprotonated forms have been determined from titration curves, and have been correlated with reduction potentials.[360] A comparison of the protonation behaviors of $[Ru(bpy)_{3-n}(bpz)_n]^{2+}$ and $[Ru(bpy)_{3-n}(\mathbf{39})_n]^{2+}$ has been made, and pK_a values for monoprotonation of the ground state and first-excited MLCT state complexes containing ligand (**39**) have been determined. Luminescence is quenched by organic buffers even at concentrations in which protonation does not occur; this phenomenon is explained in terms of hydrogen bonding between the carboxylic acid and the non-coordinated N atoms of the ligand.[361] Values of pK_a have also been determined for a series of protonated Ru^{II} complexes containing bpm, bpz and bpy ligands. The excited states of the complexes are described as containing a one-electron reduced ligand with the electron localized on the most easily reduced ligand: bpz > bpm > bpy.[362,363]



(**39**)

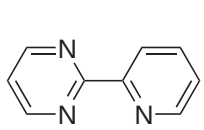
The fluorescence emission of 7-amino-4-methylcoumarin is quenched by $[Ru(bpy)_3]^{2+}$, and data in aqueous solution are consistent with a static quenching mechanism.[364]

That the excited-state redox potentials can be varied systematically over a series of luminescent Ru^{II} complexes has been illustrated for $[Ru(bpy)_nL_{3-n}]^{2+}$ where L = bpm and bpz.[365] A wider range of ruthenium(II) diimine complexes has been studied in order to gain insight into correlations between charge transfer emission energies and redox potentials, and the applicability of relationships involving ground state redox potentials to excited state redox potentials is discussed.[366]

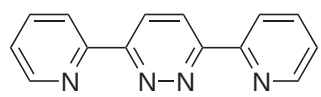
Complexes in the series $[MLL'_2]^{2+}$ where M = Ru or Os, L = bpz or bpm, and L′ = 2-(phenylazo)pyridine or 2-(4-tolylazo)pyridine have been prepared and characterized. They exhibit MLCT transitions in the visible region, and for M = Os, low-intensity, spin-forbidden transitions are observed. Electrochemical data illustrate the effects of differing π-acceptor abilities of the ligands.[367] Assignments of the MLCT bands in the absorption spectra of $[Os(bpy)(CN)_4]^{2-}$ and $[Ru(bpz)(CN)_4]^{2-}$ have been made and the effects of solvent on the spectra and redox potentials of the complexes have been studied. The π-acceptor ability of bpy or bpz is increased in weakly acceptor solvents and this is attributed to CN^--solvent interactions. The complexes are poor emitters in aqueous solution at 29 K; the excited states are very strong reductants.[368] $[Ru(bpz)(CN)_4]^-$ and $[Ru(bpz)(CN)_4]^{3-}$ have been generated spectroelectrochemically from $[Ru(bpz)(CN)_4]^{2-}$; their Fe analogs have also been studied. $[M(bpz)(CN)_4]^{3-}$ are shown to be M^{II} species with a radical anion π-acceptor ligand.[369]

Tuning the photophysical properties of $[Ru(bpy)_3]^{2+}$-related species is discussed in several sections in this chapter, and in this section, examples are restricted to mononuclear complexes. The photochemical and photophysical properties of the series of complexes $[Ru(bpy)_n\{5,5'\text{-}(CF_3)_2\text{-}bpy\}_{3-n}]^{2+}$ and $[Ru(bpy)_n\{4,4'\text{-}(CF_3)_2bpy\}_{3-n}]^{2+}$ ($n = 0, 1, 2$) have been investigated. Compared to bpy, each of 4,4′-$(CF_3)_2$bpy and 5,5′-$(CF_3)_2$bpy has lower lying π^* levels, and the lowest-lying emitting CT states of the mixed ligand complexes involve the $Ru^{III}\{(CF_3)_2bpy^{\bullet-}\}$ chromophore. Excited state lifetimes (in MeOH) lie in the range 42–1,050 ns depending on the number and substituent pattern of $(CF_3)_2$bpy ligands; the longest lifetime is observed for the excited state of $[Ru\{4,4'\text{-}(CF_3)_2bpy\}_3]^{2+}$.[370] Excited-state lifetime and photochemical ligand-loss studies for the complexes $[Ru(bpy)_nL_{3-n}]^{2+}$ (L = (**40**)) and some related species show that the order of decreasing quantum yield towards ligand loss is $[RuL_3]^{2+} > [Ru(bpy)L_2]^{2+} > [Ru(bpy)_2L]^{2+} > [Ru(bpy)(bpz)(py)_2]^{2+}$. In the latter complex, there is significant suppression of photochemical ligand loss, making the $[Ru(bpy)(bpz)]^{2+}$-unit a suitable one on which to build photostable light-induced electron-transfer systems.[371] Comparisons have been made between the photophysical properties of $[Ru(bpy)_3]^{2+}$, $[Ru(bpz)_3]^{2+}$, and $[Ru(bpz)_2(bpm)]^{2+}$ in MeCN and in MeCN/H_2O mixtures. The dependence of the emission energy on the solvent composition indicates that the excited states are preferentially solvated by H_2O molecules. Nonradiative decay and the temperature-dependent thermal population of the metal centered *d–d* state depend strongly on both solvent composition and temperature.[372]

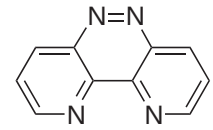
Tris(ligand) complexes involving ligand (**41**), or derivatives thereof, have been synthesized and characterized. Appending electron-releasing Ph or cyclic alkyl groups to the ligand leads to a blue



(40)

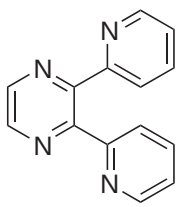


(41)

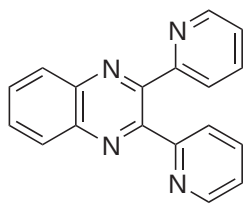


(42)

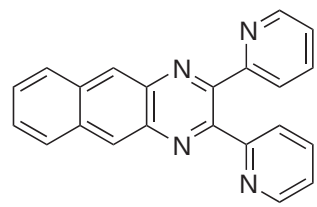
shift in the electronic spectrum; trends in redox potentials are discussed and it is noted that the variation of first reduction potentials of the complexes is small.[373] The absorption spectra, emission spectra and emission lifetimes of $[Ru(bpy)_nL_{3-n}]^{2+}$ (L = 2,2′-biisoquinoline; $n = 1$, 2, 3) have been compared with those of $[Ru(bpy)_3]^{2+}$. The 2,2′-biisoquinoline ligand is not involved in the low-energy excited states responsible for the luminescence emission of the heteroleptic species. Electrochemical studies on the complexes have also been carried out. The combined data illustrate that $[Ru(bpy)_3]^{2+}$, $[Ru(bpy)_2L]^{2+}$, and $[Ru(bpy)L_2]^{2+}$ (L = 2,2′-biisoquinoline) contain single bpy-localized excited states although where there is more than one bpy ligand, there is weak inter-bpy interaction.[374] The syntheses and photophysical properties of the complexes $[Ru(bpy)_n(\mathbf{42})_{3-n}]^{2+}$ ($n = 0$–3) have been reported. The first reduction potentials of the complexes containing ligand (**42**) are similar (≈−0.72 V vs. SCE) to each other but significantly less negative than that of $[Ru(bpy)_3]^{2+}$. The lifetimes of the emitting states of the complexes containing ligand (**42**) are ≈1 μs at 77 K and in the region of 0.1 μs at 298 K.[375] Ruthenium(II) complexes incorporating the ligands (**43**), (**44**), and (**45**) have been studied. It is concluded that the electrochemical and electronic spectroscopic properties are governed by the ligand reduction potential and the steric crowding of the ligands around the Ru^{II} center. $[Ru(\mathbf{45})_3]^{2+}$ exhibits an extremely low-energy emission and this is consistent with the "energy gap law."[376]



(43)



(44)

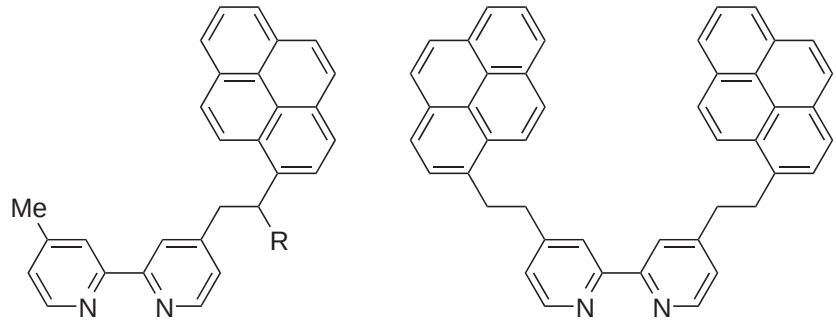


(45)

From photophysical data recorded for the series of complexes $[Ru(4,4'\text{-}Me_2bpy)_3]^{2+}$, $[Ru(4,4'\text{-}Me_2bpy)_2(\mathbf{46})]^{2+}$, $[Ru(4,4'\text{-}Me_2bpy)(\mathbf{46})_2]^{2+}$, $[Ru(\mathbf{46})_3]^{2+}$, $[Ru(4,4'\text{-}Me_2bpy)_2(\mathbf{47})]^{2+}$, $[Ru(4,4'\text{-}Me_2bpy)(\mathbf{47})_2]^{2+}$, $[Ru(\mathbf{46})_2(\mathbf{47})]^{2+}$, $[Ru(\mathbf{46})(\mathbf{47})_2]^{2+}$, and $[Ru(\mathbf{47})_3]^{2+}$, it is concluded that the excited state lifetime of the complex is linearly related to the number of pyrenyl chromophores present; lifetimes lie in the range 0.8–18.1 μs.[377] An analysis of the absorption spectra of $[Ru(4,4'\text{-}Me_2bpy)_2(\mathbf{48})]^{2+}$ and $[Ru(\mathbf{48})_3]^{2+}$ shows that there is no significant electronic interaction between the 4,4′-Me_2bpy and ligand (**48**) chromophores. In complexes containing ligand (**48**), there is rapid and efficient singlet–singlet energy transfer from the pyrene groups to the $Ru(bpy)_3$ unit.[378]

Experimental data for the interligand electron transfer kinetics following photoexcitation of $[Os(bpy)_3]^{2+}$ are in agreement with a reaction/diffusion model; measurements were made in a range of solvents. The variable parameters in the model are interligand electronic coupling and solvent polarization barrier height.[379]

The photolysis of $[Ru(bpy)_3]^{2+}$ in dmf in the presence of Cl^- leads to a mixture of *cis*-$[Ru(bpy)_2Cl_2]$ and *cis*-$[Ru(bpy)_2Cl(dmf)]^+$ along with the thermally unstable *cis*-$[Ru(bpy)_2Cl_2]^+$, $[Ru(bpy)_3]^{3+}$ and a dinuclear species, proposed to be $[Ru_2(bpy)_4Cl_2]^{n+}$ ($n = 3$ or 4). Interconversion of *cis*-$[Ru(bpy)_2Cl_2]$ and *cis*-$[Ru(bpy)_2Cl(dmf)]^+$ can be achieved thermally or photochemically.[380] The role of the lowest-lying π* level localized in a diimine ligand in directing photosubstitution has been investigated through reactions of $[Ru(bpz)_2(bpm)]^{2+}$, $[Ru(bpz)(bpm)_2]^{2+}$, $[Ru(bpy)(bpm)(bpz)]^{2+}$, $[Ru(bpm)_2(MeCN)Cl]^+$, $[Ru(bpz)_2(MeCN)Cl]^+$, $[RuL_2(py)_2]^{2+}$ (L = 4,4′-Me_2bpy, bpy, bpm, bpz) and $[Ru(bpy)_nL'_{3-n}]^{2+}$ (L′ = bpz, bpm; $n = 0$–3). The substitution quantum yields (ϕ_p) varied from 0.35 for $[Ru(bpz)_3]^{2+}$ to 1.7×10^{-4} for $[Ru(bpy)_2(bpz)]^{2+}$. A linear correlation was observed between ln ϕ_p(obs) and $\Delta E_{1/2}$ where $\Delta E_{1/2}$ is the difference between the first oxidation potential and first reduction potential of the Ru^{II}



(**46**) R = H (**47**)

(**48**) R = OH

complexes. Separation correlations (which relate to the "energy gap law") were noted for complexes containing only bpy-type ligands and those containing bpm and bpz ligands.[381]

The kinetics of the oxidation of $[Ru(bpy)_3]^{2+}$ by Tl^{3+}, catalyzed by $RuO_2 \cdot xH_2O$ dispersed in HNO_3 (3 M), have been studied, varying the concentrations of $[Ru(bpy)_3]^{2+}$, Tl^{3+}, Tl^{+}, catalyst and temperature. The kinetic data are consistent with an effect involving electron transfer between the electrochemically reversible redox couples $[Ru(bpy)_3]^{3+}/[Ru(bpy)_3]^{2+}$ and Tl^3/Tl^{+}, the transfer being mediated by $RuO_2 \cdot xH_2O$.[382]

5.5.3.1.3 *Mononuclear complexes of general formula $[Ru(bpy)_2L_2]^{n+}$ and complexes containing functionalized bpy ligands*

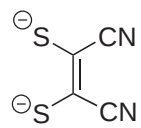
There is necessarily some overlap between some of the complexes covered in the previous and following sections. The main themes running through the next part of the chapter are mononuclear $[Ru(bpy)_2L_2]^{2+}$ species in which L_2 is a didentate or two monodentate ligands, and complexes containing functionalized bpy ligands. Of general interest is a review covering coordination complexes of bpy.[276] Lack of symmetry in complexes of the type $[Ru(bpy)_2L_2]^{2+}$ where L_2 is an unsymmetrical diimine leads to difficulties in assigning ^1H NMR spectra. A useful method to overcome the problem involves the use of $[Ru(bpy\text{-}d^8)_2L_2]^{2+}$ in place of the protio analog.[383] A general method of preparing mixed ligand complexes $[Ru(bpy^1)(bpy^2)L_2]^{2+}$ where bpy^1 and bpy^2 are different 2,2′-bipyridine derivatives and L_2 = various ligands (two monodentate or one didentate) uses $[Ru(bpy^1)(bpy^2)(CO)_2]^{2+}$ as a starting material. Removal of the CO ligands by Me_3NO oxidation can be difficult in the presence of reducing ligands. This problem can be avoided by making use of $[Ru(bpy^1)(bpy^2)(MeCN)_2]^{2+}$.[384]

Complexes of the type $[Ru(bpy)_2L_2]^{2+}$ in which L is a simple, monodentate ligand will be surveyed first. The structure of *trans*-$[Ru(bpy)_2(H_2O)_2][PF_6]_2$ has been determined; steric interactions result in the bpy ligands being "bowed".[385] Similar deformations are observed in *trans*-$[Ru(bpy)_2(MeCN)_2]^{2+}$ and *trans*-$[Ru(bpy)_2(NH_3)_2]^{2+}$.[386] The structure of *cis*-$[Ru(bpy)_2(MeCN)_2][PF_6]_2$ has also been determined.[387] The isocyanide complexes $[Ru(bpy)_2(CN)(CNMe)]^{+}$, $[Ru(bpy)_2(CNMe)_2]^{2+}$, and $[Ru(bpy)(CNMe)_4]^{2+}$ have been prepared and their photophysical and redox properties described. Compared to analogous cyanide complexes, the strong electron-withdrawal properties of the CNMe ligands result in significant blue shifts in the Ru → bpy MLCT transitions, and in anodic shifts in the Ru^{2+}/Ru^{3+} oxidation potentials.[388] Studies of $[Ru(bpy)_2(CN)_2]$ and its Fe^{II} analog show that there are significant differences in the excited state electronic spectra; whereas the excited state of $[Ru(bpy)_2(CN)_2]$ absorbs much more strongly than the ground state, the opposite is true for the Fe^{II} complex. Absorptions at 370 and 430 nm in the spectrum of excited $[Ru(bpy)_2(CN)_2]$ are characteristic of the bpy^- chromophore.[389] Oxidation of NH_3 in *cis*-$[Ru(bpy)_2(NH_3)_2]^{2+}$ by acidic aqueous Cl_2 generates *cis*-$[Ru(bpy)_2(NH_3)(NO)]^{3+}$; the reaction kinetics have been studied by stopped-flow methods and a mechanism has been proposed.[390] Photosubstitution in $[Ru(bpy)_2(N_3)_2]$ occurs when the sample is irradiated in $CHCl_3$ at $\lambda \leq 313$ nm; irradiation above this wavelength results in either slow or no photoreaction. Since $CHCl_3$ absorbs at 313 nm, it is concluded that $CHCl_3$, and not Ru^{II}, is

the photoactive species in the reaction; a radical mechanism is proposed for the conversion of $[Ru(bpy)_2(N_3)_2]$ to $[Ru(bpy)_2Cl_2]$ under these conditions.[391] The oxidation of $[Ru(bpy)_2Cl_2]$ to $[Ru(bpy)_2Cl_2]^+$ in several aerated solvents occurs under UV irradiation and a radical mechanism is proposed. If $[Ru(bpy)_2Cl_2]^+$ is irradiated in the blue or UV region in the same solvents, reduction to $[Ru(bpy)_2Cl_2]$ is observed. Depending on the solvent, a photostationary mixture, or the fully reduced or oxidized complexes can be obtained.[392] When irradiated in the ligand field band, the quantum yield for the photoaquation of *trans*-$[Ru(bpy)_2Cl_2]^+$ is 1.5×10^{-2}; the data reveal that *trans*-$[Ru(bpy)_2Cl_2]^+$ has a higher quantum efficiency than *trans*-$[Ru(en)_2Cl_2]^+$.[393]

The preparation, electrochemical and electronic spectroscopic properties and crystal structure of *cis*-$[Ru(bpy)_2(dmso\text{-}S)Cl]X$ ($X = PF_6$ or ClO_4) have been reported.[394,395] Methods of preparing both *cis* and *trans*-complexes of this type have been described.[396] Selective, photochemical monosubstitution of dmso can be achieved with complete enantiomeric retention, e.g., replacement by 4,4′-bipyridine.[397] Similarly, Δ-$[Ru(bpy)_2(dmso\text{-}S)Cl]^+$ can be converted to Δ-$[Ru(bpy)_2(4,4'\text{-}Me_2bpy)]^{2+}$ in 97% yields and with 96.8% retention of configuration. The crystal structure of one enantiomer of $[Ru(bpy)_2(4,4'\text{-}Me_2bpy)]^{2+}$ has thus been determined.[398] The family of sulfoxide complexes has been expanded to include $[Ru(4,4'\text{-}Me_2bpy)_2(dmso)Cl]^+$, $[Ru(bpy)_2(ttso)Cl]^+$ and $[Ru(4,4'\text{-}Me_2bpy)_2(ttso)Cl]^+$. Starting from *cis*-$[Ru(bpy)_2Cl_2]$ or *trans*-$[Ru(4,4'\text{-}Me_2bpy)_2Cl_2]$ and using a thermal route, all the sulfoxide products are *cis*. Photoirradiation of *cis*-$[Ru(bpy)_2Cl_2]$ in dmso yields a *trans* product, but in contrast, photoirradiation of *trans*-$[Ru(4,4'\text{-}Me_2bpy)_2Cl_2]$ in dmso gives *cis*-$[Ru(4,4'\text{-}Me_2bpy)_2(dmso)Cl]^+$.[399] The reactions of *cis* or *trans*-$[Ru(bpy)_2Cl_2]$ with either (*R*)-(+) or (*S*)-(–)-methyl 4-tolyl sulfoxide (mtso) results in the diastereoselective formation of *cis*-Δ-$[Ru(bpy)_2\{(R)\text{-}(+)\text{-}(mtso)\}Cl]^+$ (49.6% de) or *cis*-Λ-$[Ru(bpy)_2\{(S)\text{-}(-)\text{-}(mtso)\}Cl]^+$ (48.4% de). The diastereoselectivity of these and related reactions depend entirely on the chirality of the sulfoxide nucleophile.[400] This methodology has been extended to the first "one-pot" synthesis of derivatives of $[Ru(bpy)_3]^{2+}$ starting from racemic $[Ru(bpy)_2X_2]$ precursors and using the mtso derivatives as intermediates.[401]

The reaction of $[Ru(bpy)_2Cl_2]$ with $Na_2S_2C_2(CN)_2$ or $(PhCH_2)_2S_2C_2(CN)_2$ leads to the formation of $[Ru(bpy)_2\{S_2C_2(CN)_2\}]$ or $[Ru(bpy)_2\{(PhCH_2)_2S_2C_2(CN)_2\}]^{2+}$. The introduction of the $[S_2C_2(CN)_2]^{2-}$ ligand (**49**) results in the presence in the complex of a low-lying $d\pi$ (Ru) $\rightarrow \pi^*$(ligand) MLCT state.[402]



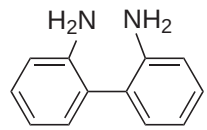
(**49**)

The crystal structures of a number of $[Ru(bpy)_2(phosphine)_2]^{2+}$ and $[Ru(bpy)_2(phosphine)Cl]^+$ have been reported: *trans*-$[Ru(bpy)_2(PMePh_2)_2]^{2+}$,[403] *cis*-$[Ru(bpy)_2\{PPh_2(2\text{-}MeC_6H_4)\}Cl]^+$,[404] *cis*-$[Ru(bpy)_2\{PPh(2\text{-}MeC_6H_4)_2\}Cl]^+$,[405] *cis*-$[Ru(bpy)_2(PPr_3)Cl]^+$,[406] *cis*-$[Ru(bpy)_2(PPh_3)Cl]^+$,[407] *cis*-$[Ru(bpy)_2(PMe_3)Cl]^+$,[408] *cis*-$[Ru(bpy)_2\{PMe_2(2\text{-}MeC_6H_4)\})Cl]^+$,[408] and *cis*-$[Ru(4,4'\text{-}{}^tBu_2bpy)_2(PPh_3)Cl]^+$.[409] Irradiation ($\lambda = 460$ nm) of *rac*-$[Ru(bpy)_2\{PhP(OMe)_2\}Cl]Cl$ leads to the photochromic generation of a new atropisomer and inversion, there being a low energy barrier to rotation around the Ru—P bond. Complex formation with γ–cyclodextrin stabilizes the new atropisomeric conformation.[410] The luminescence properties of *cis*-$[Ru(bpy)(dppe)X_2]$, *cis*-$[Ru(bpy)_2(PPh_3)X]^+$ and *cis*-$[Ru(bpy)_2X_2]$ ($X^- = CN^-$, NO_2^-) adsorbed on SiO_2 at 77 K and room temperature have been studied.[411,412] The introduction of the phosphine ligands raises the singlet and triplet CT state energies.[412]

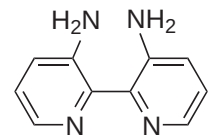
Bis(bpy) complexes incorporating Ru^{II}-bound carbonyl ligands include $[Ru(bpy)_2(CO)H]^+$, the structure of which has been determined. In acidic solution, H_2 is eliminated from $[Ru(bpy)_2(CO)H]^+$, and the results of a study of this reaction are discussed in terms of their relevance to the homogeneous water–gas shift reaction catalyzed by $[Ru(bpy)_2(CO)Cl]^+$.[413] The complex *cis*-$[Ru(bpy)_2(CO)(NO_2)][PF_6]$ has been structurally characterized. Over a pH range of 1–12 in aqueous solutions, the electronic spectrum of the complex showed no change, indicating that the coordinated CO and NO_2^- in $[Ru(bpy)_2(CO)(NO_2)]^+$ are less reactive than those in $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(NO_2)_2]$, respectively. When Bu_4NOH in MeOH is used as the source of OH^-, reaction does occur: at low concentrations of OH^-, $[Ru(bpy)_2(COOH)(NO_2)]$ is formed, while at high concentrations of OH^-, the Ru^{II} complex decomposes.[414] The crystal

structures of salts of $[Ru(bpy)_2(CO)_2]^{2+}$ and $[Ru(bpy)_2(CO)(CO_2Me\text{-}C)]^{+}$ and of $[Ru(bpy)_2(CO)(CO_2\text{-}C)]\cdot 3H_2O$ have been determined; $[Ru(bpy)_2(CO)(CO_2Me\text{-}C)]^{+}$ is used as a model for $[Ru(bpy)_2(CO)(CO_2H\text{-}C)]^{+}$. From the structural data, it is proposed that the extra electron pair in $[Ru(bpy)_2(CO)(CO_2\text{-}C)]$, made available after formally deprotonating $[Ru(bpy)_2(CO)(CO_2H\text{-}C)]^{+}$, is localized on the CO_2 ligand.[415] The complex *cis*-$[Ru(bpy)_2(CO)(CHO)]^{+}$ reacts with concentrated HCl at 298 K to give *cis*-$[Ru(bpy)_2(CO)(CH_2Cl)]^{+}$ and $[Ru(bpy)_2(CO)_2]^{2+}$. If $[Ru(bpy)_2(CO)(CHO)]^{+}$ is left standing in dry MeOH for 7 h at 298 K under a fluorescent light, $[Ru(bpy)_2(CO)(CO_2Me)]^{+}$ is formed more or less quantitatively. No reaction takes place if the reagents are left in the dark. The effects of further varying the reaction conditions, and the conditions required for the reaction of $[Ru(bpy)_2(CO)(CHO)]^{+}$ with H_2O are discussed.[416] The complexes $[Ru(bpy)_2(CO)_2]^{2+}$, $[Ru(4,4'\text{-}Me_2bpy)_2(CO)_2]^{2+}$, $[Ru(bpy)(4,4'\text{-}Me_2bpy)(CO)_2]^{2+}$, $[Ru(bpy)(CO)_2Cl_2]$, $[Ru(4,4'\text{-}Me_2bpy)(CO)_2Cl_2]$, $[Ru(phen)_2(CO)_2]^{2+}$, and $[Ru(phen)_2(CO)Cl]^{+}$ catalyze the electrochemical reduction of CO_2. When the solvent is acetonitrile/H_2O (4/1), no difference between the catalysts is observed, but in MeOH, the amounts of CO produced exceed HCO_2^- when 4,4′-Me_2bpy is present in the Ru^{II} complex.[417] The preparation and characterization of $[Ru(4,4'\text{-}Me_2bpy)(4\text{-}Me\text{-}4'\text{-}CH_2{}^tBubpy)(CO)_2]^{2+}$ and $[Ru(4\text{-}Me\text{-}4'\text{-}CH_2{}^tBubpy)_2(CO)_2]^{2+}$ have included the identification of geometrical isomers. Both complexes can be used as precursors to $[Ru(4,4'\text{-}Me_2bpy)(4\text{-}Me\text{-}4'\text{-}CH_2{}^tBubpy)_2]^{2+}$, and the three geometrical isomers of the latter have been separated by cation exchange chromatography. Geometrical isomers of $[Ru(4\text{-}Me\text{-}4'\text{-}CH_2{}^tBubpy)_3]^{2+}$ have also been prepared, separated and characterized.[418]

Lengthening the spacer in $H_2N(CH_2)_nNH_2$ from $n=2$ to 3 in the complexes $[Ru(bpy)_2\{H_2N(CH_2)_nNH_2\}]^{2+}$ has little effect on their emission properties and luminescent lifetimes at 77 K. For both complexes, the quantum yields for the photosubstitution of the amine ligand by Cl^- are low in CH_2Cl_2 and MeCN solutions. Prolonged photolysis resulted in the oxidation of the diamine ligands.[419] In $[Ru(bpy)_2(dien)]^{2+}$ and $[Ru(bpy)_2L]^{2+}$ (L = 1,4,8-triazaoctane), the triamines act as didentate ligands. The photophysical properties of these complexes have been compared with those of $[Ru(bpy)_3]^{2+}$ and $[Ru(bpy)_2L']^{2+}$ where L′ = en, $MeHNCH_2CH_2NHMe$ or $Me_2NCH_2CH_2NMe_2$. The emission of the complexes is quenched at pH > 12 and this is attributed to the deprotonation of the coordinated amine groups in the excited-state complexes. The protonation/deprotonation of the pendent NH_2 groups has little effect on the photophysical properties of the Ru-containing chromophore.[420] Ligands (**50**) and (**51**) exhibit hindered rotation about the central C—C bond making each of $[Ru(bpy)_2(\mathbf{50})]^{2+}$ and $[Ru(bpy)_2(\mathbf{51})]^{2+}$ diastereomeric. In the solid state, each complex exhibits only one diastereoisomer; structural data confirm that ligand (**50**) bonds through the two NH_2 groups, while (**51**) coordinates in a bpy-like mode.[421]



(**50**)

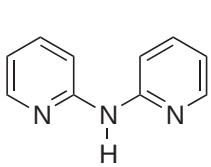


(**51**)

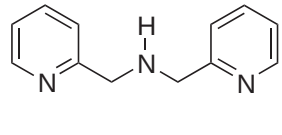
The next group of $[Ru(bpy)_2L_2]^{2+}$ complexes to be considered involves pyridine-based ligands. The structural and spectroscopic properties of *cis*-$[Ru(bpy)_2(py)_2]^{2+}$ have been reported.[422] Hydrolysis of *cis*-$[Ru(bpy)_2(py)Cl]^{+}$ gives *cis*-$[Ru(bpy)_2(py)(H_2O)]^{2+}$ with 80% retention of configuration. Retention of configuration also accompanies the oxidation of the latter to *cis*-$[Ru(bpy)_2(py)(O)]^{2+}$, racemization of which is slow; the use of this Ru^{IV} complex as a chiral oxidant has been examined.[423] The kinetics of the comproportionation reaction between $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and $[Ru(bpy)_2(py)(H_2O)]^{2+}$ in MeCN have been studied using stopped-flow methods. The Ru^{III} product is unstable, and in MeCN solution undergoes disproportionation to $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ and $[Ru(bpy)_2(py)(H_2O)]^{2+}$, followed by MeCN-for-$H_2O$ substitution in the latter to give $[Ru(bpy)_2(py)(MeCN)]^{2+}$; reaction of $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ with the solvent also leads to $[Ru(bpy)_2(py)(MeCN)]^{2+}$, via the aqua complex.[424] The complex *trans*-$[Ru(bpy)_2(py')(dmso)]^{2+}$ can be prepared by reaction of *trans*-$[Ru(bpy)_2(dmso)_2]^{2+}$ with py′ where py′ is 4-ethylpyridine, 4-(dimethylamino)pyridine or ethyl isonicotinate. The reaction of *trans*-$[Ru(bpy)_2(4\text{-}Etpy)(dmso)]^{2+}$ with LiCl in dmf/H_2O yields *trans*-$[Ru(bpy)_2(4\text{-}Etpy)Cl]^{+}$, abstraction of Cl^- from which provides a route by which a second pyridine ligand can be introduced specifically *trans* to the first py.[425]

The cyclometallated complex $[Ru(bpy)_2(ppy)]^+$ (Hppy = 2-phenylpyridine) can be prepared from $[Ru(bpy)_2Cl_2]$ and Hppy in the presence of Ag^I; Ru^{II} to Ru^{III} oxidation in $[Ru(bpy)_2(ppy)]^+$ is significantly more facile than in $[Ru(bpy)_3]^{2+}$ (+0.47 compared to +1.354 V vs. NHE).[426] Theoretical calculations on $[Ru(bpy)_{3-n}(ppy)_n]^{(2-n)+}$ reveal that the electronic structures of the heteroleptic complexes exhibit a separation of the Ru—C and Ru—N σ-bonding character.[301] Electrophilic bromination and iodination of $[Ru(bpy)_2(ppy)]^+$ are regioselective, giving halo-substitution at the 5′-position, i.e., at C_{phenyl} opposite to the Ru—C bond. These halogenated complexes can, via Sonogashira coupling, provide a route into alkyne-functionalized tris(bpy)-related complexes.[427]

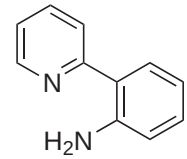
Full ^1H and ^{13}C NMR spectroscopic assignments have been made for the series of complexes $[Ru(bpy)_n(\mathbf{52})_{3-n}]^{2+}$ ($n = 0$, 1, 2). In solution, the apparent symmetries of the complexes are C_2 for $[Ru(bpy)_2(\mathbf{52})]^{2+}$ and $[Ru(bpy)(\mathbf{52})_2]^{2+}$, and D_3 for $[Ru(\mathbf{52})_3]^{2+}$.[428] The emission lifetimes and quantum yield of photoracemization for $[Ru(bpy)_n(\mathbf{52})_{3-n}]^{2+}$ ($n = 0$–3) have been measured in aqueous solution. The lifetime for $[Ru(bpy)_2(\mathbf{52})]^{2+}$ varies from 80 ns to 200 ns over the temperature range 293–33 K; in contrast, $[Ru(bpy)(\mathbf{52})_2]^{2+}$ and $[Ru(\mathbf{52})_3]^{2+}$ are nonemitters in this temperature range.[429] In the complex $[Ru(bpy)_2(\mathbf{53})]^{2+}$, one py unit of ligand (**53**) is pendent; the luminescence lifetime of the complex is similar to that of $[Ru(bpy)_3]^{2+}$.[430] The osmium(II) complex $[Os(bpy)_2L]^{2+}$, where L = 2-(aminomethyl)pyridine, has been prepared and characterized. In aqueous solution, it undergoes an irreversible two-electron oxidative dehydrogenation to give the corresponding imine complex, and the kinetics of this reaction are consistent with initial oxidation of Os^{II} to Os^{III}, with an Os^{IV} intermediate being formed during ligand dehydrogenation.[431] Ligand (**54**) acts as an *N,N*′-chelate in $[Ru(bpy)_2(\mathbf{54})]^{2+}$, and the Ru^{2+}/Ru^{3+} couple is cathodically shifted by 0.34 V compared to that of $[Ru(bpy)_3]^{2+}$.[432] $[Ru(bpy)_2(\mathbf{55})]^{2+}$ is one of a group of Ru^{II} bpy and tpy complexes incorporating tertiary amine ligands to be reported. The spectroscopic, electrochemical and photochemical properties of $[Ru(bpy)_2(\mathbf{55})]^{2+}$ are compared to those of $[Ru(bpy)_2(\mathbf{56})]^{2+}$. On going from primary to tertiary amine, the UV-vis absorption spectrum is blue shifted by ≈8 nm, and the Ru^{2+}/Ru^{3+} couple is shifted to more positive potential by ≈100 meV. When an acetonitrile solution of $[Ru(bpy)_2(\mathbf{55})]^{2+}$ is irradiated, photochemical ligand substitution occurs to give $[Ru(bpy)_2(MeCN)_2]^{2+}$. Analogous studies have been carried out on $[Ru\{4,4'\text{-}(CF_3)_2bpy\}_2(\mathbf{55})]^{2+}$.[433] The syntheses and spectroscopic and electrochemical characterizations of $[Ru(bpy)_{3-n}L_n]^{2+}$ ($n = 0$–3) in which L is an aryl(2-pyridylmethylene)amine have been described.[434] Structural isomers of *trans*-$[Ru(bpy)_2(4\text{-}Etpy)_2]^{2+}$ and *trans*-$[Ru(bpy)_2(4\text{-}Etpy)(\mathbf{57})]^{2+}$ in which the bpy ligands are planar or "bowed" have been investigated by use of spectroscopic methods. In the ground state of the complexes in low-temperature glasses, the "bowed" forms are preferred. At higher temperatures and in MeOH/EtOH solutions, the two forms of bpy are in equilibrium. The "bowed" form converts to the planar form in the MLCT excited state of $[Ru(bpy)_2(4\text{-}Etpy)_2]^{2+}$.[435] The complexes $[Ru(bpy)_2(4\text{-}NH_2py)_2]^{2+}$ (used as a reference compound), $[Ru(bpy)_2(\mathbf{58})_2]^{2+}$ and $[Ru(bpy)_2(\mathbf{59})_2]^{2+}$ have been prepared and their photochemical properties compared. For $[Ru(bpy)_2(\mathbf{58})_2]^{2+}$ and $[Ru(bpy)_2(\mathbf{59})_2]^{2+}$, excitation into the ^{3}MLCT state is followed by rapid intramolecular energy transfer to the lowest triplet state of the anthryl group. Quenching is complete for $[Ru(bpy)_2(\mathbf{58})_2]^{2+}$, but is only partially achieved in $[Ru(bpy)_2(\mathbf{59})_2]^{2+}$ in which the spacer is relatively rigid.[436]



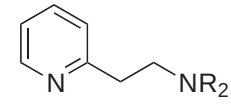
(**52**)



(**53**)



(**54**)

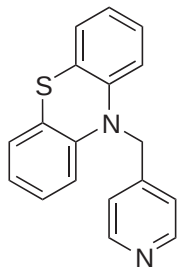


(**55**) R = Me
(**56**) R = H

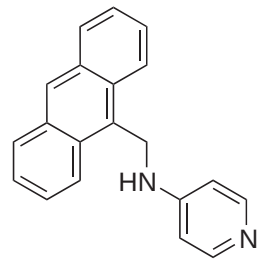
Structural characterization of $[Ru(bpy)_2(napy\text{-}N)(MeCN)][PF_6]_2$ has confirmed that the 1,8-naphthyridine (napy) ligand is monodentate; the two monodentate ligands are mutually *cis*.[437]

In the next part of the section, $[Ru^{II}(bpy)_2L_2]^{n+}$ complexes containing oximes, dioximes and quinones are considered. We then move to $[Ru(bpy)_2L]^{n+}$ complexes with other *O,O*- and *N,O*-donors as well as *N,S*- and *P,O*-donor ligands.

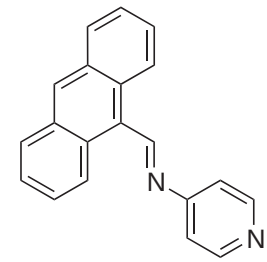
The reaction of *cis*-$[Ru(bpy)_2Cl_2]$ with $AgSO_3CF_3$ followed by H_2dmg yields *cis*-$[Ru(bpy)_2(H_2dmg)]^{2+}$. Values of $pK_a(1)$ and $pK_a(2)$ of 4.60 and 7.33 have been determined for deprotonation steps involving the H_2dmg ligand.[438] $[Ru(bpy)_2(H_2dmg)]^{2+}$ has also been



(**57**)



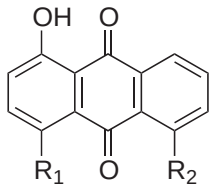
(**58**)



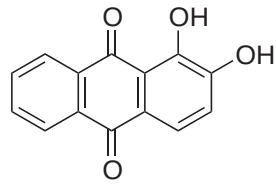
(**59**)

included in a study of a series of oxime-containing complexes of type *cis*-$[Ru(bpy)_2L]^{2+}$ (L = H_2dmg, cyclohexanedione dioxime, diphenylglyoxime, difurilglyoxime and 2-acetylpyridine oxime). The complexes exhibit solvent and pH-dependent electronic spectra; pK_a values have been determined for the complexes. The MLCT absorption energies correlate with the Ru^{3+}/Ru^{2+} redox potentials.[439] The reaction between *cis*-$[Ru(bpy)_2Cl(NO)]^{2+}$ and camphor in boiling MeOH/NaOMe results in the formation of $[Ru(bpy)_2L]^+$ where HL is camphorquinone monoxime; $[Ru(bpy)_2L]^+$ can also be prepared by the direct reaction of HL with *cis*-$[Ru(bpy)_2Cl_2]$.[440]

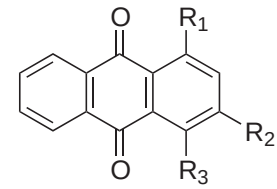
Complexes of type $[Ru^{II}(bpy)_2L]^{n+}$ and $[Ru^{II}(py)_4L]^{n+}$ in which L = 1,2-$(OH)_2C_6H_4$, 2-NH_2 C_6H_4OH and 1,2-$(NH_2)_2C_6H_4$ have been synthesized and their electrochemical and electronic, photoelectron and ESR spectroscopic properties reported. The results illustrate extensive metal–ligand orbital overlap in many of the complexes, leading to ambiguities in ruthenium oxidation state. However, it is concluded that Ru^{II} is the best overall description.[441] Following from work of Lever and co-workers who reported data for $[Ru^{II}(bpy)_2L]^{n+}$ and $[Ru^{II}(py)_4L]^{n+}$ where L = catechol, semiquinone or quinone forms of dioxolene ligands[442] (see also Section 5.5.3.4 for $[Ru^{II}(bpy)(dioxolene)_2]^{n+}$), resonance Raman spectroscopy has been used to probe the assignments of absorption bands and study relevant electronic states in $[Ru(bpy)_2(DTBSq)]^+$ and $[Ru(bpy)_2(Q)]^{2+}$ where DTBSq is 3,5,di-*tert*-butyl-1,2-semiquinonate(1−) and Q is the corresponding 1,2-quinone.[443] Reactions of an excess of (**60**) or (**61**) with $[Ru(bpy)_2Cl_2]$ yields $[Ru(bpy)_2(\mathbf{60})]^+$ or $[Ru(bpy)_2(\mathbf{61})]^+$ respectively. In the electronic spectra, the lowest energy band in the visible region is assigned to an MLCT transition to the dihydroxyanthraquinone ligand. pK_a values for both complexes in aqueous solution are 10.1 ± 0.2, illustrating that the coordinated ligands are less acidic than the free ligands.[444] Alizarin (**62**) coordinates to the $Ru(bpy)_2^{2+}$ unit as either a catechol or acetylacetonate-like ligand, thereby forming a pair of linkage isomers, distinguishable by IR and ^{1}H NMR spectroscopies.[445,446] The reaction of $[Ru(bpy)_2Cl_2]$ with 1,4-diaminoanthroquinone (**63**) leads to a dinuclear product[447] (see Section 5.5.3.1.4), but with 1,2-diaminoanthroquinone (**64**), mononuclear $[Ru(bpy)_2(\mathbf{64})]^{2+}$ (containing the ligand in its oxidized form) is produced.[448] The complex has been structurally characterized. Ligand (**64**) is a strong π acceptor, and results of theoretical calculations along with spectroscopic and electrochemical data are consistent with extensive π-backbonding between ligand (**64**) and the Ru center. Reduction and oxidation of $[Ru(bpy)_2(\mathbf{64})]^{2+}$ in protic or aprotic solutions lead to various species, many of which can exist in several tautomeric forms.[449] The complexes $[Ru(bpy)_2L]^+$ in which L is 1,4-dihydroxy-2,5-bis(pyrazol-1-yl)benzene (**65**) or 1,4-dihydroxy-2,3-bis(pyrazol-1-yl)benzene have been investigated. The spectroscopic properties of both these complexes and their oxidized forms have been studied; the first redox process is hydroquinone-based and the lowest-energy absorption is assigned to a hydroquinone → bpy interligand transition. The oxidation products are considered to be Ru^{II} quinone complexes, each with a lowest energy transition assigned to Ru^{II} → quinone charge transfer.[450] The complex $[Ru(bpy)_2(\mathbf{66})]^{2+}$ exhibits two intense electronic transitions in the visible region. The strong solvent dependence of these absorptions is rationalized in terms of the availability of the amino lone pairs and their coupling to the benzenequinone diimine ring. When the lone pairs are not involved in solvent interactions, ligand (**66**) tends towards being planar, but when the lone pairs are engaged in interactions with solvent molecules, the ligand twists out of plane. Interest in this system therefore stems from its potential as a component in molecular switching devices.[451]



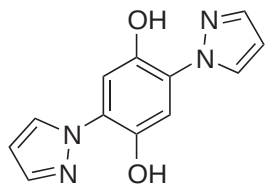
(**60**) $R_1 = OH$; $R_2 = H$
(**61**) $R_1 = H$; $R_2 = OH$



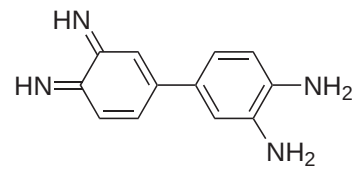
(**62**)



(**63**) $R_1 = NH_2$; $R_2 = H$; $R_3 = NH_2$
(**64**) $R_1 = H$; $R_2 = NH_2$; $R_3 = NH_2$



(**65**)



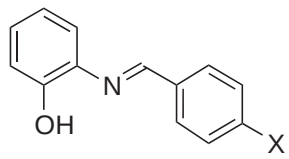
(**66**)

Riboflavin, folic acid and lumiflavin each bind one $Ru(bpy)_2^{2+}$ unit. The MLCT spectra of the complexes are pH dependent, and an α-iminocarbonyl chelating mode for each ligand is proposed. Coordination results in a lowering of the pK_a values (≈9 to 5) of the N(3)-H protons.[452]

The complexes $[Ru(bpy)_2L]^+$ (HL = acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, tropolone or dibenzoylmethane) have been prepared and characterized; they act as catalysts for the oxidation of alcohols, 3,5-di-*tert*-butylcatechol and alkanes in the presence of appropriate co-oxidants.[453] Perchlorate salts of $[Os(bpy)_2L]^+$ in which HL = salicylaldehyde, 2-hydroxyacetophenone or 2-hydroxynaphthaldehyde, are formed from reactions of $[Os(bpy)_2Br_2]$ with HL. The structure of the salicylaldehyde derivative has been determined. Chemical and electrochemical oxidations of $[Os(bpy)_2L]^+$ yield the corresponding low-spin Os^{III} species from which $[Os(bpy)_2L]^+$ can be regenerated.[454] $[Ru(bpy)_2L]^+$ (HL = salicylic acid) has been prepared and structurally characterized as the tetrahydrate. Absorptions at 590 nm, 400 nm, and 290 nm in the electronic spectrum have been assigned to Ru → bpy CT transitions; electrochemical oxidations of the complex have been investigated.[455]

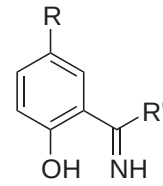
Pyridine-2-olate and pyridine-2-thiolate (L^-) complexes $[Ru(bpy)_2L]^+$ have been prepared and characterized. Both complexes are room-temperature emitters; the excited state lifetimes are 100 ns and 90 ns for the pyridine-2-thiolato and pyridine-2-olato complexes, respectively. The electrochemical properties of both complexes have been described.[456]

Ligands L^- derived from the Schiff bases HL = (**67**) act as *N,O*-chelates in the complexes $[Ru(bpy)_2L]^+$. Cyclic voltammograms of $[Ru(bpy)_2L]^+$ show reversible Ru^{II}/Ru^{III} and irreversible Ru^{III}/Ru^{IV} processes, except in the case of ligand (**67**) with $X = NMe_2$ where both processes are reversible. All the complexes are luminescent at room temperature.[457] The complexes $[Ru(bpy)_2L]^+$ in which HL = (**68**), have been prepared and characterized, including a single-crystal structure of $[Ru(bpy)_2L][ClO_4]$ for HL with $R = R' = H$. Electronic spectroscopic and electrochemical data have been discussed; the paramagnetic one-electron oxidized species convert to diamagnetic dimers in which the Ru^{III} centers are antiferromagnetically coupled.[458] 1,3,-Dimethyllumazine (**69**) binds to the ruthenium center in $[Ru(bpy)_2(\mathbf{69})]^{2+}$ through the N(5) and O(4) atoms. The electrochemical properties of the complex have been studied, and in the electronic spectrum, the absorptions at 242 and 285 nm are assigned to bpy $\pi \rightarrow \pi^*$ transitions, at 350–365 nm to transitions associated with ligand (**69**), and at 431 and 509 nm to MLCT transitions.[459] It has been reported that the emission spectrum and luminescent lifetime of $[Ru(bpy)_2(HL)]^+$ (H_2L = 3,3′-dinicotinic acid) are influenced by the presence of heavy metal ions (e.g., Pb^{2+}) in solution, even at concentrations as low as 1 μM. Crystallographic data for the complex show that the bpy rings of the dinicotinic acid are twisted with respect to each other by 19.3°. From the results of molecular mechanics and extended Hückel MO calculations, it is concluded that the interaction with Pb^{2+} leads to the dinicotinic acid ring system tending towards planarity, and as a consequence, the π^* energy levels of the ligand are affected.[460]



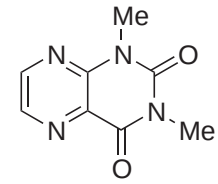
X = NO_2, Cl, F, Me, OMe, NMe_2

(**67**)



R = H, R' = H
R = H, R' = Me
R = NO_2, R' = H

(**68**)

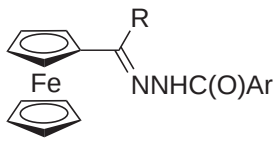


(**69**)

The complex $[Ru(bpy)_2(2\text{-}MeOC_6H_4PPh_2\text{-}P,O)]^{2+}$ exhibits a significant red shift of the absorption and emission spectra that is concentration dependent. From NMR spectroscopic data, it is concluded that this observation arises from equilibration with an aqua complex. Structural data and the solution properties of $[Ru(bpy)_2(2\text{-}PrOC_6H_4PPh_2\text{-}P,O)]^{2+}$ have been reported.[461] These results expand on an earlier report of $[Ru(bpy)_2(2\text{-}ROC_6H_4PPh_2\text{-}P,O)]^{2+}$ (R = Me, Et).[462]

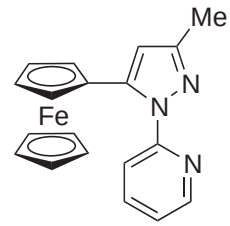
The ferrocenyl ligands (**70**) in $[Ru(bpy)_2(\mathbf{70})]^{2+}$ act as *N,O*-chelates through the azomethine N and carbonyl O atoms. Each complex exhibits several one-electron redox processes.[463] The properties of $[Ru(bpy)_2(\mathbf{71})]^{2+}$ and $[Ru(bpy)_2(\mathbf{72})]^{2+}$ have been compared with those of complexes containing corresponding non-ferrocenyl ligands. Electrochemical data show that each of $[Ru(bpy)_2(\mathbf{71})]^{2+}$ and $[Ru(bpy)_2(\mathbf{72})]^{2+}$ exhibits two oxidation waves, the first of which is assigned to oxidation of the ferrocenyl unit and the second to the Ru^{II} center. Electronic spectroscopic data are also reported.[464] These complexes lead us into a discussion of a range of compounds involving imidazole, triazole, tetrazole and related heterocyclic ligands. *cis*-$[Ru(bpy)_2(im)(H_2O)]^{2+}$, *cis*-$[Ru(bpy)_2(im)_2]^{2+}$, *cis*-$[Ru(bpy)_2(1\text{-}Meim)_2]^{2+}$, *cis*-$[Ru(4,4'\text{-}Me_2bpy)_2(im)(H_2O)]^{2+}$, and *cis*-$[Ru(4,4'\text{-}Me_2bpy)_2(1\text{-}Meim)(H_2O)]^{2+}$ have been prepared in aqueous solution at pH 7, and a comparative study has been made of electrochemical and spectroscopic properties. The crystal structures of the BF_4^- salts of the bpy-containing complexes have been determined.[465] When *cis*-$[Ru(bpy)_2(im)(H_2O)]^{2+}$ is treated with horse heart cytochrome *c*, the $[Ru(bpy)_2(im)]^{2+}$-unit binds to the His 33 and His 26 sites. For binding at the His 33 site, a diastereomeric $[Ru(bpy)_2L]$-His-cyt *c*(II) mixture is formed which shows a preference for the Λ-form, irrespective of the presence of substituents on the bpy ligand. For binding at the His 26 site, an isomeric distribution is formed which is influenced by bpy-substituents.[466] Solution studies of *cis*-$[Ru(bpy)_2L_2]^{2+}$ where L = 1-Meim, 1,2-Me_2im or 1-Mebim show that the different steric requirements of the non-bpy ligands result in different fluxional behaviors of the complexes. In $[Ru(bpy)_2(1\text{-}Meim)_2]^{2+}$, rotation about the Ru—N(imidazole) bonds occurs at all temperatures over the range 178–328 K, whereas for the more bulky imidazole ligands, three atroisomers can be distinguished at low temperatures.[467] Related studies have also been carried out for *cis*-$[Ru(bpy)_2L_2]^{2+}$ where L = 4-picoline.[468] The acid–base and redox chemistry of $[M(bpy)_2L]^{2+}$ in which L = 2,2′-dibenzimidazole have been examined; the Os^{III} and Os^{IV} species are more readily accessed electrochemically than their Ru analogs.[469] The complex $[Ru(bpy)_2L]^{2+}$, where L = 2-(2′-pyridyl)benzimidazole, interacts with aromatic nitrogen-containing heterocycles through hydrogen bonding. The equilibrium constant for this interaction depends on the pK_a value of the *N*-heterocycle. Analogous hydrogen bonding interactions involving the corresponding Ru^{III} complex are stronger than for the Ru^{II} species.[470] For the series of ligands (**73**), the complexes $[Ru(bpy)_2(\mathbf{73})]^{2+}$, $[Ru(bpy)(\mathbf{73})_2]^{2+}$ and $[Ru(\mathbf{73})_3]^{2+}$ have been prepared and characterized. The substituent R in ligand (**73**) affects the stereochemistry observed for $[Ru(bpy)(\mathbf{73})_2]^{2+}$ and $[Ru(\mathbf{73})_3]^{2+}$.[471] The coordination of 9-methylhypoxanthine (**74**) and 9-ethylguanine (**75**) to the$[Ru(bpy)_2]^{2+}$-unit has been studied in the complexes $[Ru(bpy)_2L(H_2O)]^{2+}$ and $[Ru(bpy)_2LCl]^+$(L = (**74**) or (**75**)). Details of the solid-state structure of $[Ru(bpy)_2(\mathbf{75})Cl]Cl$ have been discussed.[472]

The acid–base properties of the ground and excited states of $[Ru(bpy)_2(im)_2]^{2+}$ and $[Ru(bpy)_2(1,2,4\text{-triazole})_2]^{2+}$ have been investigated. Both complexes are stronger acids in the excited than the ground states.[473] Representative triazoles, L or HL, have been incorporated into the complexes $[Ru(bpy)_2L]^{n+}$ ($n = 1$ or 2). Electronic spectroscopic and electrochemical properties have been reported; all the ligands are weaker π acceptors than bpy.[474] The crystal structures of

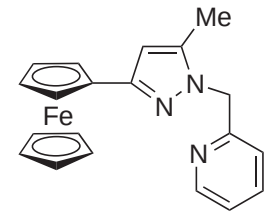


R = H, Me
Ar = Ph, 2-HOC_6H_4, 2-$C_{10}H_7$

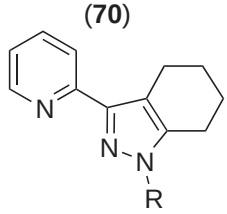
(**70**)



(**71**)

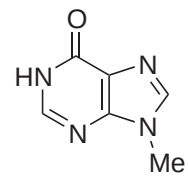


(**72**)

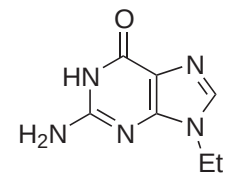


R = H, Me, Ph, 4-$CO_2MeC_6H_4$, 4-$CO_2HC_6H_4$, 4-$CO_2EtC_6H_4$

(**73**)



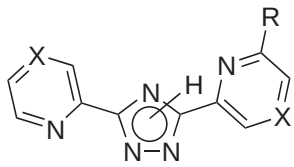
(**74**)



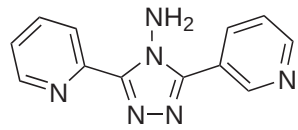
(**75**)

$[Ru(bpy)_2L][PF_6]_2$ where L = 3,5-bis(2-pyridyl)-1,2,4-triazole[475] or 3-(2-hydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole[476] have been determined. Spectroscopic and electrochemical properties of the latter complex,[476] as well as those of $[Ru(bpy)_2(H_2L)][PF_6]_2$ with H_2L = 3,3′-dimethyl-5,5′-bis(1,2,4-triazole)[477] have also been reported. In the latter complex, deprotonation of H_2L leads to lower oxidation potentials and a red shift of the lowest energy $d\pi$–π^* absorption band.[477] The acid–base properties of the two coordination isomers of $[Ru(bpy)_2(HL)]^{2+}$ where HL = 3-(pyrazin-2-yl)-1,2,4-triazole are characterized by ground state pK_a values of 3.1 and 5.3 for the N(2) and N(4) isomers respectively. These values indicate that the N(2) site is a stronger σ-donor than the N(4) site; pK_a values for the excited states are consistent with the lowest π^* level of the HL-containing complexes possessing predominantly pyrazinyltriazole character, while deprotonation switches this level to being bpy-based.[478] The syntheses, and spectroscopic and electrochemical properties of the complexes $[Ru(bpy)_2(HL)]^{2+}$ in which HL = 3-(pyrazin-2-yl)-1,2,4-triazole, 1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole, 1-methyl-5-(pyrazin-2-yl)-1,2,4-triazole or 3-methyl-5-(pyrazin-2-yl)-1,2,4-triazole, have been reported. The emission lifetime and absorption data suggest that pH changes affect the character (i.e., bpy or triazole-based) of the emitting states.[479] Related complexes containing the conjugate bases of (**76**)–(**78**)[480] and ligands (**79**) and (**80**)[481] have also been investigated. Comparisons have been made between the absorption spectra, and luminescence and electrochemical properties of $[Ru(bpy)_2L]^{2+}$ and $[Ru(2,2'\text{-biq})_2L]^{2+}$ (L = (**79**) or (**80**)).[481] For HL = (**76**), $[Os(bpy)_2L]^+$ and $[\{Os(bpy)_2\}_2(\mu\text{-}L)]^{3+}$ have been reported. For both complexes, the lowest energy absorption and luminescence bands are assigned to Os → bpy MLCT singlet and triplet excited states respectively. Comparisons are made between the properties of these complexes and those of $[Os(bpy)_3]^{2+}$ and of the Ru^{II} analogs.[482,483] The luminescence lifetimes of the deprotonated forms of $[Ru(bpy)_2(HL)]^{2+}$ where HL = 3-(pyridin-2-yl)-1,2,4-triazole bound to Ru through either N(2) or N(4), is much longer than that of the protonated complexes, and the results of a detailed study of the pH control of the photoreactivity of these complexes have been reported.[484]

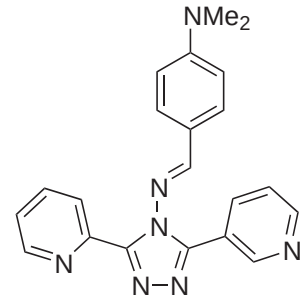
The crystal structure of *cis*-$[Ru(bpy)_2(4\text{-allyl-}1,2,4\text{-triazole})_2][PF_6]_2$ has been determined.[485] Linkage isomers of 3-(pyridin-2-yl)-1,2,4-triazole have been separated by use of HPLC.[486] Structural data for 3-methyl-5-(pyridin-2-yl)-1,2,4-triazole (L) derivative $[Ru(bpy)_2L]^{2+}$ have been determined.[487] The photolysis of $[Ru(bpy)_2L]^{2+}$ (L = 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole) in MeCN proceeds through an intermediate that has been isolated and characterized; in this species, the triazole ligand is monodentate, and the photochemically induced change in coordination mode can be reversed in a thermal reaction.[488] These observations have been further explored with related ligands, and the crystal structure of $[Ru(bpy)_2ClL][PF_6]$ in which L = 3-methyl-1-(pyridin-2-yl)-1,2,4-triazole has been determined, confirming the monodentate mode of the triazole ligand.[489]



(**76**) X = CH, R = H
(**77**) X = N, R = H
(**78**) X = CH, R = Me



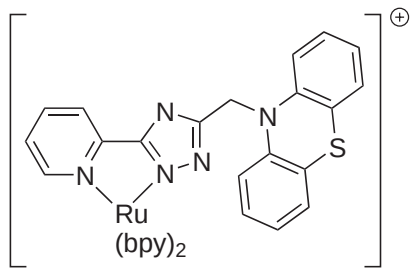
(**79**)



(**80**)

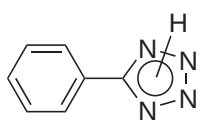
A method to distinguish the emitting and spectator ligands in heteroleptic complexes such as $[Ru(bpy)_2L]^+$ (HL = 5-phenyl-3-(pyridin-2-yl)-1,2,4-triazole) by comparing data obtained for complexes containing deuterated bpy and non-deuterated bpy has been developed.[500] For the complex $[Ru(bpy)_2L]^+$ (HL = 3-(pyrazin-2-yl)-1,2,4-triazole), two emission maxima are observed in EtOH/MeOH solution between 120 K and 260 K. The dual emission is rationalized in terms of two emitting states, one bpy in origin and one pyrazine-based.[501] Detailed studies that apply the use of deuterated ligands have examined the differing emission behaviors of $[Ru(bpy)_2L]^+$ and $[Ru(bpy)_2(HL)]^{2+}$ where HL = 3-(pyrazin-2-yl)-1,2,4-triazole) or 3-(pyridin-2-yl)-1,2,4-triazole.[502] Related complexes in which 2,2′-biquinoline replaces bpy have also been studied.[503]

In complex (**81**), the electron-donating phenothiazine moiety is separated from the $Ru(bpy)_2^{2+}$ unit by a triazole bridge that carries a formal negative charge. An investigation of this system shows that such anionic bridges can mediate electron transfer between chromophore and quencher.[504]

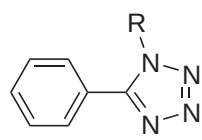


(**81**)

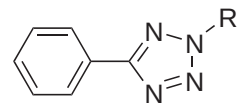
Tetrazole complexes of Ru^{II} have received far less attention than triazole or, in general,[505] other heterocyclic ligands. Complex formation of $Ru(bpy)_2^{2+}$ and $Ru(4,4'\text{-}Me_2bpy)_2^{2+}$ groups with the tetrazole ligands (**82**)–(**84**) has been studied, and electronic spectroscopic and electrochemical properties reported.[496]



(**82**)



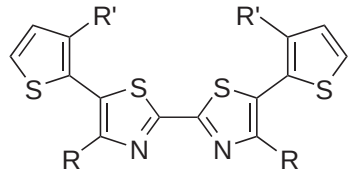
R = Me, ^{t}Bu
(**83**)



R = Me, ^{t}Bu
(**84**)

The thiophene-functionalized ligand 4-(5-bromothiophene)-2,2′-bipyridine, L, reacts with $[Ru(bpy)_2Cl_2]$ to give $[Ru(bpy)_2L]^{2+}$. The reactivity of the bromo site in coordinated L can be utilized to derivatize (e.g., by Pd(0) coupling) this ligand further.[497] Ligands (**85**) form the

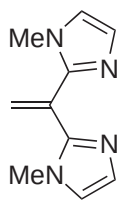
complexes $[M(bpy)_2(\mathbf{85})]^{2+}$ (M = Ru, Os), and both ligands and complexes may be electropolymerized. The metallopolymers show reversible M^{2+}/M^{3+} electrochemistry and there is no evidence for electronic coupling between the Ru or Os centers. When the organic backbone of the polymer is oxidized, the process is localized on the thiophene units; in contrast, reduction of the backbone is bithiazole-based.[498] In 5,5′-dimethyl-2,2′-bi-1,3,4-thiadiazole (L) complex $[Ru(bpy)_2L]^{2+}$, L is a strongly π-accepting ligand; the π* level is low-lying and is available to be involved in the emission process; the complex exhibits a low-energy emission at 760 nm (300 K).[499]



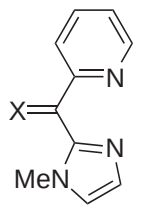
R = R' = H
R = Me, R' = H
R = Me, R' = OMe

(**85**)

Reactions of *cis*-$[Ru(bpy)_2Cl_2]$ with ligands (**86**) or (**87**) (X = CH_2) in EtOH(aq) lead to $[Ru(bpy)_2(\mathbf{86})]^{2+}$ and $[Ru(bpy)_2(\mathbf{87}, X = CH_2)]^{2+}$ respectively. When X = O in ligand (**87**), the product is the pyridine carboxylate complex $[Ru(bpy)_2(pyCO_2)]^{+}$, the structure of which is confirmed by X-ray crystallography.[500] Complexes of the type $[Ru(bpy)_2L]^{2+}$ in which L represents a series of mono- and dihydrazones have been prepared and characterized by spectroscopic methods (including variable temperature ^{1}H NMR) and a structure determination for L = biacetyl di(phenylhydrazone). When L is 2-acetylpyridine hydrazone or 2-acetylpyridine phenylhydrazone, $[Ru(bpy)_2L]^{2+}$ shows an emission, but none is observed for the dihydrazone complexes.[501] The pyrazoline complex $[Ru(bpy)_2L]^{2+}$ (L = 5-(4-nitrophenyl)-1-phenyl-3-(2-pyridyl)-2-pyrazoline) can be isolated in two diastereoisomeric forms. At 298 K, these exhibit similar MLCT absorptions, but at 77 K, their emission maxima and lifetimes are significantly different.[502]

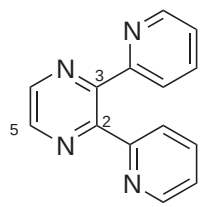


(**86**)



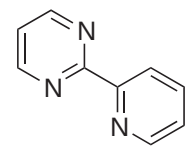
X = CH_2, O

(**87**)



2,3-dpp

(**88**)

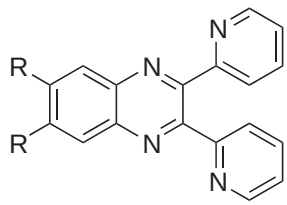


pypm

(**89**)

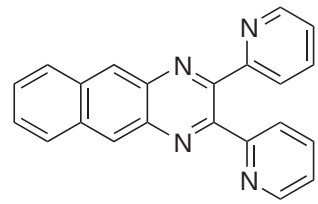
2,3-Bis(2-pyridyl)pyrazine (2,3-dpp, (**88**)) and its 2,5-analog (2,5-dpp) form the complexes $[Ru(bpy)_2(dpp)]^{2+}$, the ^{1}H NMR spectra of which have been fully assigned; ^{99}Ru NMR shifts are at δ 4,535 and 4,528 for the 2,3- and 2,5-dpp complexes respectively. The crystal structure of $[Ru(bpy)_2(2,3\text{-}dpp)]Cl_2 \cdot 3H_2O \cdot MeCN$ confirms that the dpp ligand acts as the expected *N,N′*-chelate.[503] The electrochemical behavior of $[Ru(bpy)_{3-n}(2,3\text{-}dpp)_n]^{2+}$ ($n = 1$–3) involves redox steps that are essentially localized on a particular ligand; the results are compared with those of $[Ru(bpy)_3]^{2+}$, and data for the uncoordinated 2,3-dpp ligand are also given.[504] An investigation of the acid–base and electrochemical properties of the MLCT states and one-electron reduced forms of $[Ru(bpy)_{3-n}(pypm)_n]^{2+}$ ($n = 1$–3; pypm = (**89**)) has included measurements of pK_a values of the conjugate acids of the excited states and reduced species, and the kinetics of the second-order decay of each reduced species.[505] The lifetimes of the luminescent MLCT states of $[Ru(bpy)_{3-n}(pypm)_n]^{2+}$ have been measured as a function of temperature over the range 170–36 K; from the data obtained, it is concluded that decay of the excited state of $[Ru(bpy)_2(pypm)]^{2+}$ involves a higher lying MLCT, while a metal-centered excited state is involved in the decay of the excited states of $[Ru(pypm)_3]^{2+}$ and $[Ru(bpy)(pypm)_2]^{2+}$.[506] The

complexes $[Ru(bpy)_2\{4,6\text{-}(EtO)_2pypm\}]^{2+}$ and $[Ru(bpy)_2\{5\text{-}Me\text{-}4,6\text{-}(EtO)_2pypm\}]^{2+}$ have been prepared in EtOH via complexes containing the 4,6-dihalo-2-(2-pyridyl)pyrimidine ligands. A change in reaction conditions gives a route to the related species $[Ru(bpy)_2L]^{2+}$ where L is a derivative of 2-(2-pyridyl)pyrimidinone. The photophysical and electrochemical properties of the complexes have been discussed.[507] High-yield syntheses of a series of 2-substituted 4-(2-pyridyl) pyrimidine ligands have been described. The ligands, L, have been incorporated into complexes of the type $[Ru(bpy)_2L]^{2+}$. Electrochemical data indicate that the first reduction potential of each complex involves a process centered on the pyrimidine ligand.[508] A series of complexes $[Ru(bpy)_{3-n}L_n]^{2+}$ containing 2-(2-pyridyl)-quinoxaline (L) has been reported. It is proposed on steric grounds that $[RuL_3]^{2+}$ has a *mer*-conformation; this complex undergoes photoinduced dissociation of one L ligand. The PF_6^- salt of $[Ru(bpy)L_2]^{2+}$ was isolated as a mixture of the three geometrical isomers.[509] 2,3-Bis(2-pyridyl)benzoquinoxaline (**90**, R = H) forms the complex $[Os(bpy)_2L]^{2+}$, and the electrochemical and spectroscopic properties of this and its 2,3-dpp (**88**) analog have been studied.[510] A study has been made of the electronic and resonance Raman spectra of $[Ru(bpy)_2(2,3\text{-}dpp)]^{2+}$ and $[Ru(bpy)_2L]^{2+}$ where L = 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline (**90**, R = Me), and of the reduced and oxidized forms of these complexes. The initial oxidation is ruthenium-based, while the first reduction process involves the pyrazine or quinoxaline ligand.[511] A new group of near-IR emitters in which the emission energies and lifetimes can be tuned in a systematic manner has been reported; the complexes that make up the series of emitters are $[Ru(4,4'\text{-}Me_2bpy)\{4,4',5,5'\text{-}Me_4bpy\}(\mathbf{90},R=H)]^{2+}$, $[Ru(4,4'\text{-}Me_2bpy)\{4,4'\text{-}(CO_2Et)_2bpy\}(\mathbf{91})]^{2+}$, $[Ru\{4,4'\text{-}(CO_2Et)_2bpy\}(\mathbf{91})(Et_2dtc)]^{+}$, $[Ru(bpy)_2(\mathbf{92})]^{2+}$, $[Os(bpy)_2(\mathbf{91})]^{2+}$ and $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{92})]^{4+}$. Each possesses a low-lying π^* acceptor orbital centered on ligand (**90**), (**91**) or (**92**). The emission maxima of the complexes range from 802 to 1,440 nm, the longest wavelength being for $[Ru\{4,4'\text{-}(CO_2Et)_2bpy\}(\mathbf{91})(Et_2dtc)]^{+}$, and the excited-state lifetimes range from 5 to 322 ns.[512] Studies of the photophysical behavior of $[Ru(bpy)_2L]^{2+}$ where L = 2-(2-pyridyl)quinoline or 2-(2-pyridyl)benzoquinoline in MeCN solution and in EtOH–MeOH glasses reveal that luminescence from each complex originates from an MLCT excited state. The complex containing 2-(2-pyridyl)benzoquinoline exhibits a transient absorption spectrum with a decay rate constant ≈30 times less than the luminescence decay constant. This implies that two non-equilibrated excited states exist.[513] The synthesis, luminescence and electrochemical properties of $[Ru(bpy)_2L]^{2+}$ where L = 4-phenyl-2-(2-pyridyl)quinoline have been discussed,[514] and the crystal structure of $[Ru(bpy)(L')_2][PF_6]_2$ in which L′ = 4-methoxycarbonyl-2-(2-pyridyl)quinoline has been determined.[515]

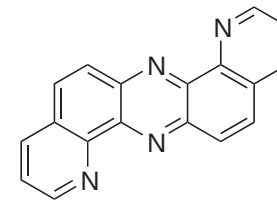


R = H or Me

(**90**)



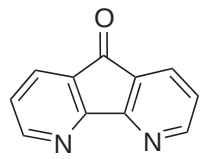
(**91**)



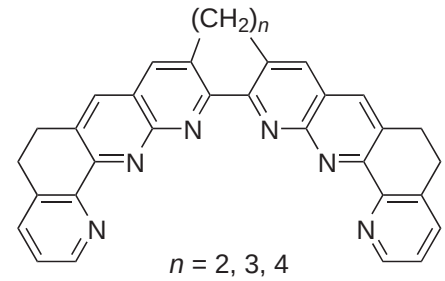
(**92**)

The structural and photophysical properties of $[Ru(bpy)_2(dafo)][PF_6]_2$ (dafo = **93**) have been reported; the emission lifetime of the complex is 420 ns;[516] the study has been extended to the properties of the series of complexes $[Ru(bpy)_n(dafo)_{3-n}]^{2+}$.[517] The nonplanar ligands (**94**) have been prepared, and form complexes of type $[Ru(bpy)_2(\mathbf{94})]^{2+}$ for $n = 2$, 3 or 4, and $[\{Ru(bpy)_2\}_2(\mathbf{94})]^{4+}$ for $n = 3$ or 4. By using deuterated bpy ligands, more easily interpretable ^1H NMR spectra are obtained. For the diruthenium complexes, there is limited inter-metal communication.[518]

Complexes of the $[Ru(bpy)_2L]^{2+}$ type in which L is a phen-based ligand are discussed next. Perchlorate salts of $[Ru(bpy)_2(phen)]^{2+}$ and $[Ru(bpy)_2(5\text{-}Mephen)]^{2+}$ have been prepared and structurally characterized. The steric strain within the coordination sphere is relieved in part by twisting of each bpy ligand.[519] Time-resolved resonance Raman spectroscopy has been used to investigate the localization of the excited electron in the MLCT state of $[Ru(bpy)_2(4,7\text{-}Ph_2\text{-}phen)]^{2+}$. In neutral micelles, the electron is localized on the bpy ligands, but in the presence of DNA and anionic surfactants, it is localized on 4,7-Ph_2phen; when the complex is in aqueous

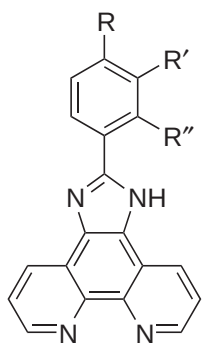


(**93**)

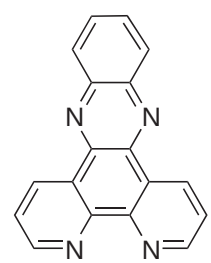


(**94**)

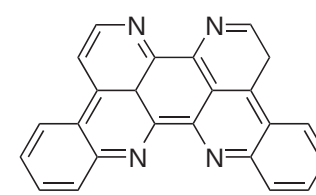
solution, both bpy and 4,7-Ph_2phen host the excited electron.[520] Starting from $[Ru(bpy)_2(3\text{-Brphen})]^{2+}$ (3-Brphen = 3-bromo-1,10-phenanthroline), cross-coupling reactions with a number of aromatic acetylenes in the presence of $PdCl_2(PPh_3)_2$, CuI and NEt_3 have been carried out; mono-, di- and trinuclear products have been isolated and characterized.[521] It has been found that the luminescent quantum yields of $[Ru(bpy)_2(HL)]^{2+}$ in which ligands HL are imidazo[f]-1,10-phenanthrolines are controlled by pH because of intramolecular, photoinduced electron transfer.[522] Related ligands are (**95**)–(**97**) (HL); their complexes, $[Ru(4,4'\text{-}Me_2bpy)_2(HL)]^{2+}$, and those in which HL has been deprotonated, have been prepared and characterized. These complexes show NLO absorption and self-defocusing effects; the NLO properties depend on the substitution (i.e., comparing within the series (**95**)–(**97**)) and level of protonation in the phenanthroline-based ligands;[523] (see also structures (**209**)–(**211**) and discussion). Electrochemical and electronic spectroscopic data for the complex $[Ru(bpy)_2(\mathbf{98})]^{2+}$ indicate that it contains two electronically separate units, one behaving in a similar manner to $[Ru(bpy)_3]^{2+}$ and the other resembling a phenazine-like acceptor.[524] A series of complexes $[ML_2(\mathbf{99})]^{2+}$ (M = Ru, Os) in which L is bpy, phen, 2,9-Me_2phen or biq, have been reported. Crystallographic and ^{1}H NMR spectroscopic methods were used to investigate the dimerization of the complexes by means of π–π stacking interactions between pairs of coordinated ligands (**99**). The dimerization constants are independent of M^{2+} but are highly dependent on steric effects of ligands L.[525] Ligand (**100**) and its naphthoquinone analog (**100′**) have been incorporated into the complexes $[Ru(bpy)_2(\mathbf{100})]^{2+}$ and $[Ru(bpy)_2(\mathbf{100'})]^{2+}$. The results of photophysical studies using steady-state emission spectroscopy evidence quenching of the Ru^{II}-based ^{3}MLCT emissive state in both complexes; this arises from intramolecular electron transfer between the excited Ru^{II} and the electron-accepting quinone moieties.[526] Chromophore-quencher dyads related to $[Ru(bpy)_2(\mathbf{100'})]^{2+}$ have been developed in order to investigate the effectiveness of rigid alicyclic frameworks in mediating electron and energy transfer.[527]



(**95**) R = NO_2, R′ = R″ = H
(**96**) R′ = NO_2, R = R″ = H
(**97**) R″ = NO_2, R = R′ = H

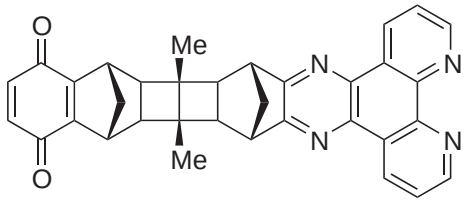


(**98**)

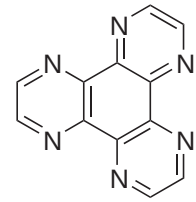


(**99**)

By comparing the results of photophysical studies on $[Ru(bpy)_2(hat)]^{2+}$, $[Ru(phen)_2(hat)]^{2+}$, $[Ru(bpy)(tap)(hat)]^{2+}$, $[Ru(bpy)(hat)_2]^{2+}$, $[Ru(tap)_2(hat)]^{2+}$, $[Ru(tap)(hat)_2]^{2+}$ and $[Ru(hat)_3]^{2+}$ (hat = **101**, tap = **102**), it has been concluded that the energy difference between the ^{3}MLCT

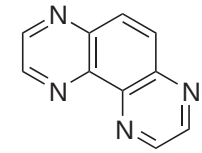


(**100**)



hat

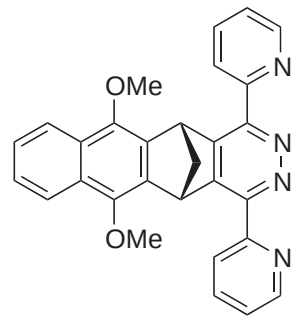
(**101**)



tap

(**102**)

and ^{3}MC states increases as the emission energy decreases. For $[Ru(bpy)_2(hat)]^{2+}$, for example, the ^{3}MC state is not accessible at room temperature.[528] The complex $[Ru(bpy)_2(\mathbf{103})]^{2+}$ exists in two diastereoisomeric forms. The crystal structure of the less soluble diastereoisomer has been determined, and the ^{1}H NMR spectra of the two isomers have been analyzed.[529]

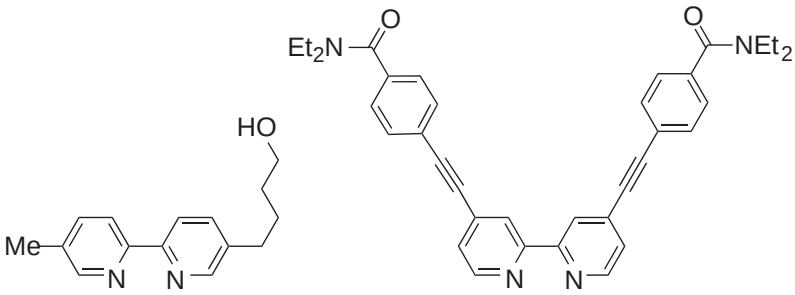


(**103**)

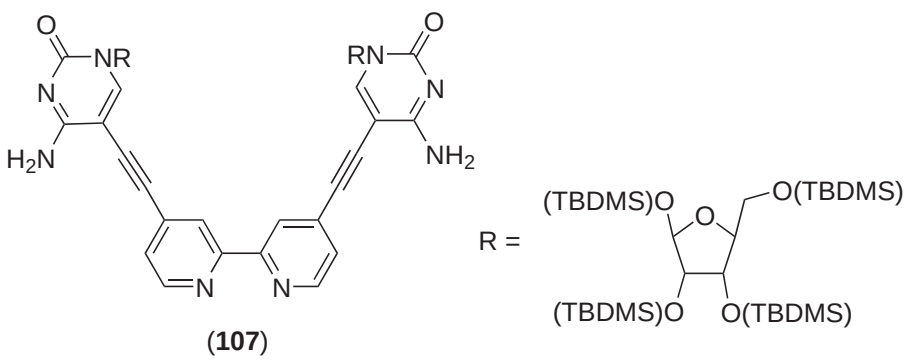
The discussion now moves to complexes containing functionalized bpy ligands. A general preparative procedure for tris(didentate)ruthenium(II) complexes in which there are three different ligands has been described. The precursor is $[Ru(CO)_2Cl_2]_n$ and the method involves the sequential introduction of polypyridyl ligands.[530] A significant number of investigations involving the 4,4′-Me_2bpy ligand have already been mentioned.[43,306,329,330,339,377,378,381,398,399,417,418,465,466,512,523] The emission properties of $[Ru(4,4'\text{-}Me_2bpy)_3]^{2+}$ and $[Ru(4,4'\text{-}Ph_2bpy)_3]^{2+}$ have been compared,[531] and the complexes have been studied using femtosecond visible electronic absorption spectroscopy, and the excited-state differential absorption spectra have been assigned.[532] For the 3,3′-dimethyl-2,2′-bipyridine-containing complex $[Ru(bpy)_2(3,3'\text{-}Me_2bpy)]^{2+}$, a short period of irradiation generates an intermediate with a monodentate 3,3′-Me_2bpy ligand; the lifetime of this species is 2–10 min in neutral or acidic (up to 1 mol dm^{-3}) solutions at 298 K.[533] The resonance Raman and time-resolved resonance Raman spectra of the ground state of $[Ru(4\text{-}Mebpy)_3]^{2+}$ can be interpreted essentially in terms of vibrationally isolated pyridine and 4-methylpyridine rings.[534] A series of $[RuR_2(4,4'\text{-}{}^tBu_2bpy)_2]$ complexes (R = alkyl) has been reported, and the structure of *cis*-$[RuEt_2(4,4'\text{-}{}^tBu_2bpy)_2]$ has been determined.[535] The ^{1}H NMR spectra of the unsymmetrical 4,4′-RR′bpy ligands and of the complexes $[Ru(bpy)_2(4,4'\text{-}RR'bpy)]^{2+}$ have been analyzed.[536] A useful route to tris{4,4′-bis(halomethyl)bpy}ruthenium(II) complexes has been described; the method involves initial formation of $[RuL_3]^{2+}$ in which L = 4,4′-$(CH_2OH)_2$bpy, followed by treatment with oxalyl chloride and dmf in thf or MeCN.[537] Tris-(ligand) complexes containing the unsymmetrical alkyl-substituted bpy ligands 5-Mebpy, 5-Etbpy, 5-Prbpy, 5-(2-MePr)bpy and 5-(2,2-Me_2Pr)bpy have been prepared and characterized. The *mer*- and *fac*-isomers of each complex have been isolated by use of cation-exchange column chromatography; as the steric requirements of the R group increase, the percentage of the *fac*-isomer decreases. Enantiomers of $[Ru(5\text{-}Prbpy)_3]^{2+}$ were separated on SP Sephadex C-25.[538] Electrokinetic chromatography has been used to separate the enantiomers of $[Ru(\mathbf{104})_3]^{2+}$; anionic carboxymethyl-$\beta$-cyclodextrin was employed as the chiral mobile phase additive.[539]

The ligand 6-phenyl-2,2′-bipyridine has the potential to be an *N,N*′-donor or undergo cyclometallation of the phenyl ring and become an *N,N′,C*-donor. This chemistry has been investigated, and as part of the study, *cis*-$[Ru(6\text{-}Phbpy\text{-}N,N')_2Cl_2]$ has been isolated and structurally

characterized.[540] The photophysical properties of Ru^{II} complexes containing bpy and 4,4′-Ph_2bpy have been described.[541] Incorporating phenylene ethynylene substituents into $[Ru(bpy)_3]^{2+}$ complexes has been addressed in a study of the photophysical properties of $[Ru(bpy)_2(\mathbf{105})]^{2+}$ and $[Ru(bpy)_2L]^{2+}$ in which L is the 5,5′-disubstituted analog of (**105**). In both Ru^{II} complexes, the MLCT excited state is localized on the functionalized ligand; the effects of changing the position of substitution (4,4′ or 5,5′) have been examined.[542] An ethynylated-pyrene group attached to a bpy ligand (ligand **106**) has a dramatic effect on the photophysical properties of Ru^{II} tris(bpy) complexes; the emission spectrum of $[Ru(bpy)_2(\mathbf{106})]^{2+}$ is typical of the Ru(bpy)-unit, but emission is extremely long-lived with a triplet lifetime of 42 μs.[543] The synthesis and characterization of the cytidine-containing $[Ru(bpy)_2(\mathbf{107})]$ $[PF_6]_2$ have been reported; the interest in the complex (which has an emission band at 655 nm) is in its potential use as a photodonor and/or acceptor in redox-active electron-transfer model systems.[544]



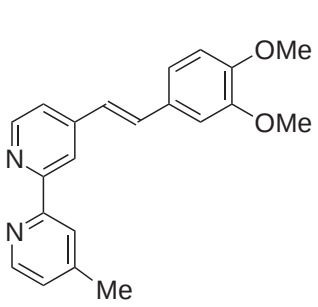
(**104**) (**105**) (**106**)



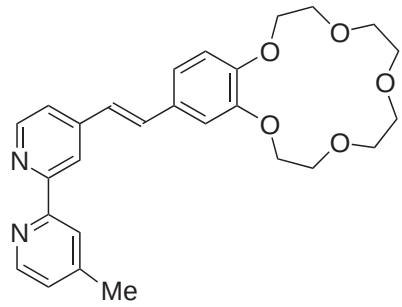
(**107**)

The complex $[RuL_3]^{2+}$ in which L = 4-methyl-4′-(*E*-prop-2-enyl)-2,2′-bipyridine, has been synthesized and characterized.[545] Problems associated with the preparation of 4-methyl-4′-vinyl-2,2′-bipyridine (vbpy) and the electropolymerization of $[Ru(vbpy)_3]^{2+}$ have been addressed; ^{1}H NMR spectroscopy can be used to determine the relative proportions of complexes in mixtures formed prior to electropolymerization.[545] Size exclusion chromatography has been used to separate polymers produced from $[M(vbpy)_3][PF_6]_2$ (M = Ru, Os) by radical polymerization. On going from mononuclear complex to polymer, there is a shift in the emission energy to higher values; the emission energy of each polymer is related to the concentration of vinyl groups remaining in the polymer.[546] The outcomes of different methods of polymerization of $[M(vbpy)_3][PF_6]_2$ (M = Ru, Os) have been discussed.[547] $[RuL_3]^{2+}$ and $[Ru(bpy)_2L]^{2+}$ complexes containing the ligands (**108**) and (**109**), and analogous 4,4′-bpy ligands bearing two bis(methoxy)phenyl or crown ether substituents, have been prepared and characterized. Electropolymerization studies reveal that of the two classes of complex $[RuL_3]^{2+}$ and $[Ru(bpy)_2L]^{2+}$, only $[RuL_3]^{2+}$ undergoes polymerization.[548] The photophysical properties of $[RuL_3]^{2+}$ and $[Ru(bpy)_2L]^{2+}$ complexes in which L is one of ten methoxy or vinyl linked benzo-crown ether ligands have been investigated; the excited ^{3}MLCT state lifetimes are in the range 0.85 ± 0.12 μs for almost all the complexes. Quenching in MeCN of the ^{3}MLCT states by molecular O_2 ($^3\Sigma_g^-$) has also been studied.[549] Electroactive polymer films have been produced by the electropolymerization of $[RuL_3]^{2+}$ and $[Ru(bpy)_2L]^{2+}$ where L = 4-methyl-4′-(3-methoxystyryl)-2,2′-bipyridine and 4,4′-di(3-methoxystyryl)-2,2′-bipyridine.[550]

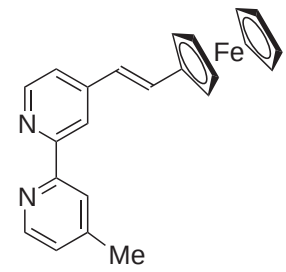
The PF_6^- salts of $[Ru(bpy)_2(\mathbf{110})]^{2+}$, and $[Ru(\mathbf{110})_3]^{2+}$ and analogous complexes containing 4,4′-bis(substituted) ferrocenyl ligands (**110′**), have been synthesized and characterized; the tris(chelate) complexes are either poorly soluble or insoluble. Electropolymerization of $[Ru(\mathbf{110}')_3][PF_6]_2$ produces an electrochromic film.[551] The complex $[Ru(bpy)_2(\mathbf{111})]^{2+}$ undergoes electropolymerization on Pt and glassy carbon electrodes, although the related complex $[Ru(bpy)_2(\mathbf{112})]^{2+}$ does not. Electrochemical and spectroscopic properties of the films indicate that they form by both head-to-tail and tail-to-tail monomer coupling.[552]



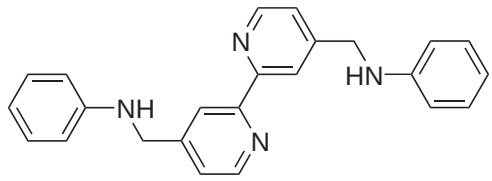
(**108**)



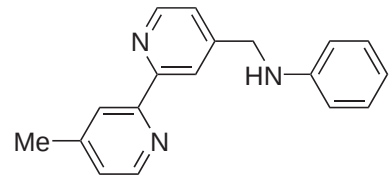
(**109**)



(**110**)



(**111**)



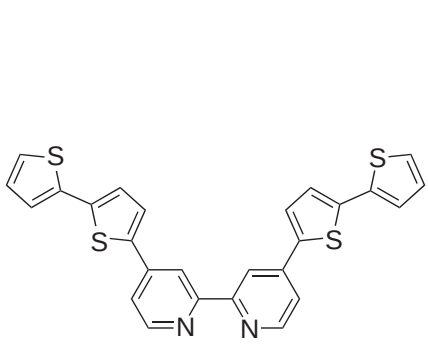
(**112**)

It has been observed that, in EtOH and in the presence of Et_3N, *cis*-$[Ru(6,6'\text{-}Cl_2bpy)_2(H_2O)_2][CF_3SO_3]_2$ is an effective catalyst for the hydrogenation of CO_2 to HCO_2H.[553]

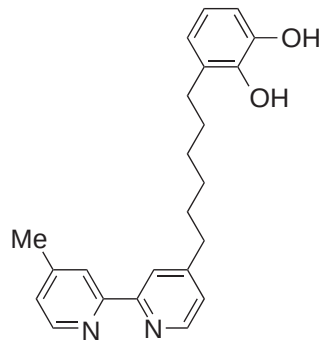
Complexes involving amino-derivatives of bpy include $[Ru(6,6'\text{-}(NH_2)_2bpy)_3]^{2+}$, the photophysical and electrochemical properties of which have been reported.[554] The complexes $[Ru(4,4'\text{-}Me_2bpy)_{3-n}\{4,4'\text{-}(NEt_2)_2bpy\}_n]^{2+}$ ($n = 0$–3) have been the focus of electronic and vibrational spectroscopic studies. The MLCT absorption shifts from 458 nm when $n = 0$–518 nm when $n = 3$; however, emission data are consistent with an energy-gap order (values of n) of $0 > 1 > 3 > 2$. This apparent difference in data is understood in terms of the localization of the ^{3}MLCT state on the 4,4′-Me_2bpy ligand when this is possible, leaving $[Ru\{4,4'\text{-}(NEt_2)_2bpy\}_3]^{2+}$ as a unique case.[555] An improved method of preparing the 4,4′-$(NEt_2)_2$bpy ligand has been reported, and it is observed that the Ru^{III} complex $[Ru\{4,4'\text{-}(NEt_2)_2bpy\}_2Cl_2]^+$ is a useful precursor to complexes such as $[Ru\{4,4'\text{-}(NEt_2)_2bpy\}_2(bpy)]^{2+}$ and $[Ru\{4,4'\text{-}(NEt_2)_2bpy\}_2\{2\text{-}(2\text{-pyridyl})bim\}]^{2+}$. These complexes exhibit low Ru^{3+}/Ru^{2+} redox potentials.[556] Unsymmetrical bpy ligands (bpy′) possessing amino or carboxyl groups linked to the bpy ligand via an alkyl chain have been prepared. The $[Ru(bpy')_3]^{2+}$ complexes exhibit MLCT bands close to 480 nm, and reduction potentials are ≈200 mV lower than for $[Ru(bpy)_3]^{2+}$.[557]

The presence of SMe groups in the 4,4′-positions of bpy make little difference to the photophysical properties of $[Ru(bpy)_2\{4,4'\text{-}(SMe)_2bpy\}]^{2+}$ compared to those of $[Ru(bpy)_3]^{2+}$. However, $[Ru(bpy)_2\{4,4'\text{-}(SMe)_2bpy\}]^{2+}$ does possess the ability to provide strong binding sites for pentacyanoferrate groups providing a route to polynuclear species that can be immobilized on Ni electrode surfaces.[558] The thienyl complexes $[Ru(\mathbf{113})_3]^{2+}$ and $[Ru(bpy)_2(\mathbf{113})]^{2+}$, those involving the 5,5′-analog of (**113**), and $[Ru(\mathbf{113}')_3]^{2+}$ where (**113′**) is the monosubstituted analog of (**113**), have been prepared and characterized. Electropolymerization generates poly-$[Ru(\mathbf{113})_3]^{2+}$ and poly-$[Ru(\mathbf{113}')_3]^{2+}$ which exhibit high redox conductivity.[559]

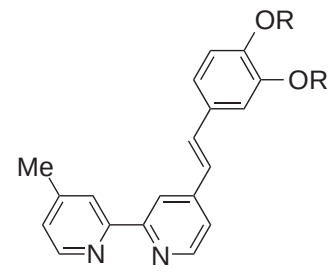
Tris(bpy) complexes of ruthenium(II) with pendant catechol units are represented by $[Ru(bpy)_2(\mathbf{114})]^{2+}$, isolated as the BF_4^- salt. Interest in this fluorescent complex stems from its use as a potential skin sensitizer.[560] In the complex $[Ru(bpy)_2(\mathbf{115})]^{2+}$ (R = H), the deprotonated catechol unit can act as a binding site for other metal fragments, thereby forming homo- and



(**113**)



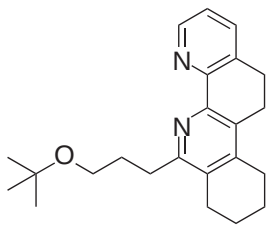
(**114**)



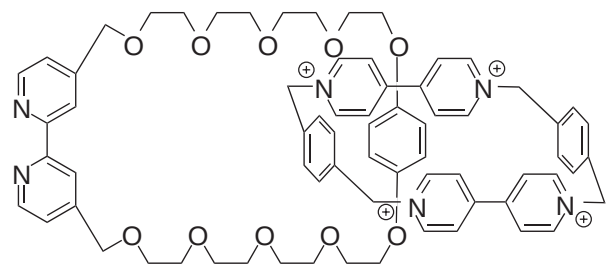
R = H, Me

(**115**)

heterometallic species. The complex $[Ru(bpy)_2(\mathbf{115})]^{2+}$ (R = Me) has also been prepared and characterized.[561] The complexes $[M(bpy)_2(bpy\text{-}O\text{-}bpy)]^{2+}$ (M = Ru, Os; bpy-O-bpy = bis (4-(2,2′-bipyridinyl))ether) interact with 1-pyreneacetic acid via coordination to a common Zn^{2+} ion. In the $\{Ru^{II}–Zn^{II}–pyrene\}$ system, the excited state lifetime of the Ru^{II} complex is prolonged into the microsecond range at 298 K as a result of an equilibrium involving the triplet excited state of the pyrene unit.[562] Two annelated bpy ligands L (e.g., **116**) carrying *tert*-butoxypropyl chains and which exhibit fluorescence emission, form $[Ru(bpy)_2L]^{2+}$ complexes that show similar photophysical and spectroscopic properies to $[Ru(bpy)_3]^{2+}$ at 298 K and 77 K, although the heteroleptic complexes show less intense emission quantum yields and lifetimes at 298 K. Structural data evidence significant distortion in the octahedral structure of the $[Ru(bpy)_2L]^{2+}$ complexes.[563] By designing cages consisting of three polyether-linked bpy ligands, it has been possible to synthesize $[RuL]^{2+}$ complexes in which L is the cage ligand. The inter-bpy linkers are -C(O)O$(CH_2)_2$O$(CH_2)_2$O$(CH_2)_2$OC(O)- and -C(O)O$(CH_2)_2$O$(CH_2)_2$O$(CH_2)_2$O$(CH_2)_2$O$(CH_2)_2$OC(O)- connected to the 4 and 4′- or 5 and 5′-positions of adjacent bpy ligands. The coronate complexes exhibit very high photostabilities, and electron transfer to MV^{2+} proceeds by a bimolecular process in a hydrogen-producing cycle.[564,565] The catenane $[(\mathbf{117})][PF_6]_4$ reacts with $[Ru(4,4'\text{-}Me_2bpy)_2Cl_2]$ to give $[Ru(4,4'\text{-}Me_2bpy)_2(\mathbf{117})][PF_6]_6$. This complex exhibits effective photoinduced electron transfer between the noncovalently linked sensitizer and acceptor domains, and the rate of transfer in water is estimated to be $\geq 2.1 \times 10^8\ s^{-1}$. The system is proposed as a model for a photosynthetic reaction center.[566] The macrocyclic ligand (**118**) contains both bpy and phen binding sites. Treatment of (**118**) with $[Ru(bpy)_2Cl_2]$ results in selective coordination at the bpy domain in (**118**) to yield $[Ru(bpy)_2(\mathbf{118})]^{2+}$. Reaction of the latter with $[Cu(MeCN)_4]^+$ leads to $[(MeCN)_2Cu(\mathbf{118})Ru(bpy)_2]^{3+}$; this complex reacts with 2,9-di(4-methoxy)phenyl-1,10-phenanthroline (dap) to give $[(dap)Cu(\mathbf{118})Ru(bpy)_2]^{3+}$, a precatenate species. The absorption spectrum and electrochemical data for this complex show that in the ground state, the two chromophores are independent. The emission behavior is interpreted in terms of one of two processes: energy transfer between $*Ru^{II}$ and Cu^I, or reductive quenching of $*Ru^{II}$ by Cu^I.[567]

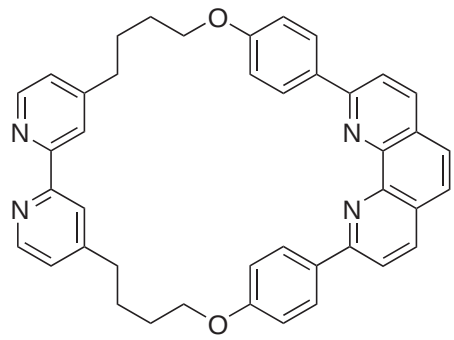


(**116**)



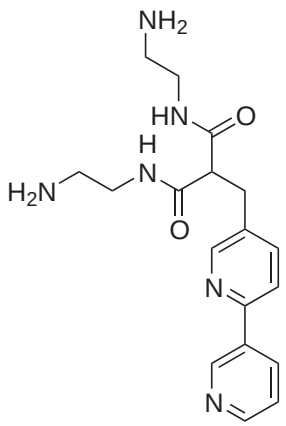
(**117**)

The complexes $[Ru(bpy)_2(3,3'\text{-}X_2bpy)]^{2+}$ and $[Ru(4,4'\text{-}Me_2bpy)_2(3,3'\text{-}X_2bpy)]^{2+}$ in which X = CH_2OH, CO_2H, CO_2Me, CO_2Et and CO_2CH_2Ph have been prepared and characterized, and the structure of $[Ru(bpy)_2\{3,3'\text{-}(CO_2Me)_2bpy\}][PF_6]_2$ has been determined. In the UV–vis

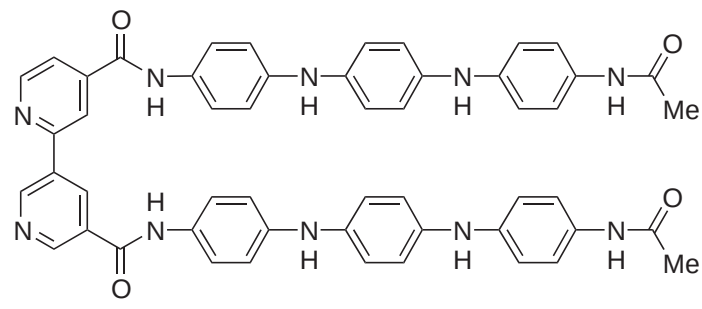


(**118**)

spectra of the complexes, bands in the 400–550 nm region are assigned to MLCT transitions and those between 250 nm and 350 nm to intraligand processes. Emission maxima (298 K, MeCN) range from 711 nm for X = ester functionality to 614 nm for X = CH_2OH, and the emission lifetimes lie in the range 258–940 nm.[568] Viscous, room-temperature ionic liquids are produced when bpy′ ligands containing $C(O)O(CH_2CH_2O)_7Me$ chains attached to the 4- and 4′-positions are incorporated into $[Ru(bpy)_{3-n}(bpy')_n]^{2+}$ complexes.[569] The presence of electron-withdrawing groups (e.g., ester, nitrile, imide, amide) in 5,5′-bpy ligands in Ru^{II} tris(bpy) complexes leads to shifts in the reduction potentials of each complex to more positive values, making it possible to observe up to six ligand-based reductions. In the reduced oxidation states, the complexes exhibit multicolor electrochromism.[570] The optical absorption and luminescence spectroscopic and electrochemical properties of $[Ru(bpy)_2\{5,5'\text{-}(NH_2)_2bpy\}]^{2+}$, $[Ru(bpy)_2\{5,5'\text{-}(CO_2Et)_2bpy\}]^{2+}$ and $[Ru(bpy)_2\text{-}\{5,5'\text{-}(NHCO_2Et)_2bpy\}]^{2+}$ have been investigated.[571] Coupling of the $CONEt_2$ group in Ru^{II}-coordinated 4-Me-4′-$(CONEt_2)$bpy to appropriate amino acids gives a route to amino acid-functionalized complexes $[Ru(bpy)_2(4\text{-Me-}4'\text{-Xbpy})]^{3+}$ where $X = CONH(CH_2)_n$ $CH(NH_3^+)CO_2^-$. The characteristics of the absorption spectra for the complexes with $n = 1$–4 are pH-independent because there is little electronic communcation between the amino acid group and the Ru^{II} chromophore. However, the luminescence intensities and excited-state lifetimes are pH-dependent.[572] The complex $[Ru(bpy)_2$(**119**)$][PF_6]_2$ is water-soluble and is able to sense Cu^{2+} and Ni^{2+} ions because coordination of the pendant donor set to these metal ions results in strong quenching of the $Ru(bpy)_3$-fluorescence.[573] The reaction of *cis*-$[Ru(bpy)_2Cl_2]$ with ligand (**120**) leads to the formation of $[Ru(bpy)_2$(**120**)$]^{2+}$, isolated as the PF_6^- salt. Oxidation of this complex with Ag_2O produces $[Ru(bpy)_2$(**120-ox**)$]^{2+}$ in which ligand (**120**) has been oxidized at the central $-NHC_6H_4NH-$ unit; this step can be reversed on treatment with $N_2H_4 \cdot H_2O$. The electrochemistry of $[Ru(bpy)_2$(**120**)$]^{2+}$ has been studied; when the complex (in MeCN) is excited at 477 nm, the emission spectrum is almost completely quenched, and it is concluded that the π-conjugated chains in (**120**) contribute to this effect.[574]

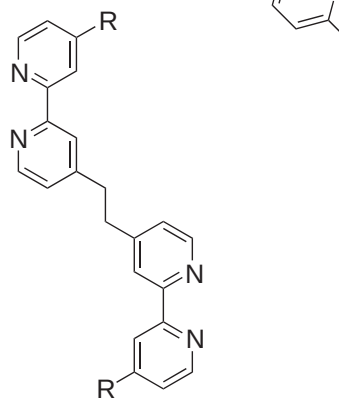


(**119**)

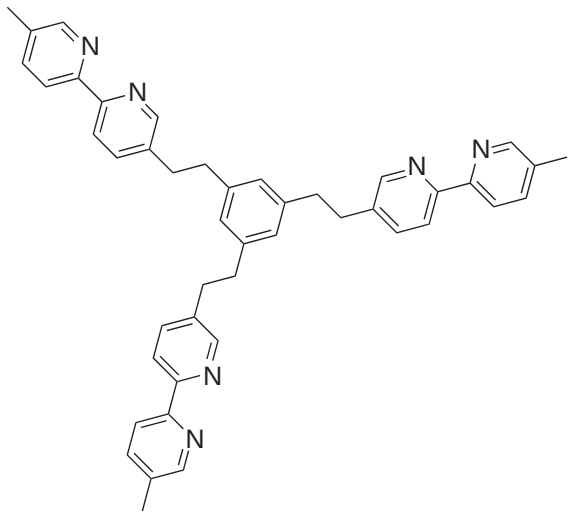


(**120**)

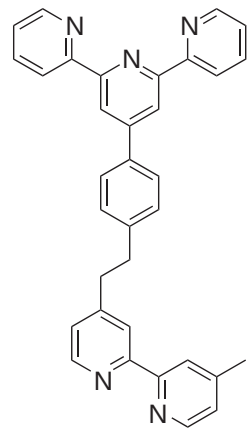
The complexes $[Ru(\mathbf{28})_3]^{2+}$ containing polymethylene bridged bpy ligands (**28**)[312] have been prepared by reactions of $RuCl_3 \cdot xH_2O$ with the appropriate ligands. The absorption and emission energies of the complexes resemble those of $[Ru(bpy)_3]^{2+}$, but the emission intensities are reduced when $[Ru(\mathbf{28})_3]^{2+}$contains bridged bpy ligands that are highly distorted away from planarity. Structural data confirm the degree of twisting of the ligand containing the longest polymethylene bridge.[575] The photophysical properties of $[Ru(bpy)_2(4,4'\text{-}Me_2bpy)]^{2+}$, $[Ru(bpy)_2(\mathbf{121})]^{2+}$, $[Ru(bpy)_2(\mathbf{122})]^{2+}$, $[Ru(bpy)(\mathbf{121})]^{2+}$, $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{121})]^{4+}$, and $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{122})]^{4+}$ have been reported. The complexes exhibit MLCT transitions at ≈450 nm, intraligand $\pi \rightarrow \pi^*$ transitions at wavelengths <300 nm, emission (λ(em) = 598–610 nm) from an ^{3}MLCT excited state. The electrochemistry of the complexes is characterized by a reversible, Ru-centered oxidation between 1.25 V and 1.40 V (vs. SSCE), and a series of ligand-based reductions between −1.3 V and ≈−1.9 V.[576] Complex formation between Ru^{II} and three tripodal-type ligands, exemplified by (**123**), has been described. The three bpy domains may bind a single Ru^{2+} ion, although dimetallic and polymetallic species have also been isolated. The excited-state lifetime and emission quantum yield for $[Ru(\mathbf{123})]^{2+}$ are 2,800 ns and 0.271 respectively.[577] The syntheses of ligand (**124**) and its analog containing two tpy-binding domains (**124′**) have been reported. Pendant tpy domains are present in the complexes $[Ru(bpy)_2(\mathbf{124})]^{2+}$ and $[Ru(bpy)_2(\mathbf{124'})]^{2+}$.[578]



(**121**) R = H
(**122**) R = Me



(**123**)



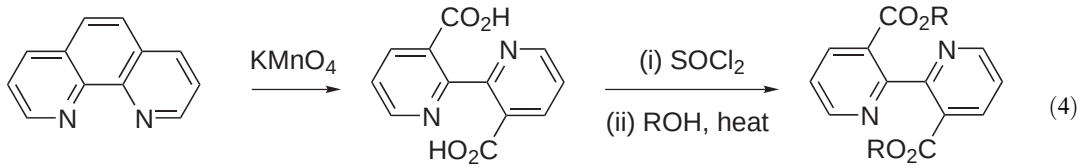
(**124**)

Attaching a C_{60} cluster to an $[Ru(bpy)_3]^{2+}$ core has been achieved by 1,3-dipolar cycloaddition of azomethine ylides to the fullerene. The electrochemistry of the complex is complicated: a one-electron reversible oxidation of the Ru center, five one-electron reversible reductions associated with the C_{60} cage, and five more reversible reductions centered on the bpy ligands. The photophysical properties of the complex have been discussed.[579]

Among functionalized bpy ligands, those with carboxylic acid or carboxylate groups attached have been a particular focus of attention, especially with respect to finding efficient photosensitizers for use in TiO_2-based solar cells. One of the most efficient photosensitizers for this purpose is *cis*-$[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2(NCS)_2]$.[580] Acceptor–donor complexes are formed by intermolecular interactions between $[Ru(4,4'\text{-}X_2bpy)_2\{4\text{-}Me\text{-}4'\text{-}(CO_2)bpy\}]^{2+}$ (X = H, CO_2Et) and *N,N′*-dimethylaminobenzamidinium ion. Electron transfer across the bridging unit has been examined.[581] A series of complexes containing carboxylate or ester-functionalized bpy ligands has been prepared; these include $[Ru(bpy)_2\{6\text{-}(CO_2)bpy\}]^+$ and $[Ru(bpy)_2\{6\text{-}(CO_2H)\ bpy\}]^{2+}$. In $[Ru(bpy)_2\{6\text{-}(CO_2)bpy\}]^+$, an unusual temperature dependence of the rate of radiative decay is observed.[582] The emission lifetimes of $[Os(bpy)_2\{4,4'\text{-}(CO_2)_2bpy\}]$ and $[Os(bpy)_2\{3,5\text{-}(CO_2)_2bpy\}]$ show different dependences on temperature. For aqueous solutions of the former complex, the emission lifetime decreases as the temperature increases; in contrast, the latter complex (in EtOH) exhibits longer lifetimes as the temperature increases.[583] The synthesis and photophysical properties of

$[Ru(bpy)_2\{3,5\text{-}(CO_2H)_2bpy\}]Cl_2$ have been reported. The complex exhibits a long-lived excited state ($\lambda(em) = 637\,nm$, $\tau = 846 \pm 11\,ns$), the decay of which involves an activated crossing to higher energy ligand-field states.[584] The energy of the CT band can be varied systematically in the series of complexes $[Ru\{4,4'\text{-}(CO_2)_2bpy\}_2L_2]$ where L_2 is a wide variety of ligands, either one didentate or two monodentate.[585] The pK_a value of the complex $[Ru(bpy)_2\{3\text{-}(CO_2H)bpy\}]^{2+}$ is 0.82 ± 0.07,[586] and for $[Ru(bpy)_2\{3,3'\text{-}(CO_2H)_2bpy\}]^{2+}$, pK_a values are 0.2 and 2.2.[587] Values for $[Ru(bpy)_2\{4,3'\text{-}(CO_2H)_2bpy\}]^{2+}$ are 1.7 and 2.9. The difference in values between $[Ru(bpy)_2\{3,3'\text{-}(CO_2H)_2bpy\}]^{2+}$ and $[Ru(bpy)_2\{4,3'\text{-}(CO_2H)_2bpy\}]^{2+}$ is attributed to differences in hydrogen-bonded interactions. Values of pK_a for the excited-state complexes show that the latter are slightly stronger bases than the corresponding ground state complexes.[586,587] The syntheses and characterization[588] of *trans*-$[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2Cl_2]$, *trans*-$[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2(H_2O)_2]^{2+}$, and *trans*-$[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2(NCS)_2]$ have been reported. The absorption and emission maxima of the *trans*-complexes are red-shifted with respect to their *cis*-analogs, and this red-shift makes the complexes suited to their use as dyes in dye-sensitized TiO_2 electrodes.[589] General synthetic strategies have been described for the incorporation of carboxylate groups in polypyridyl ligands in Ru^{II} complexes; one method involves the hydrolysis of CO_2Et groups to CO_2H, while the second method relies on the conversion of Me to CO_2H substituents.[590] The electrochemical properties of $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}(CO)_2Cl_2]$, $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2Cl_2]$, $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2Br_2]$, $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2\{4,4'\text{-}(CO_2)_2bpy\}]$, and $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_3]Cl_2$ have been studied in MeCN and dmso. The presence of electron-withdrawing $4,4'\text{-}(CO_2H)_2bpy$ ligands make oxidation of the Ru^{I} center more difficult. The photochemical behavior of the complexes has also been examined.[591] The complex $[Ru(PPh_3)_2\{4,4'\text{-}(CO_2H)_2bpy\}Cl_2]$ has been prepared for use as a TiO_2 sensitizer in regenerative photoelectrochemical cells; it exhibits a reversible Ru^{2+}/Ru^{3+} couple.[592] The photoluminescent properties of $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_3]^{2+}$ are pH-dependent. At pH 3, the emission intensity and excited-state lifetime are at a minimun while $\lambda(em)$ is at a maximum value. pK_a measurements have been made. The study is extended to include electrochemical data.[593] The photophysical properties of *cis*-$[Ru\{3,3'\text{-}(CO_2H)_2bpy\}_2(NCS)_2]$, *cis*-$[Ru\{5,5'\text{-}(CO_2H)_2bpy\}_2(NCS)_2]$ and *cis*-$[Ru(4,4'\text{-}X_2bpy)_2(NCS)_2]$ (X = various substituents) have been compared. Steric factors influence the energy of the excited state; compared to 4,4′-substituted bpy-containing sensitizers, the 3,3′- and 5,5′-analogs are less efficient at converting visible photons into electrons.[594] Starting from *cis*-$[RuCl_2(dmso)_4]$, the sequential introduction of bpy ligands carrying different substituents has been used as a general method of preparing $[Ru\{4\text{-}CO_2H\text{-}4'\text{-}(CO_2)bpy\}(4,4'\text{-}Me_2bpy)(dtc)]$ (the structure of which has been determined) and $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}(4,4'\text{-}Me_2bpy)(NCS)_2]$. The properties of these complexes have been discussed in terms of their suitability as charge-transfer photosensitizers in TiO_2-based solar cells.[595] This application has also driven an investigation of the properties of $[Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2L]^{+}$ in which HL = Hacac, 3-methyl-2,4-pentanedione or 1,3-diphenyl-1,3-propanedione. In tests as photosensitizers, these complexes perform well, giving overall solar light to electrical energy conversion efficiencies of 3.9–6.0%, compared with 5.7% for *cis*-$[Ru\{4,4'\text{-}(CO_2H)_2\ bpy\}_2(NCS)_2]$ under similar conditions.[596] The complex *fac*-$[Ru\{5\text{-}(CO_2H)_2bpy\}_3]^{2+}$ has been prepared as a single geometrical isomer. The synthetic strategy involved the use of a tripodal tris(bpy) ligand with ester linkages which could then be hydrolyzed to release the *fac*-isomer of $[Ru\{5\text{-}(CO_2H)bpy\}_3]^{2+}$.[597] The introduction of a Ph spacer between the bpy ligand and CO_2H substituent in $4,4'\text{-}(CO_2H)_2bpy$ has the effect of red-shifting the MLCT bands on going from the parent compounds to $[Ru\{4,4'\text{-}(C_6H_4\text{-}4\text{-}CO_2H)_2bpy\}_{3-n}(4,4'\text{-}Me_2bpy)_n]^{2+}$ ($n = 0$–2). However, the excited state properties of these complexes remain similar to those of the parent $4,4'\text{-}(CO_2H)_2bpy$-containing species.[598] The synthesis and characterization of *cis*-$[Ru\{4,4'\text{-}(CO_2H)_2\text{-}2,2'\text{-}biq\}_2X_2]$ ($X^- = Cl^-$, NCS^-, CN^-) have been described; the complexes exhibit intense MLCT bands in the visible region and are emissive at 298 K; $pK_a(1)$ for the ground state of the thiocyanate complex is 2.9. The results of photoelectrochemical studies of the complexes anchored to TiO_2 film electrodes indicate that they exhibit only low light-harvesting efficiencies.[599]

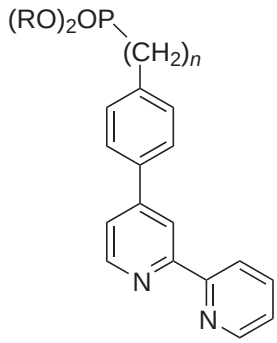
The electronic structures of the MLCT excited states of $[Ru(bpy)_2(4\text{-}CO_2Et\text{-}4'\text{-}Mebpy)]^{2+}$, $[Ru(bpy)_2\{4,4'\text{-}(CO_2Et)_2bpy\}]^{2+}$, $[Ru(bpy)\{4,4'\text{-}(CO_2Et)_2bpy\}_2]^{2+}$, $[Ru\{4,4'\text{-}(CO_2Et)_2bpy\}_3]^{2+}$, $[Ru(bpy)_2\{4,4'\text{-}(CONEt_2)_2bpy\}]^{2+}$, $[Ru(bpy)_2\{4\text{-}(CONEt_2)\text{-}4'\text{-}Mebpy\}]^{2+}$, and $[Ru\{4\text{-}(CONEt_2)\text{-}4'\text{-}Mebpy\}_3]^{2+}$ have been examined by use of step-scan FT IR absorption difference time-resolved spectroscopy. The results show that the ester- or amide-functionalized ligands are the ultimate acceptors, with the excited electron localized on one acceptor ligand on a nanosecond timescale.[600,601] Starting from phen, 3,3′-dialkoxycarbonyl-2,2′-bipyridine ligands (L) have been prepared (Equation (4)) and used to produce the complexes *trans*-$[RuL(CO)_2Cl_2]$ and *cis*-$[RuL_2Cl_2]$.[602]



(4)

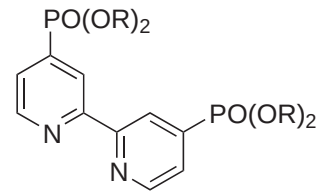
R = Me, Et, ^{i}Pr, ^{i}Bu

The sulfonic acid-functionalized bpy ligands 4,4′-$(SO_3H)_2$bpy and 5-(SO_3H)bpy have been prepared and their complexation with Ru^{II} investigated.[603] Phosphonic acid and phosphonate-functionalized bpy ligands (**125**) and (**126**) have been incorporated into complexes of type $[Ru(bpy)_2L]^{2+}$. The Ru^{3+}/Ru^{2+} reduction potentials are more positive for the phosphonate than phosphoric acid-containing complexes, and the first reduction process of each phosphonate-containing complex is centered on this ligand. The luminescence properties of the complexes are discussed, and coordination to Fe^{3+} or Cu^{2+} very efficiently quenches the luminescence of the phosphonic acid complexes.[604]



n = 0, 1
R = H, Et

(**125**)



R = H, Et

(**126**)

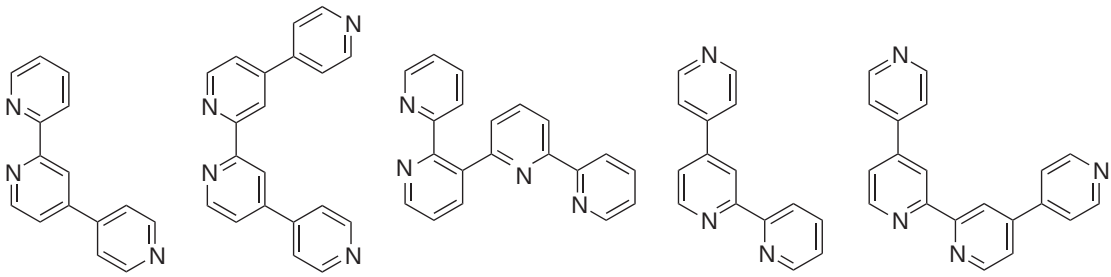
The final part of this section covers several complexes of type $[Ru(bpy)_2L]^{2+}$ in which L is a polypyridyl ligand other than 2,2′-bipyridine or 2,2′:6′,2″-terpyridine. In the complexes $[Ru(bpy)_2(\mathbf{127})]^{2+}$, protonation of the non-coordinated N atom results in a red shift of the lowest energy MLCT band by 870 cm^{-1}, consistent with the π^* level of (**127**) being lowered on addition of H^+. Protonation of the two non-coordinated N atoms in $[Ru(bpy)_2(\mathbf{128})]^{2+}$ occurs at the same time ($pK_a = 3.6$) with a concomitant red shift of the lowest energy MLCT band by 1,570 cm^{-1}. The excited states of the complexes are more basic than the corresponding ground states.[605] The electrochemical and photophysical properties of the *N*-methylated complexes $[M(bpy)_2(\mathbf{129}\text{-Me})]^{3+}$ (M = Ru, Os) have been compared with those of $[M(bpy)_2(\mathbf{129})]^{2+}$.[606] Complex $[Ru(bpy)_2(\mathbf{131})]^{2+}$ and its *N*- or *N,N′*-methylated derivatives have been investigated. $[Ru(bpy)_2(\mathbf{131})]^{2+}$ is strongly luminescent, with a lifetime >1,400 ns in MeCN. Methylation drastically reduces this lifetime to <100 ns.[607] In both $[Ru(bpy)_2(\mathbf{130})]^{2+}$ and $[Ru(bpy)_2(\mathbf{131})]^{2+}$, the orientations of the pendant pyridyl units make these complexes ideal as building blocks for photoactive polynuclear complexes containing $[Ru(bpy)_3]^{2+}$ chromophores.[608]

5.5.3.1.4 Dinuclear complexes of the general formula $[(bpy)_2M(\mu\text{-}L)M(bpy)_2]^{n+}$ (M = Ru or Os)

Stereochemical aspects of complexes including many dinuclear species are considered together in Section 5.5.3.1.6.

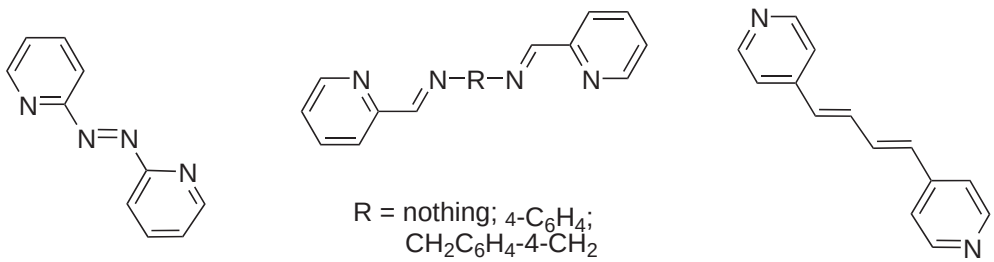
On a general note, the use of FAB mass spectrometry in the characterization of complexes of type $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{4+}$ or related species has been addressed in several papers.[609–612]

The α-azodiimine (**132**) is one of a series of related ligands used as bridges in $[(4,4'\text{-}R_2bpy)_2\text{-}Ru(\mu\text{-}L)Ru(4,4'\text{-}R_2bpy)_2]^{4+}$ (R = H or Me). Ligand (**132**) presents an *N,N′*-donor set to each Ru^{II}



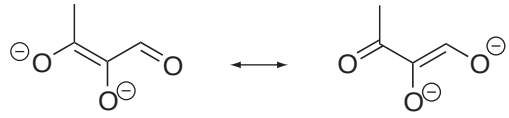
(127) **(128)** **(129)** **(130)** **(131)**

center, and the diastereoisomeric forms of each complex ΔΛ (*meso*) and ΔΔ/ΛΛ (*rac*) have been separated using cation-exchange chromatography and have been characterized.[613] The complexes $[(bpy)_2Ru(\mu\text{-}\mathbf{133})Ru(bpy)_2]^{4+}$ exhibit three MLCT transitions in the visible region, and the lowest energy band is assigned to a d $\pi(Ru) \rightarrow \pi^*$(**133**) transition; in the UV region, intense ligand-based $\pi \rightarrow \pi^*$ transitions are observed. Both Ru^{II} centers are oxidized simultaneously.[614] The complexes $[(bpy)_2ClRu(\mu\text{-}\mathbf{134})RuCl(bpy)_2]^{2+}$ and $[(NH_3)_5Ru(\mu\text{-}\mathbf{134})Ru(NH_3)_5]^{4+}$ can be deprotonated at the central CH_2 unit to give cyanine-linked complexes. Redox studies of the complexes have been carried out; attempts to prepare mixed-valence polyenyl complexes were not successful.[615]



(132) **(133)** **(134)**

Treatment of $[Ru(bpy)_2(EtOH)_2]^{2+}$ with 2-thiouracil or 6-methyl-2-uracil (H_2L) in the presence of NEt_3, yields $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{2+}$; L^{2-} coordinates to one Ru^{II} center as an *N,O*-donor and to the other as an *N,S*-donor. The thiouracil derivative exhibits two reversible one-electron redox processes assigned to successive Ru^{2+}/Ru^{3+} couples.[616] The reaction between $[Ru(bpy)_2Cl_2]$ and ethylene glycol at elevated temperature produces $[(bpy)_2Ru(\mu\text{-}\mathbf{135})Ru(bpy)_2]^{2+}$ in which there is a strong electronic interaction between the two metal centers.[617] Alkoxy-bridged complexes in this general family include $[(bpy)_2Ru(\mu\text{-}OR)_2Ru(bpy)_2]^{2+}$ (R = Me, Et), both of which are chiral as a result of the $Ru(bpy)_2$ units in each complex possessing the same absolute configuration. Each complex undergoes two one-electron oxidations to give $Ru^{II}Ru^{III}$ and $Ru^{III}Ru^{III}$ species.[618,619]

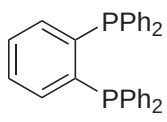


(135)

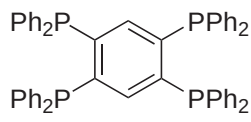
A number of cyano-bridged complexes are included here even though they strictly do not fall in the general family-type defined for the section. The syntheses and photophysical properties of $[(NC)(bpy)_2Ru(\mu\text{-}NC)Cr(CN)_5]^{2-}$ and $[(NC)_5Cr(\mu\text{-}CN)Ru(bpy)_2(\mu\text{-}NC)Cr(CN)_5]^{4-}$ have been described. Absorption of visible light by the $Ru(bpy)_2^{2+}$ unit results in phosphorescence from the $Cr(CN)_6^{3-}$ luminophore, and the results evidence fast intramolecular exchange energy transfer from the ^{3}MLCT state of the $Ru(bpy)_2^{2+}$ chromophore to the doublet state of the Cr^{III}-based unit.[620] Time-resolved resonance Raman and transient UV-vis absorption spectroscopies have been employed to investigate the MLCT excited states of $[(NC)(bpy)_2Ru(\mu\text{-}CN)Ru(bpy)_2(CN)]^+$, $[(NC)(bpy)_2Ru(\mu\text{-}CN)Ru(phen)_2(CN)]^+$, $[(NC)(phen)_2Ru(\mu\text{-}CN)Ru(bpy)_2(CN)]^+$, $[(NC)(bpy)_2$

$Ru(\mu\text{-}CN)Ru(bpy)_2(\mu\text{-}NC)Ru(bpy)_2(CN)]^{2+}$, and $[(NC)(bpy)_2Ru(\mu\text{-}CN)Ru\{4,4'\text{-}(CO_2)_2bpy\}_2(\mu\text{-}NC)Ru(bpy)_2(CN)]^{2-}$. The data indicate that distinct Ru^{II} and Ru^{III} centers are present in the excited states of the complexes.[621] In systems in which an $Ru(NH_3)_5^{3+}$ acceptor is linked through a cyano bridge to $[(NC)(bpy)_2Ru(\mu\text{-}CN)\{Ru(bpy)_2(\mu\text{-}NC)\}_nRu(bpy)_2(CN)]^{(n+1)+}$ ($n = 0$ or 1), there is complete quenching of the excited states of the polychromophoric species.[622] Absorption of visible light by the Ru-based chromophore in $[Ru(bpy)_2\{(\mu\text{-}NC)Cr(cyclam)(CN)\}_2]^{4+}$ (the structure of which has been determined)[623] results in emission from the Cr-based luminophore; there is a rapid and efficient chromophore–luminophore exchange energy-transfer process.[624]

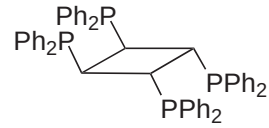
Phosphine bridged systems containing terminal $M(bpy)_2$ units are represented by a few examples. $[(bpy)_2XRu(\mu\text{-}trans\text{-}Ph_2PCH{=}CHPPh_2)RuX(bpy)_2]^{2+}$ (X = Cl, NO_2) and related complexes containing pyz or 4,4′-bpy bridges, have been prepared. The phosphine-bridged complex with X = Cl is photochemically inert, as is $[Ru(bpy)_2Cl(trans\text{-}Ph_2PCH{=}CHPPh_2\text{-}P)]^{2+}$.[625] In the excited states of the mixed metal complexes [(**136**)M(μ-**137**)Os$(bpy)_2]^{4+}$ (M = Ni, Pd, Pt), there is significant interaction between the metal centers, and there is quenching of the Os^{II} MLCT state by the group 10 metal center.[626] The photochemical reaction of [$(bpy)_2Ru(\mu$-**138**) $Ru(bpy)_2]^{4+}$ in MeCN leads, unexpectedly, to the formation of $[(bpy)(MeCN)_2Ru(\mu$-**138**$)Ru(bpy)(MeCN)_2]^{4+}$. The driving force for the reaction appears to be release of steric strain.[627]



(**136**)

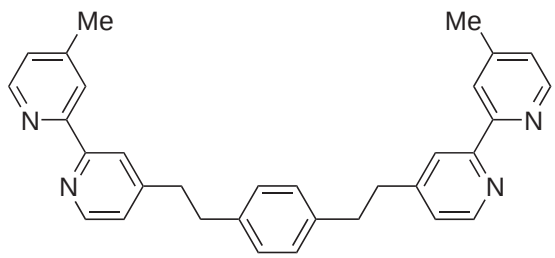


(**137**)

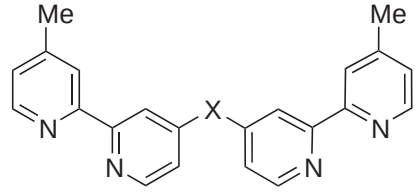


(**138**)

In the next part of this section, we consider $[(bpy)_2M(\mu\text{-}L)M(bpy)_2]^{n+}$ (M = Ru, Os) and related complexes in which L is a bridged bis(bpy) ligand. A number of relevant reviews should be consulted;[628–636] these provide detailed accounts of a wide range of systems covering mono-, di- and polynuclear species. The mono- and dinuclear complexes $[Ru(4,4'\text{-}Me_2bpy)_2($**139**$)]^{2+}$, $[(4,4'\text{-}Me_2bpy)_2Ru(\mu$-**139**$)$ $Ru(4,4'\text{-}Me_2bpy)_2]^{4+}$ and $[(4,4'\text{-}Me_2bpy)_2Ru(\mu$-**139**$)Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2]^{4+}$ as well as higher nuclearity species (see Section 5.5.3.1.5) have been prepared and characterized. In $[(4,4'\text{-}Me_2bpy)_2Ru(\mu\text{-}139)Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2]^{4+}$, there is efficient intramolecular quenching by energy transfer of the emission of the $Ru^{II}(4,4'\text{-}Me_2bpy)_2$ center.[637] An efficient intramolecular triplet–triplet annihilation process has been observed for the complexes $[(bpy)_2Ru(\mu$-**140**$)$-$Ru(bpy)_2]^{4+}$ under conditions of laser-light irradiation.[638] This series of complexes has been extended to Ru–Os complexes containing the bridging ligands (**141**) and (**142**). For all the complexes, there is essentially complete quenching by energy transfer of the Ru-based MLCT emission, and enhancement of the $Os^{II} \rightarrow \pi^*$(bpy) MLCT emission.[639] The related heteronuclear complex $[(bpy)_2Ru(\mu$-**141**$)Os(bpy)_2]^{4+}$ has also been investigated; there is efficient intramolecular energy transfer from the excited $Ru^{II}(bpy)_2$ to the $Os(bpy)_2$ domain.[640] In the excited state of $[\{4,4'\text{-}(CF_3)_2bpy\}_2Ru(\mu$-**141**$)Os\{4,4'\text{-}(CF_3)_2bpy\}_2]^{4+}$, quenching of the MLCT state is again observed. In MeOH at room temperature, the rate of reductive quenching is $5.3 \times 10^8\ s^{-1}$ and the rate of energy transfer from the excited Ru^{II} state to Os^{II} is $7.8 \times 10^7\ s^{-1}$. In ^{n}BuOH, these processes compete with one another.[641] Ligands (**140**) and related ligands in which $X = (CH_2)_4$,

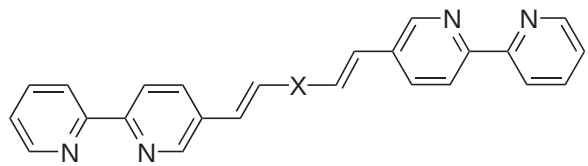


(**139**)

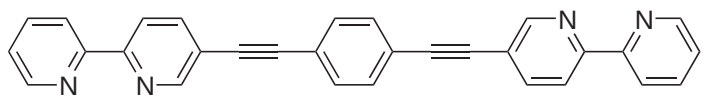


(**140**) X = $(CH_2)_2$, $(CH_2)_3$
(**141**) X = $CH_2CH(OH)CH_2$
(**142**) X = $(CH_2)_5$, $(CH_2)_7$

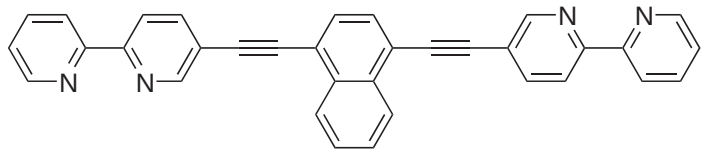
$(CH_2)_5$, CH_2OCH_2, CH_2SCH_2 or 1,3-$(CH_2)_2C_6H_4$ bridge Ru^{II} and Fe^{II} centers in the complexes $[Ru(\mu\text{-}L)_3Fe]^{4+}$. From the photophysical data it is observed that the emission decay rates depend on the Ru–Fe separation, but do not depend on the nature of the group X in the bridging ligand.[642] Ligands (**143**)–(**148**) contain rigid spacers. A comparison of the absorption spectra of $[Ru(4,4'\text{-}Me_2bpy)_3]^{2+}$ and $[(4,4'\text{-}Me_2bpy)_2Ru(\mu\text{-}\mathbf{143})Ru(4,4'\text{-}Me_2bpy)_2]^{4+}$ shows that the latter exhibits an extra band at 500 nm; the dinuclear complex emits at 750 nm compared to 640 nm for $[Ru(4,4'\text{-}Me_2bpy)_3]^{2+}$. Other differences between the complexes have been discussed.[643] The lifetimes of the excited states of $[(4,4'\text{-}Me_2bpy)_2Ru(\mu\text{-}\mathbf{143})Ru(4,4'\text{-}Me_2bpy)_2]^{4+}$ and $[Ru(4,4'\text{-}Me_2bpy)_2(\mathbf{143})]^{2+}$ are relatively long (1.31 μs and 1.15 μs in MeCN at 298 K). These studies have been extended to the diosmium(II) analog.[644] The complexes $[(bpy)_2M(\mu\text{-}\mathbf{144})M(bpy)_2]^{4+}$ where M–M = Ru–Ru, Os–Os, or Ru–Os, have been reported. In the heterometallic species, 91% of the Ru-based luminescence is quenched by energy transfer to the Os^{II} unit. The oxidized complexes M^{II}–M^{III} have also been investigated.[645] The effects of changing the spacer to 1,3-adamantane (ligand **145**) have been examined.[646] An adamantane spacer has also been incorporated as a spacer between two 4,5-diazafluorene units in a bridging ligand, L, in the complexes $[(bpy)_2M(\mu\text{-}L)M(bpy)_2]^{4+}$ (M–M = Ru–Ru, Os–Os, or Ru–Os). In the heterometallic complex, there is electronic energy transfer from Ru to Os ($k = 2.6 \times 10^8 s^{-1}$).[647] The phenylene spacer in ligand (**146**)–(**148**) (L) has little effect on the photophysical properties of the $M(bpy)_2M^{2+}$units in $[(bpy)_2M(\mu\text{-}L)M(bpy)_2]^{4+}$ (M–M = Ru–Ru or Os–Os). However, in the related tpy complexes, it is observed that $[(tpy)Ru(\mu\text{-}L')Ru(tpy)]^{4+}$ (L′ = 4′-tpy substituted analogs of ligands (**146**)–(**148**)) exhibits very long triplet lifetimes.[648]



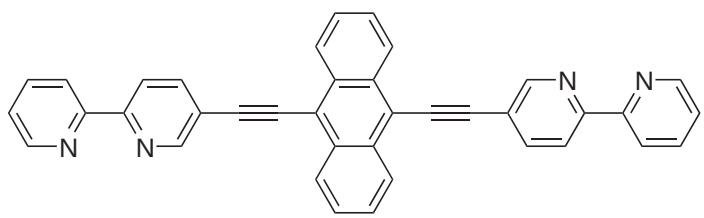
(**144**) X = 1,4-bicyclo[2.2.2]octane
(**145**) X = 1,3-adamantane



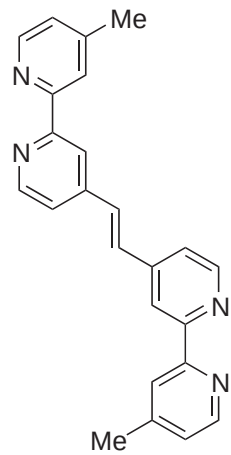
(**146**)



(**147**)



(**148**)



(**143**)

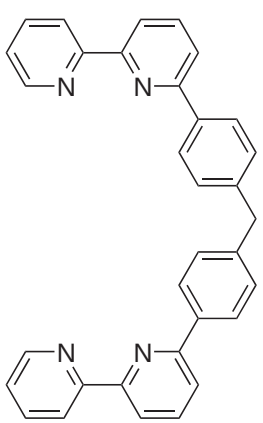
A series of bridged dinuclear $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{4+}$ and $[(bpy)_2Ru(\mu\text{-}L)Os(bpy)_2]^{4+}$ complexes have been prepared in which the bridge coordination domains are phen ligands and the spacer is constructed by the stereoselective coupling of units through norbornene and epoxide functionalities.[649,650]

The ligand (**149**), H_2L, may act as a bis(*N,N′*-donor) as in the complex $[(bpy)_2Ru(\mu\text{-}H_2L)Ru(bpy)_2]^{4+}$. However, cyclometallation is also an option, as is observed in $[(tpy)Ru(\mu\text{-}L)Ru(tpy)]^{2+}$ in which L^{2-} acts as an *N,N′,C*-donor to each Ru^{II} center.[651] Ligands (**150**) have been prepared and used as bridges in the complexes $[(bpy)_2M(\mu\text{-}\mathbf{150})M(bpy)_2]^{4+}$ (M–M = Ru–Ru, Os–Os, Ru–Os), all of which show MLCT absorption and luminescence bands in the visible region; excited-state lifetime measurements have been made, and the homonuclear complexes exhibit long lifetimes. The addition of Ce^{4+} generates the corresponding mixed valence complexes.[652] The pyrene-bridged complex $[(bpy)_2Ru(\mu\text{-}\mathbf{151})Ru(bpy)_2]^{4+}$ exhibits MLCT and pyrene-centered transitions in the absorption spectrum as well as a band at ≈400 nm. At 298 K, the emission lifetime is 130 μs, and it is proposed that this arises from a ^{3}ILCT (intraligand charge transfer) state or a ^{3}ILCT state with significant pyrene character.[653]

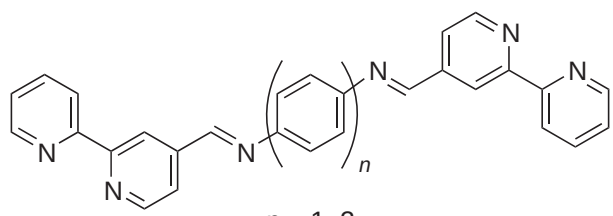
Thienyl-bridged ligands are of particular interest. Bridging ligands in which two bpy ligands are connected by one (L^1), three (L^3) or six (L^6) thienyl units have been developed. In $[(bpy)_2Ru(\mu\text{-}L^1)Ru(bpy)_2]^{4+}$, both Ru^{2+} centers are oxidized at the same potential, and initial reduction processes are terminal bpy-centered. For $[(bpy)_2Ru(\mu\text{-}L^3)Ru(bpy)_2]^{4+}$, concurrent Ru^{2+} oxidation processes come between two terthiophene oxidations, whereas in $[(bpy)_2Ru(\mu\text{-}L^6)Ru(bpy)_2]^{4+}$, oxidations of the Ru^{2+}centers follow two sequential sexithiophene oxidation processes.[654]

The complex $[(bpy)_2Ru(\mu\text{-}\mathbf{152})Ru(bpy)_2]^{4+}$ exhibits a luminescence spectrum that is concentration-dependent; the emission maximum appears at 650 nm for dilute solutions but at 670 nm when the concentration is raised. These observations can be understood in terms of excimers formed as a result of energy transfer between the Ru centers.[655] The MLCT emission of $[L_2Ru(\mu\text{-}\mathbf{153})OsL_2]^{4+}$ (L = bpy or 4,4′-$(CF_3)_2$bpy) and of the analogous leucine-containing peptide-bridged complex is almost completely quenched. When L = 4,4′-$(CF_3)_2$bpy, the data are consistent with competitive energy and electron-transfer processes.[656] A series of complexes $[(bpy)_2M(\mu\text{-}\mathbf{154})M(bpy)_2]^{4+}$ (M–M = Ru–Ru, Os–Os, Ru–Os) has been developed in which energy transfer occurs in a predetermined direction, and in which the efficiency and rate of transfer can be lowered by a self-photosensitized reaction involving O_2.[657]

The dinuclear complexes $[(bpy)_2M(\mu\text{-}2,5\text{-}dpp)M(bpy)_2]^{4+}$ (M–M = Os–Os, Ru–Os) and $[(bpy)_2Os(\mu\text{-}2,3\text{-}dpp)Os(bpy)_2]^{4+}$ (dpp = bis(2-pyridyl)pyrazine; 2,3-dpp = 88) have been investigated as part of a larger series of polynuclear complexes containing $M(bpy)_2^{2+}$ or $M(bpq)_2^{2+}$ units and 2,3-dpp or 2,5-dpp bridging ligands. All the complexes show a luminescence band in the near IR region (850–1,000 nm) assigned to triplet MLCT levels localized on Os-based fragments. For the Ru–Os species, Os-centered luminescence is observed. Exoergonic electronic energy transfer in the polynuclear "cascade" systems is fully efficient.[658] Quaterpyridine (quatpy) ligands (**129**) and (**155**) contain two bpy domains, and can effectively connect two $[M(bpy)_3]^{2+}$ units, i.e., in $[(bpy)_2M(\mu\text{-quatpy})M(bpy)_2]^{4+}$. The reaction of two equivalents of $[Ru(bpy)_2Cl_2]$ with ligand (**155**) leads to a mixture of the *meso* and *rac*-forms of $[(bpy)_2Ru(\mu\text{-}155)Ru(bpy)_2]^{4+}$. The Ru–Ru interaction in the latter is not strong, but there is extensive electronic coupling between the two

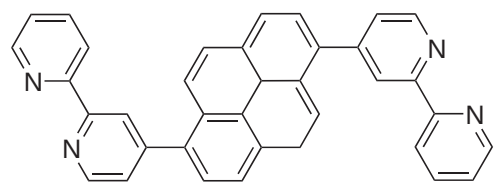


(**149**)

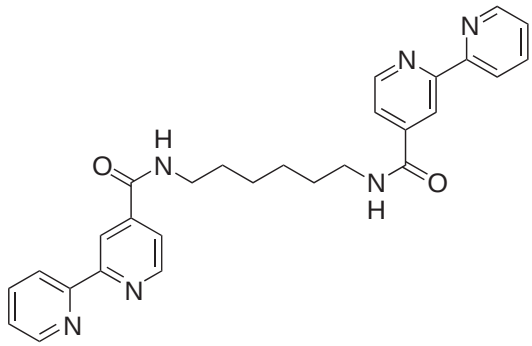


n = 1, 2

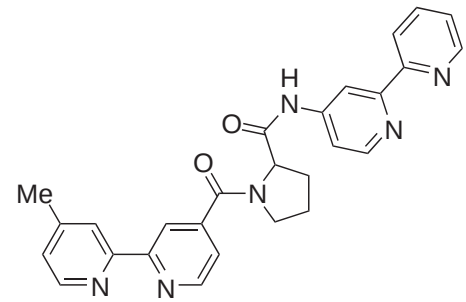
(**150**)



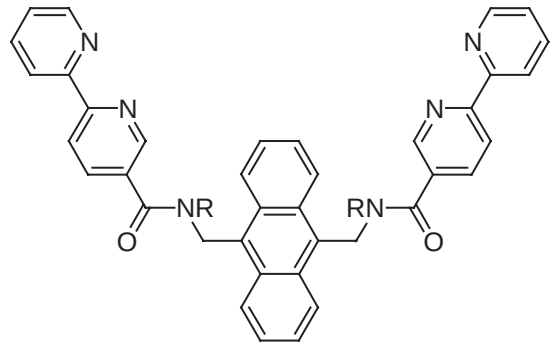
(**151**)



(**152**)

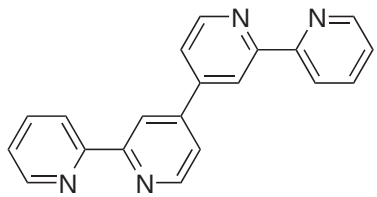


(**153**)

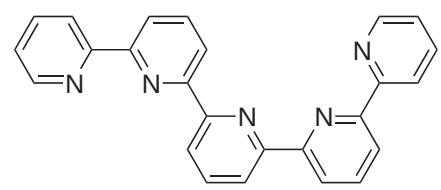


(**154**)

bpy domains in the bridging ligand; the first reduction process of the complex is quatpy-centered.[659] The unsymmetrical quaterpyridine (**129**) is an isomer of (**155**), and has been incorporated into the complexes $[(bpy)_2M(\mu\text{-}129)M(bpy)_2]^{4+}$ (M–M = Ru–Ru, Os–Os, Ru–Os, Os–Ru). The crystal structure of the Os–Ru species has been determined. Due to the unsymmetrical nature of (**129**), the homometallic dinuclear complexes have distinct metal environments, and the M^{II} center associated with the less sterically crowded site is the easier one to oxidize. Despite this, the center that is easier to oxidize in the Ru–Os or Os–Ru species is always Os^{2+}. In both mixed metal compounds, luminescence is Os-centered.[660] Related Ru–Re complexes bridged by ligand (**129**) have also been studied, including by time-resolved IR spectroscopy to investigate the nature of their MLCT excited states.[661,662] Lengthening the bridging polypyridyl ligand to 2,2′:6′,2″:6″,2‴:6‴,2″-quinquepyridine (**156**) provides the potential for the formation of double helical complexes, as exemplified by $[Ru_2(\mathbf{156})_2(ox)]^{2+}$ in which each ligand (**156**) presents a bpy donor set to one Ru^{II} center (an additional ox^{2-} ligand coordinates to complete the octahedral environment) and a tpy donor set to the second Ru^{II} center.[663]



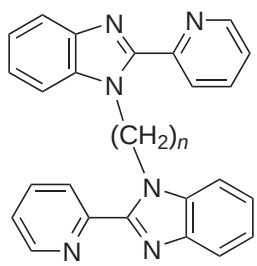
(**155**)



(**156**)

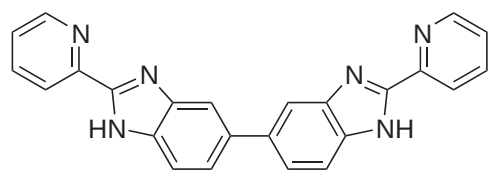
Detailed electrochemical studies of $[(bpy')_2M(\mu\text{-}H_2bibzim)M(bpy')_2]^{2+}$ (M–M = Ru–Ru, Os–Os, Ru–Os; H_2bibzim = 2,2′-bibenzimazole; bpy′ = bpy, Mebpy, Me_2bpy or CO_2Etbpy) have been carried out; the complexes exhibit numerous reversible one-electron oxidation and reduction processes.[664] Starting from $[Ru(4,4'\text{-}R_2bpy)_2Cl_2]$ (R = H, Me, ^{t}Bu), either $[Ru(4,4'\text{-}R_2bpy)_2\text{-}H_2bibzim]^{2+}$ or $[(4,4'\text{-}R_2bpy)_2Ru(\mu\text{-bibzim})Ru(4,4'\text{-}R_2bpy)_2]^{2+}$ can be prepared depending on the reaction conditions; structural data are discussed.[665] Intramolecular electron-transfer

processes involved in triplet–triplet annihilation in $[(4,4'\text{-}R_2bpy)_2Ru(\mu\text{-}\mathbf{157})Ru(4,4'\text{-}R_2bpy)_2]^{4+}$ (R = H, Me, CO_2Et, and in (**157**), *n* is 2, 3, 4, 5, 6, or 10 depending on R) have been investigated. The high-energy charge-separated Ru^{I}–Ru^{III} states were observed and the lifetimes of these states depend on the intermetallic separation and on the energy gap between the charge-separated state and the single excited state, (^{3}CT)Ru–Ru^{II}.[666] The study has been extended to Ru–Os systems.[667] The absorption spectra and redox potentials for $[(bpy)_2Ru(\mu\text{-}\mathbf{158})Ru(bpy)_2]^{4+}$ depend strongly on the pH of the solution and consequent protonation state of ligand (**158**); the electronic interaction between the metal centers can be increased by removal of an imidazole proton.[668,669] On going from $[Ru(bpy)_2(\mathbf{158})]^{2+}$ to $[(bpy)_2Ru(\mu\text{-}\mathbf{158})Ru(bpy)_2]^{4+}$, or from the analogous mono- to diosmium species, the MLCT bands remain virtually the same.[669] Electronic communication is observed in related ruthena- and osmapolymers.[670,671] Both mono- and dinuclear complexes containing $Ru(bpy)_2^{2+}$ units and the terminal or bridging ligand 2,2′-bis(benzimidazol-2-yl)-4,4′-bipyridine (H_2L) have been studied, and the crystal structure of $[Ru(bpy)_2(H_2L)][ClO_4]_2\cdot MeOH$ has been determined. The series of complexes show CT bands at 420–520 nm and emissions at 660–720 nm in MeCN with lifetimes of 200–800 ns (298 K). The photophysical properties of the complexes can be altered by changing the protonation state of H_2L.[672] Pyrazole-3,5-bis(benzimidazole) (H_3L) has been used as a terminal or bridging ligand in the complexes $[Ru(bpy)_2(H_3L)]^{2+}$, $[Ru(phen)_2(H_3L)]^{2+}$, $[(bpy)_2Ru(\mu\text{-}H_2L)Ru(bpy)_2]^{3+}$, $[(bpy)_2Ru(\mu\text{-}H_2L)Ru(phen)_2]^{3+}$, $[(phen)_2Ru(\mu\text{-}H_2L)Ru(phen)_2]^{3+}$, $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{+}$ and $[(phen)_2Ru(\mu\text{-}L)Ru(phen)_2]^{+}$. Mixtures of diastereoisomers formed for the complexes with bridging H_2L^- ligands were separated by fractional crystallization. The complexes containing H_3L or H_2L^- exhibit fluorescent behavior.[673] Transient absorption spectra and spectroelectrochemical difference spectra have been used to assign the lowest excited state of $[(bpy)_2Ru(\mu\text{-}\mathbf{159}, X = S)Ru(bpy)_2]^{4+}$ to the MLCT state. The electronic coupling between the metal fragments in the latter complex is less than in the corresponding complex with X = NH.[674]

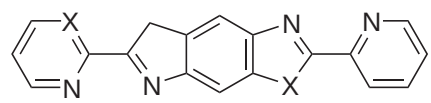


n = 2–6,10

(**157**)



(**158**)

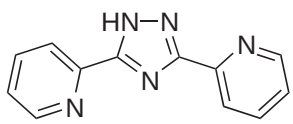


X = S or NH

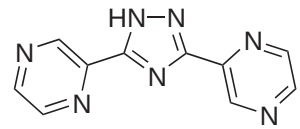
(**159**)

Studies of dinuclear complexes of type $[(bpy)_2M(\mu\text{-bpt})M(bpy)_2]^{3+}$ (Hbpt = the triazole derivative (**160**); M = Ru, Os) prior to 1991 have been reviewed by Hage.[675] Electrochemical data reveal that the LUMO is bpy-centered in each complex. The bpt^- bridge is unsymmetrical, placing the two metal centers in homonuclear species in different environments; as a result, the oxidation potentials of the two centers in each complex are widely separated. In the Ru–Os system, there is a strong interaction between the metal centers. The luminescence and photophysical properties of the isomers (i.e., by virtue of the different *N,N*-binding domains of bpt^-) of $[(bpy)_2Ru(\mu\text{-bpt})Os(bpy)_2]^{3+}$ have been explored. The complex exhibits extremely efficient energy transfer from *Ru to Os.[676] Two bpt groups have been linked via a 1,4-cyclohexanediamido spacer and the resulting bis(bpt) ligand (bpt–bpt) incorporated into the complexes $[(bpy)_2M(\mu\text{-bpt–bpt})sM(bpy)_2]^{4+}$ (M–M = Ru–Ru, Os–Os); comparisons of their properties are made with those of corresponding mononuclear complexes. The ligands and complexes are luminescent, although the fluorescence of the ligands is quenched upon complex formation. Luminescence of the complexes is attributed to the lowest energy triplet M → bpt CT excited state. The metal centers are effectively electronically isolated in the dinuclear complexes.[677] The work has been extended to the analogous Ru–Os species and here, photoinduced energy transfer is observed.[678] The Δ,Δ,

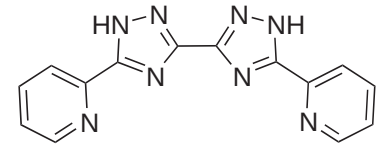
Δ,Λ, Λ,Λ, and Λ,Δ-forms of $[(bpy)_2Ru(\mu\text{-}bpt)Ru(bpy)_2]^{3+}$ have been separated and their photophysical properties compared.[679] The two different *N,N*-binding sites in bpt^- can be coordinated to $Ru(bpy)_2^{2+}$ or $Ru(phen)_2^{2+}$ units in controlled synthesis to yield two isomers of $[(bpy)_2Ru(\mu\text{-}bpt)Ru(phen)_2]^{3+}$, the properties of which have been compared with each other and with relevant mononuclear complexes. The Ru^{II} center bound to the N(1) site of the triazole ring of bpt^- is always oxidized first. Photolysis of MeCN solutions of the complexes results in labilization of the Ru center coordinated by the N(4) atom; in $MeCN/Cl^-$ or CH_2Cl_2/Cl^- media, both the N(1) and N(4) sites are photoreactive (see related $bpzt^-$ chemistry discussed below).[680] Resonance Raman and excited-state absorption spectroscopies and spectroelectrochemical techniques have been used to probe the excited-state properties of $[Ru(bpy)_2(bpzt)]^+$ and $[(bpy)_2Ru(\mu\text{-}bpzt)Ru(bpy)_2]^{3+}$ (Hbpzt = **161**). The π^* level of $bpzt^-$ is lowered on going from a terminal to bridging ligand and this results in a changeover from a bpy-based to bzpt-based lowest excited state.[681] The complexes $[Ru(bpy)_2(H_2bbpt)]^{2+}$, $[(bpy)_2Ru(\mu\text{-}H_2bbpt)Ru(bpy)_2]^{4+}$, and $[\{(bpy)_2Ru\}_3(\mu\text{-}bbpt)]^{4+}$ have been prepared and characterized; FAB-MS fragmentation patterns have been analyzed. Mixed-valence derivatives of the di- and trinuclear complexes are formed by chemical oxidation and these species exhibit strong absorptions in the IR region assigned to intervalence transitions.[682] A derivative of (**162**) in which a dihydroxybenzene spacer is placed between the two triazole rings has also been prepared and the mono- and dinuclear $Ru(bpy)_2^{2+}$-containing complexes (which show emissive behavior) investigated. Electrochemical data are consistent with the central hydroquinone unit being oxidized before the Ru^{II} centers.[683] Reactions of (**163**) with $[Ru(bpy)_2Cl_2]$ or $[Os(bpy)_2Cl_2]$ lead to the formation of $[Ru(bpy)_2(\mathbf{163})]^{2+}$, $[Os(bpy)_2(\mathbf{163})]^{2+}$, $[Os(bpy)_2(\mathbf{163})Cl]^+$, $[(bpy)_2Ru(\mu\text{-}\mathbf{163})Ru(bpy)_2Cl]^{3+}$, $[(bpy)_2Os(\mu\text{-}\mathbf{163})Os(bpy)_2Cl]^{3+}$, $[(bpy)_2Ru(\mu\text{-}\mathbf{163})Os(bpy)_2Cl]^{3+}$, and $[(bpy)_2Os(\mu\text{-}\mathbf{163})Ru(bpy)_2Cl]^{3+}$. The bridging ligand coordinates to one metal center in a didentate mode through triazole N(4) and pyrazine N(1), and to the other in a monodentate mode through pyrazine N(4). There is a weak interaction betweeen the metal centers in the dinuclear species, but the emission behavior is consistent with with efficient energy transfer in the excited state complexes.[684] Mono- and dinuclear Ru^{II} complexes containing bpt^- (see **160**), $bpzt^-$ (see **161**) and the conjugates bases L^{2-} and L'^{2-} of ligands (**164**) and (**165**) have been prepared, the dinuclear species by Ni(0) coupling of brominated derivatives of the mononuclear complexes. The protonation state of the ligands influences the electronic interaction between the Ru centers in $[(bpy)_2Ru(\mu\text{-}bpt)Ru(bpy)_2]^{3+}$, $[(bpy)_2Ru(\mu\text{-}bpzt)Ru(bpy)_2]^{3+}$, $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{2+}$, and $[(bpy)_2Ru(\mu\text{-}L')Ru(bpy)_2]^{2+}$.[685] Photolysis of $[(bpy)_2Ru(\mu\text{-}bpzt)Ru(bpy)_2]^{3+}$ results in labilization of the Ru center coordinated by the triazole N(4) donor (see discussion of related bpt^- chemistry above).[686]



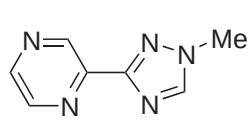
Hbpt
(**160**)



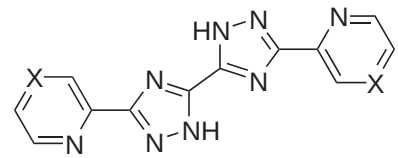
Hbpzt
(**161**)



H_2bbpt
(**162**)



(**163**)



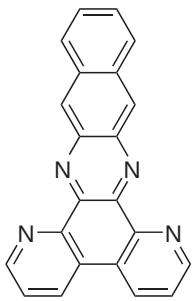
(**164**) X = CH H_2L
(**165**) X = N H_2L'

2,3-Bis(2-pyridyl)pyrazine (2,3-dpp = (**88**)), 2,3-bis(2-pyridyl)quinoxaline and 2,3-bis(2-pyridyl) benzoquinoxaline (**91**) find numerous applications as bridging ligands in homo- and heterometallic complexes. At this point, we consider some dinuclear species; complexes containing ≥3 metal centers are covered in Section 5.5.3.1.5. By using the complexes in the series $[(bpy)_2M(\mu\text{-}L)M(bpy)_2]^{4+}$ (M–M = Ru–Ru, Os–Os, Ru–Os; L = (**88**), 2,3-bis(2-pyridyl)quinoxaline or (**91**))

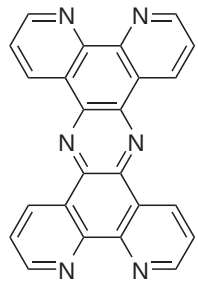
as a test set, it has been concluded that the visible spectra of mixed metal systems can be accurately interpreted by comparison with the spectra of homometallic analogs.[687] Coordinaion of the $Ru(bpy)_2^{2+}$ fragment to the pendant ligand (**88**), 2,3-bis(2-pyridyl)quinoxaline or (**91**) (L) in $[Os(bpy)_2L]^{2+}$ causes a shift to lower energies of the MLCT transitions involving the π^*-orbital of L. There is also a shift to more positive potential of the L-based electrochemical reductions.[688] The mixed valence Os^{II}–Os^{III} and Os^{III}–Ru^{II} members of this series of complexes exhibit significant near-IR spectra; the complexes are more weakly coupled Robin and Day class II systems than earlier electrochemical data had suggested.[689] For the same bridging ligands, L, cyclic voltammograms (in dmf) of $[(bpy)_2Ru(\mu\text{-L})Ru(bpy)_2]^{4+}$ show six reversible reductions for each complex. From resonance Raman, ESR and electronic spectra, it is concluded that the first two electrons occupy an L-centered MO, and the next four electrons occupy bpy-centered orbitals. Differences associated with the character of the bridging ligand are discussed.[690] The properties of $[Ru(bpy)_2L]^{2+}$ and $[(bpy)_2Ru(\mu\text{-L})Ru(bpy)_2]^{4+}$ complexes in which L is 6,7-dichloro-2,3-bis (2-pyridyl)quinoxaline (Cl_2dpq) or 6,7-dimethyl-2,3-bis(2-pyridyl) quinoxaline (Me_2dpq) have been compared with those of complexes with L = (**88**), 2,3-bis (2-pyridyl)quinoxaline (dpq) or (**91**). Values of $E_{1/2}$(reduction) of the complexes follow the sequence (by ligand L) (**88**) < Me_2dpq < dpq < Cl_2dpq < (**91**).[691] From absorption, luminescence and redox behavior, the lowest excited states of $[(bpy)_2Ru(\mu\text{-}\mathbf{88})Ru(biq)_2]^{4+}$ and $[(biq)_2Ru(\mu\text{-}\mathbf{88})Ru(biq)_2]^{4+}$ have been assigned to a CT transition involving the biq ligand.[692] Steady-state and time-resolved picosecond and nanosecond transient luminesence and absorption spectroscopies have been used to study the excited-state properties of $[(NH_3)_4Ru(\mu\text{-}\mathbf{88})\ Ru(bpy)_2]^{4+}$. The excited state complex is nonemissive (aqueous solution, 298 K). A transient species exhibiting an exponential decay ($\tau = 290 \pm 80$ ps) was observed.[693] Keene and co-workers have been the first to investigate the influence of stereochemical factors on intervalence charge transfer; properties of *meso*- and *rac*-$[(bpy)_2Ru(\mu\text{-}\mathbf{91})Ru(bpy)_2]^{5+}$ and of *meso*- and *rac*-$[(bpy)_2Ru(\mu\text{-}\mathbf{166})Ru(bpy)_2]^{5+}$ have been compared. The intensities of the intervalence bands for the *meso*-diastereoisomers are higher than those for the analogous *rac*-forms.[694] The heterometallic complexes $[(bpy)_2M(\mu\text{-L})PtCl_2]^{2+}$ where M = Ru or Os, and L is 2,3-bis(2-pyridyl) quinoxaline or (**91**), have been prepared and characterized. The lowest lying excited states are M → L charge transfer transitions.[695]

We now turn to dinuclear complexes containing $M(bpy)_2^{2+}$ units bridged by derivatives of phenazine and related ligands. Depending on conditions, the reaction of $[Ru(bpy)_2Cl_2]$ with dipyrido(2,3-*a*;2′,3′-*h*)phenazine (**92**) leads to $[Ru(bpy)_2(\mathbf{92})]^{2+}$ or $[(bpy)_2Ru(\mu\text{-}\mathbf{92})Ru(bpy)_2]^{4+}$. The dinuclear complex exhibits (in MeCN) an intense MLCT absorption at 661 nm, compared to an analogous absorption at 528 nm for the mononuclear species; $[(bpy)_2Ru(\mu\text{-}\mathbf{92})Ru(bpy)_2]^{4+}$ does not show emissive properties in contrast to emission at 768 nm from the lowest lying ^{3}MLCT state for $[Ru(bpy)_2(\mathbf{92})]^{2+}$. Comparison with related complexes have been discussed.[696] Reactions of each of the enantiomers of $[Ru(bpy)_2(py)_2]^{2+}$ with one equivalent of 2,3-dpp (**88**) or pyrazino[2,3-*f*][4,7]phenanthroline (**98**) yields Δ-$[Ru(bpy)_2(\mathbf{88})]$, Λ-$[Ru(bpy)_2(\mathbf{88})]$, Δ-$[Ru(bpy)_2(\mathbf{98})]$, and Λ-$[Ru(bpy)_2(\mathbf{98})]$. Treatment of each complex with an equivalent of enantiomerically pure $[Ru(bpy)_2(py)_2]^{2+}$ allows the formation of Δ,Δ-, Δ,Λ-, and Λ,Λ-forms of $[(bpy)_2Ru(\mu\text{-}\mathbf{88})Ru(bpy)_2]^{4+}$ and $[(bpy)_2Ru(\mu\text{-}\mathbf{98})Ru(bpy)_2]^{4+}$.[697] Ligand (**167**) can be synthesized from 1,10-phenanthroline-5,6-quinone in a melt with ammonium acetate. This ligand has been used both in the preparations of $[(bpy)_2Ru(\mu\text{-}\mathbf{167})Ru(bpy)_2]^{4+}$ and the coordination polymer $[Ru(bpy)(\mu\text{-}\mathbf{167})]_n^{2n+}$.[698] In related chemistry, stereoisomers of $[(phen)_2Ru(\mu\text{-}\mathbf{167})Ru(phen)_2]^{4+}$ have been specfically prepared by the condensation of enantiomers of $[Ru(phen)_2L]^{2+}$ and $[Ru(phen)_2L']^{2+}$ where L and L′ are appropriate quinone and diamine derivatives of phen.[699] A similar synthetic strategy has been used to prepare $[Ru(bpy)_2(\mathbf{167})]^{2+}$ from a coordinated quinone and 5,6-diamino-1,10-phenanthroline; reaction of $[Ru(bpy)_2(\mathbf{167})]^{2+}$ with $[Ru(bpy)_2Cl_2]$ then produces $[(bpy)_2Ru(\mu\text{-}\mathbf{167})Ru(bpy)_2]^{4+}$. The ^{1}H NMR spectrum of $[Ru(bpy)_2(\mathbf{167})]^{2+}$ is sensitive to concentration and this is attributed to π–π interactions between ligands **167**.[700] $[Os(bpy)_2(\mathbf{167})]^{2+}$ has been prepared by an analogous route to $[Ru(bpy)_2(\mathbf{167})]^{2+}$, and again, π-stacking of ligands (**167**) is observed in solution. By using a building-block approach, the series of complexes $[(bpy)_2M(\mu\text{-}\mathbf{167})M(bpy)_2]^{4+}$ where M–M = Ru–Ru, Ru–Os, or Os–Os has been prepared. With the exception of the Os–Os system, MeCN solutions of the mono- and dinuclear complexes are luminescent.[701] The photophysical properties of these complexes have been reported; the data are consistent with ligand (**167**) being involved in the lowest MLCT excited states of the complexes. In $[(bpy)_2Ru(\mu\text{-}\mathbf{167})Os(bpy)_2]^{4+}$, there is fast energy and/or electron transfer across the bridge ($k > 10^9$ s^{-1}).[702] Ligand (**168**) is a planar, extended aromatic system closely related to (**167**). The results of electrochemical and spectroscopic studies indicate that $[(bpy)_2Ru(\mu\text{-}\mathbf{168})Ru(bpy)_2]^{4+}$ consists of four isolated components: the two $Ru(bpy)_2^{2+}$ units and two localized bridging ligand

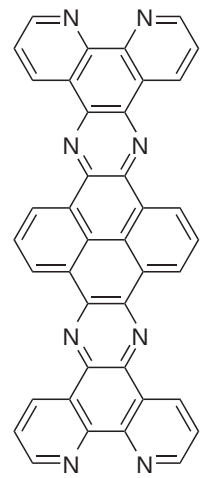
fragments.[703] In solution, $[(bpy)_2Ru(\mu\text{-}\mathbf{168})Ru(bpy)_2]^{4+}$ forms dimers as a consequence of strong π–π stacking interactions between bridging ligands.[704] In the complex $[(bpy)_2Ru(\mu\text{-}\mathbf{169})Ru(bpy)_2]^{4+}$, electronic coupling across the ligand and through the central C—C bond can be tuned as a function of the ligand oxidation state. Going from $[(bpy)_2Ru(\mu\text{-}\mathbf{169})Ru(bpy)_2]^{4+}$ to $[(bpy)_2Ru(\mu\text{-}\mathbf{169})Ru(bpy)_2]^{3+}$ and $[(bpy)_2Ru(\mu\text{-}\mathbf{169})Ru(bpy)_2]^{2+}$ causes structural and electronic changes and quenching of the MLCT emission of the excited states of the $Ru(bpy)_2^{2+}$-groups.[705]



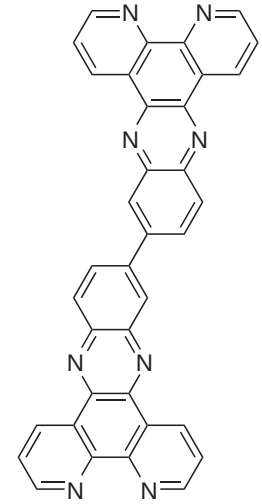
(166)



(167)



(168)

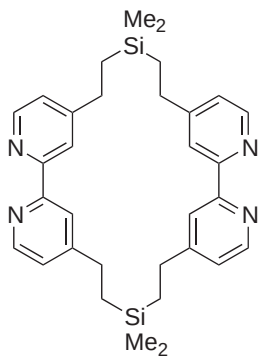


(169)

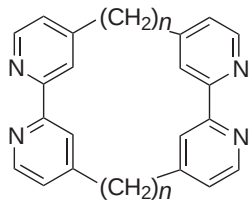
A series of mono- and dinuclear complexes containing 4,5-di(2-pyridyl)pyrimidine (L) has been reported. These include $[Ru(4,4'\text{-}R_2bpy)_2L]^{2+}$, $[(4,4'\text{-}R_2bpy)_2Ru(\mu\text{-}L)Ru(4,4'\text{-}R_2bpy)_2]^{4+}$ (R = H, Me) and $[(bpy)_2Ru(\mu\text{-}L)PdCl_2]^{2+}$.[706] The related ligand 2,6-bis-[6-(2-pyridinyl)-4-pyrimidinyl]pyridine (L′) has also been prepared. Coordination to $Ru(bpy)_2^{2+}$ takes place through the terminal bpy-type domains to give $[(bpy)_2Ru(\mu\text{-}L')Ru(bpy)_2]^{4+}$; NMR spectroscopic data and molecular mechanics calculations are used to discuss the solution conformation of the complex. In the UV–vis spectrum, $[(bpy)_2Ru(\mu\text{-}L')Ru(bpy)_2]^{4+}$ exhibits strong ligand-centered absorptions below 400 nm and MLCT absorptions above 400 nm.[707] In $[(bpy)_2Ru(\mu\text{-}L'')Ru(bpy)_2]^{4+}$ where L″ is 2,4,6-tris(2-pyridyl)triazine, the first reduction process is centered on L″ and the second on bpy. Acetonitrile solutions of the complex are emissive at 298 K.[708] The relationship between electrochemical and spectroscopic properties of $[(bpy)_2Ru(\mu\text{-}L'')Ru(bpy)_2]^{4+}$ and $[Ru(bpy)_2L'']^{2+}$[709] exhibit unusual trends contrary to those observed for similar species.[708] The preparation of 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine (L‴) and the formation of the intensely blue complex $[(bpy)_2Ru(\mu\text{-}L''')Ru(bpy)_2]^{4+}$ have been reported. The latter undergoes a one-electron reduction at −0.40 V (vs. Fc^+/Fc) and a Ru^{2+} oxidation at −1.18 V to give $[(bpy)_2Ru(\mu\text{-}L''')Ru(bpy)_2]^{5+}$.[710] A resonance Raman spectroscopic investigation of $[(bpy)_2Ru(\mu\text{-}L''')Ru(bpy)_2]^{4+}$ reveals that the bpy and L‴ vibrational modes are selectively enhanced; excited-state spectra have been analyzed.[711] Fourteen one-electron redox processes for the complex $[(bpy)_2Ru(\mu\text{-bpm})Ru(bpy)_2]^{4+}$ have been fully assigned; there are two Ru-based oxidations and twelve ligand-based reductions.[712]

Reactions of ligand (**170**) and of an acyclic analog containing only one silyl linkage with $[Ru(bpy)_2Cl_2]$ yielded $[(bpy)_2Ru(\mu\text{-}\mathbf{170})Ru(bpy)_2]^{4+}$ and the analogous complex with the acyclic bridging ligand. ^1H NMR spectroscopic data were consistent with the formation of a 1:1 mixture of $(\Delta,\Delta/\Lambda,\Lambda)$:$(\Delta,\Lambda)$ diastereoisomers of $[(bpy)_2Ru(\mu\text{-}\mathbf{170})Ru(bpy)_2]^{4+}$; the diastereoisomers were separated by crystallization of the *meso*-form. The crystal structure of $[(bpy)_2Ru(\mu\text{-}\mathbf{170})Ru(bpy)_2][PF_6]_4$ has been determined. Changes in conformation of the bridging ligand on complexation are discussed.[713] Ligand (**171**) has been prepared and structurally characterized. Its reaction with $[Ru(bpy)_2Cl_2]$ produces $[(bpy)_2Ru(\mu\text{-}\mathbf{171})Ru(bpy)_2]^{4+}$, isolated as the PF_6^- salt. The crystal structure of one of the diastereomers has been determined; the unit cell contains both the Δ, Δ- and Λ,Λ-forms.[714] Ligands (**172**) and (**173**) are related to (**171**) by an increase in the spacers between the bpy residues, and also form complexes of type $[(bpy)_2Ru(\mu\text{-L})Ru(bpy)_2]^{4+}$ (L = **172**, **173**). Compared to $[(bpy)_2Ru(\mu\text{-}\mathbf{171})Ru(bpy)_2]^{4+}$ where the diastereoisomers can be distinguished by ^1H and ^{13}C NMR spectroscopies, the diastereoisomeric differentiation is reduced as the spacer

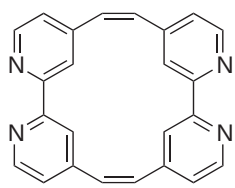
in the bridging ligand increases. The crystal structure of *meso*-[(bpy)$_2$Ru(μ-**173**)Ru(bpy)$_2$][PF$_6$]$_4$ has been determined; the Ru—Ru separation is 1,310 pm. An interesting feature of the solid-state structure is the close proximity of two PF_6^- counterions to the center of the bridging ligand.[715] Dehydrogenation of ligand (**171**) yields (**174**), and the reaction of the latter with [Os(bpy)$_2$Cl$_2$] leads to *meso*- and *rac*-[(bpy)$_2$Os(μ-**174**)Os(bpy)$_2$]$^{4+}$ which can be separated by chromatography. Structural data have been reported, and comparisons of the electrochemical behavior of *meso*- and *rac*-[(bpy)$_2$Os(μ-**174**)Os(bpy)$_2$]$^{4+}$ and a mixture of stereoisomers of [(bpy)$_2$Os(μ-**171**)Os(bpy)$_2$]$^{4+}$ have been made; *meso*- and *rac*-[(bpy)$_2$Os(μ-**174**)Os(bpy)$_2$]$^{4+}$ exhibit identical electrochemical properties and weak metal–metal interactions.[716] Like ligands (**170**)–(**174**), macrocycle (**175**) presents two bpy domains for coordination, and the complex [(bpy)$_2$Ru(μ-**175**)Ru (bpy)$_2$]$^{4+}$ has been prepared and characterized.[717]



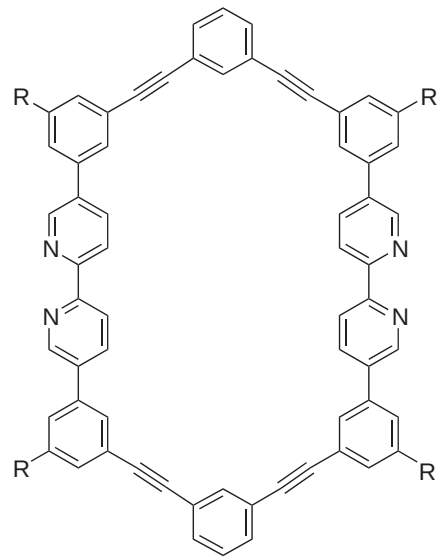
(**170**)



(**171**) $n = 2$
(**172**) $n = 3$
(**173**) $n = 4$



(**174**)

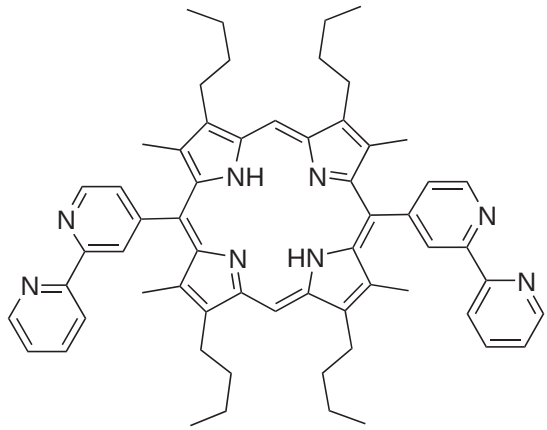


(**175**)

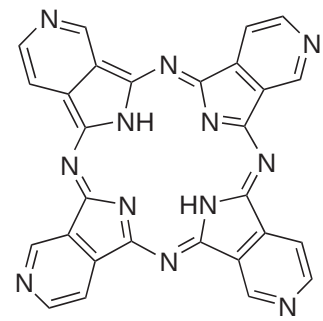
Complexes containing azamacrocyclic and porphyrin or related ligands are usefully included in this section. 1,4,8,11-Tetrakis(2,2′-bipyridyl-5′-methyl)-1,4,8,11-tetraazacyclotetradecane (L) reacts with [Ru(bpy)$_2$Cl$_2$] to give the highly fluorescent complex [{Ru(bpy)$_2$}$_4$L]$^{8+}$, isolated as the salt [{Ru(bpy)$_2$}$_4$(HL)][ClO$_4$]$_9$.[718] The porphyrin derivative (**176**) and its analog with one pendant bpy group, have been reacted with [Ru(bpy)$_2$Cl$_2$] to give di- and monoruthenium complexes, respectively. The products are formed as mixtures of structural isomers. As expected, their redox chemistry is complicated.[719] The four pyridyl groups in ligand (**177**) allow the formation of [{Ru(bpy)$_2$Cl}$_4$(**177**)]$^{4+}$. The extended π-system of the bridging ligand facilitates electronic interaction between central and outer groups; at 298 K, fluoresence emission by direct excitation at the Soret and Q bands or by excitation of the Ru(bpy)$_2^{2+}$ units, occurs from the porphyrazine.[720] The electrochemical and photoelectrochemical responses of molecular films formed by [{Ru(bpy)$_2$Cl}$_4$(**177**)]$^{4+}$ have also been studied.[721]

Ligands involving bpy units connected by ethyne spacers through the 5-positions (**178**), the 4- or 6-positions have been developed and incorporated into Ru^{II}–Os^{II} complexes, e.g., [(bpy)$_2$Ru(μ-**178**)Os(bpy)$_2$]$^{4+}$. Linking the bpy domains through the 6-positions results in a sterically crowded [(bpy)$_2$Ru(μ-L)Os(bpy)$_2$]$^{4+}$ species. The ethynylene bridge allows rapid through-bond electron exchange between the metal centers, and the rate of exchange increases with decreasing energy gap between donor and bridge.[712] Photophysical and electrochemical properties have been investigated for the series of complexes [Ru(bpy)$_2$L]$^{2+}$ and [(bpy)$_2$Ru(μ-L)Ru(bpy)$_2$]$^{4+}$ and Os^{II} analogs where L is (**178**) or a related ligand with the bpy domains linked by one or two C≡C units through the 4,4′-, 5,5′, or 6,6′-positions of the bpy ligands.[177] Related chemistry with tpy replacing bpy donor sets has also been reported (see Section 5.5.3.1.14).[178]

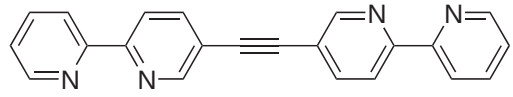
In the next part of this section, we consider bridged systems that utilize quinones and related ligands. The reactions of [Os(bpy)$_2$Cl$_2$] with H$_4$(**179**), H$_3$(**180**) or H$_6$(**181**) lead to [(bpy)$_2$Os(μ-**179**)



(**176**)

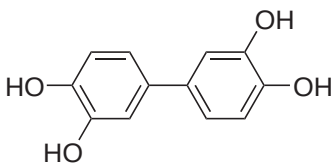


(**177**)

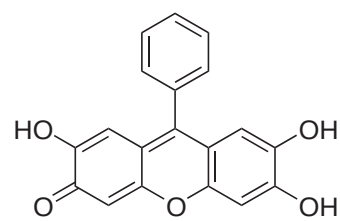


(**178**)

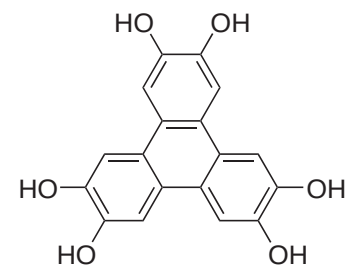
$Os(bpy)_2]^{2+}$, $[(bpy)_2Os(\mu$-**180**$)Os(bpy)_2]^{3+}$, and $[\{Os(bpy)_2\}_3(\mu$-**181**$)]^{3+}$, in which the formal oxidation state of the osmium centers is +3. The complexes exhibit metal-centered one-electron reductions and ligand-based oxidation processes. Comparisons are made with related Ru-containing species including some model, mononuclear species, e.g., for H_2cat = catechol, whereas $[Os(bpy)_2(cat)]^+$ formally contains Os^{III}, the analogous ruthenium complex is formulated as $[Ru^{II}(bpy)_2(sq)]^+$.[725] The intensely black–purple colored $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{2+}$ where H_2L is 2,5-dihydroxy-1,4-benzoquinone, is assigned as a mixed-valence $Ru^{II}Ru^{III}$ species. MO calculations (ZINDO) show that the HOMO consists of metal and bridging-ligand character, while the LUMO has L^{2-} π^* character; the extent of metal-bridging ligand mixing is less than is observed when the bridge is a simple dioxolene.[726] Ligands H_4(**182**) and H_4(**183**) react with $[Ru(4,4'\text{-}^tBu_2bpy)(H_2O)_2]^{2+}$ to give bridged diruthenium complexes containing (**182**) and (**183**) in their semiquinone states. In $[(4,4'\text{-}^tBu_2bpy)_2Ru(\mathbf{183})Ru(4,4'\text{-}^tBu_2bpy)_2]^{2+}$, the two unpaired electrons arising from the two semiquinones pair up to give a diamagnetic complex. The arrangement of the substituents in (**182**) does not allow such pairing and ESR spectroscopy confirms that $[(4,4'\text{-}^tBu_2bpy)_2Ru(\mathbf{182})Ru(4,4'\text{-}^tBu_2bpy)_2]^{2+}$ is a diradical.[727] Reactions of 1,4-dihydroxy anthraquinone, 1,5-dihydroxyanthraquinone and 1-amino-4-hydroxyanthraquinone with $[Ru(bpy)_2Cl_2]$



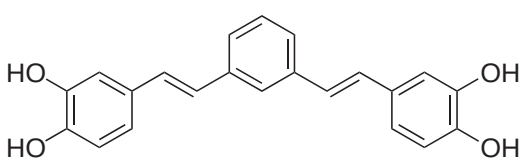
H_4(179)



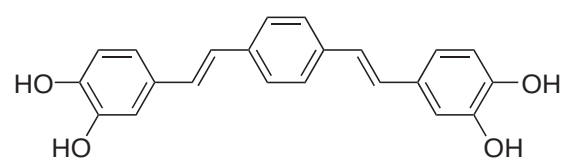
H_3(180)



H_6(181)

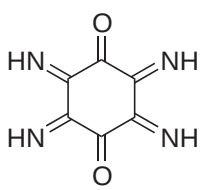


H_4(182)

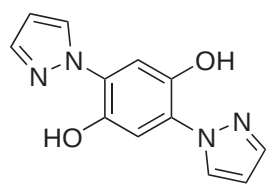


H_4(183)

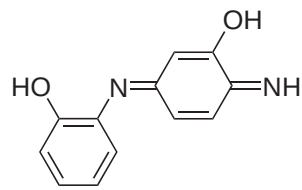
yield dinuclear complexes $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{2+}$, whereas when L is 1,8-dihydroxy anthraquinone, the mononuclear complex $[Ru(bpy)_2L]^{+}$ is obtained. Oxidation of the 1,4-dihydroxyanthraquinone and 1-amino-4-hydroxyanthraquinone bridged complexes gives stable, mixed-valence products.[728] Treatment of $[Ru(bpy)_2Cl_2]$ with 1,4-diaminoanthraquinone results in the formation of the mixed valence $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{3+}$. Data are presented for the $S_2O_8^{2-}$ oxidation of the dinuclear complexes involving 1,4-dihydroxyanthraquinone, 1-amino-4-hydroxyanthraquinone and 1,4-diaminoanthraquinone bridges.[729] Reaction of 1,2,4,5-tetraaminobenzene with $[Ru(bpy)_2(H_2O)_2]^{2+}$ in the presence of water and O_2 generates $[(bpy)_2Ru(\mu\text{-}\mathbf{184})Ru(bpy)_2]^{4+}$ from which the corresponding complexes carrying 2+ and 3+ charges can be formed via ligand-centered reductions. The crystal structure of $[(bpy)_2Ru(\mu\text{-}\mathbf{184})\ Ru(bpy)_2]\ [ClO_4]_4\cdot 4H_2O$ has been determined.[730] The first example of a $(bpy)_2Ru\text{–}Os(bpy)_2$-linked species involving a 1,4-dioxolene bridge (**185**) has been reported; homometallic Ru–Ru and Os–Os analogs have also been studied. Redox processes for the complex are reversible, with four one-electron ligand and metal-centered processes being observed; the effects of changing the metal and of going from reduced hydroquinone to semiquinone to quinone bridge have been investigated.[731] Starting from $[Ru(bpy)_2(EtOH)_2]^{2+}$ and $HOC_6H_4N{=}CHC_6H_4CH{=}NC_6H_4OH$, the diruthenium complex $[(bpy)_2Ru(\mu\text{-}\mathbf{186})Ru(bpy)_2]^{2+}$ has been obtained; the cleavage of the initial ligand was unexpected, giving a bridge that contains two nonequivalent semiquinone binding sites. The electrochemical and spectroscopic properties and the crystal structure of the perchlorate salt of $[(bpy)_2Ru(\mu\text{-}\mathbf{186})Ru(bpy)_2]^{2+}$ have been reported.[732] 2,2′-Bipyridine and semiquinone coordination domains have been linked together by different spacers in bridging ligands L, and a series of dinuclear complexes that include $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{3+}$, $[(tpzea)Ru(\mu\text{-}L)Ru(bpy)_2]^{3+}$ (tpzea = tris(*N*-pyrazolylethyl)amine), and $[(bpy)_2Os(\mu\text{-}L)Ru(bpy)_2]^{3+}$ has been synthesized. The first two redox processes for these complexes are centered on the bridging ligand.[733] 3,3′,4,4′-Tetraaminobiphenyl has been used to bridge two $Ru(bpy)_2^{2+}$ fragments and species in which the bridging ligand is in the bis(quinone diimine) form and also the successively reduced forms have been isolated. Spectroscopic properties of these complexes have been discussed in detail.[734] 3,3′-Dihydroxy-2,2′-bipyridine (H_2L) forms mononuclear $[Ru(bpy)_2(HL)]^{+}$ and dinuclear $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{2+}$ complexes. In the mononuclear complex, HL^{-} acts as an *N,N′*-donor, but in the bridged species, L^{2-} acts as an *N,O*-chelate to each Ru^{II} center. $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{2+}$ undergoes two reversible Ru^{2+}/Ru^{3+} redox processses at +0.12 V and +0.28 V (vs. Fc^{+}/Fc). Chemical oxidation produces the corresponding $Ru^{II}Ru^{III}$ complex which is classified as a valence-trapped mixed-valence species.[735] 1,10-Phenanthroline carrying a pendant dimethoxybenzene or dihydroxybenzene substituent reacts with $[Ru(bpy)_2Cl_2]$ to give mononuclear complexes; the pendant dihydroxybenzene group is oxidized to the diquinone form by 2,3-dichloro-4,5-dicyano-1,4-benzoquinone (DDQ). The bis(phen) ligands (**187**) and (**188**) react with $[Ru(bpy)_2Cl_2]$ to give $[Ru(bpy)_2(\mathbf{187})]^{2+}$ or $[(bpy)_2Ru(\mu\text{-}\mathbf{187})Ru(bpy)_2]^{4+}$, and $[Ru(bpy)_2(\mathbf{188})]^{2+}$ or $[(bpy)_2Ru(\mu\text{-}\mathbf{188})Ru(bpy)_2]^{4+}$ depending on the stoichiometry of the reaction. The bridging ligand in $[(bpy)_2Ru(\mu\text{-}\mathbf{187})Ru(bpy)_2]^{4+}$ resists oxidation by DDQ. Electrochemical data for this series of mono- and dinuclear complexes have been reported.[736]



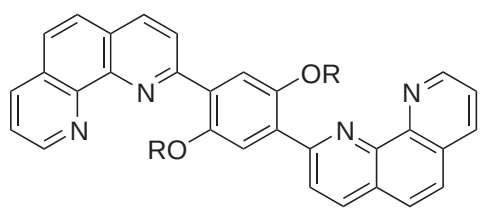
(**184**)



H$_2$(185)

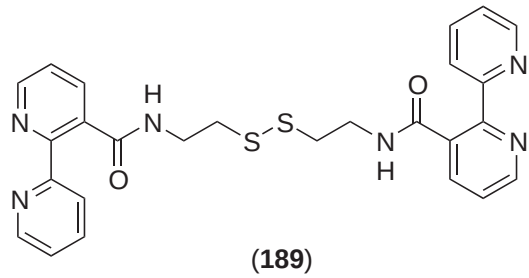


H$_2$(186)



(**187**) R = H
(**188**) R = Me

A series of bridging ligands comprising two bpy domains linked by disulfide-containing chains substituted at the 3-, 4-, 5-, or 6-positions (e.g., ligand (**189**)) has been prepared and converted to diruthenium complexes by reaction with $[Ru(bpy)_2Cl_2]$. Six of the complexes were then used in the assembly of monolayers on Sb-doped SnO_2 substrates and their electrochemical behavior examined. The highest surface coverages were observed for the longest bridge-spacer chains, probably because long alkyl chains are best suited to efficient surface packing.[737]



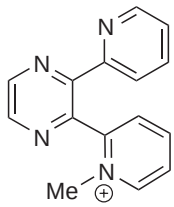
(**189**)

5.5.3.1.5 Polynuclear complexes ($M = Ru$ or Os, $n \geq 3$) containing $M(bpy)_2$ units

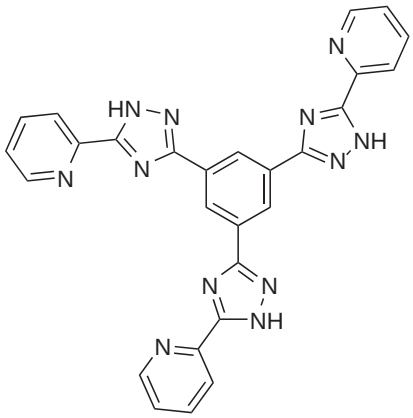
This section summarizes work carried out on polynuclear complexes containing $M(bpy)_2$ units, an area in which there is much interest, in particular with respect to energy transfer. Dendritic systems are excluded from this review, but are covered elsewhere in *CCC II*.[738] The "complexes-as-ligands" strategy is commonly exploited for the controlled construction of multinuclear complexes and examples are seen in this section.

Reaction of $RuCl_3 \cdot xH_2O$ with $[Ru(bpy)_2(2,3\text{-dpp})]^{2+}$ (2,3-dpp = (**88**)) and $[Ru(bpy)_2(2,5\text{-dpp})]^{2+}$ leads to the formation of $[Ru\{(dpp)Ru(bpy)_2\}_2Cl_2]^{4+}$ (dpp = 2,3- or 2,5-dpp). Treatment of each of these complexes with 2,3- or 2,5-dpp generates four hexanuclear species depending on the combination of 2,3- and 2,5-bridging ligands. These complexes show intense absorption bands in the UV region, assigned to ligand-based transitions, as well as intense absorptions in the visible region arising from MLCT transitions. The hexanuclear complexes are luminescent; emission lifetimes lie in the range 42–54 ns (MeCN, 298 K).[739] The syntheses and electrochemical, spectroscopic and spectroelectrochemical properties of the triruthenium complexes $[\{(bpy)_2M(2,3\text{-dpp})\}_2Ru(dpq)]^{6+}$ (dpq = 2,3-bis(2-pyridyl)quinoxaline; M = Ru, Os) have been reported. There is evidence that the peripheral Ru or Os centers are electronically remote from each other. The Ru → dpp CT state for the triruthenium complex emits at 775 nm with a lifetime of 65 ns.[740] By use of 2,3-Medpp$^+$ (**190**), a strategy of protection and deprotection has been illustrated within the "complexes-as-ligands" approach; methylation changes 2,3-dpp from a di- to monochelating ligand. The trinuclear complexes $[(2,3\text{-Medpp})Ru\{(2,5\text{-dpp})Ru(bpy)_2\}_2]^{7+}$, $[(2,3\text{-dpp})Ru\{(2,5\text{-dpp})Ru(bpy)_2\}_2]^{6+}$, $[Ru\{(2,3\text{-dpp})Ru(biq)_2\}_2Cl_2]^{4+}$, and $[Ru\{(2,3\text{-dpp})Os(bpy)_2\}_2\,Cl_2]^{4+}$ have been prepared and characterized. The trinuclear complexes have then been used as building blocks in the construction of a series of hexanuclear complexes of type $[\{ML_2(2,n\text{-dpp})\}_2Ru(2,3\text{-dpp})Ru\{(2,n\text{-dpp})M'L'_2\}_2]^{12+}$ where $n = 3$ or 5, M and M′ = Ru or Os, L and L′ = bpy or biq.[741,742] Using ligand (**101**) (1,4,5,8,9,12-hexaazatriphenylene) as a central bridging unit, stereoisomers of $[\{(bpy)_2Ru\}_2(\mu\text{-}\mathbf{101})Os(bpy)_2]^{6+}$ and of $[\{Ru(bpy)_2\}\{Ru(phen)_2\}\{Ru(4,4'\text{-}Me_2bpy)_2\}(\mu\text{-}\mathbf{101})]^{6+}$ have been prepared using a combination of stereoselective synthesis and separation by chromatography.[743,744]

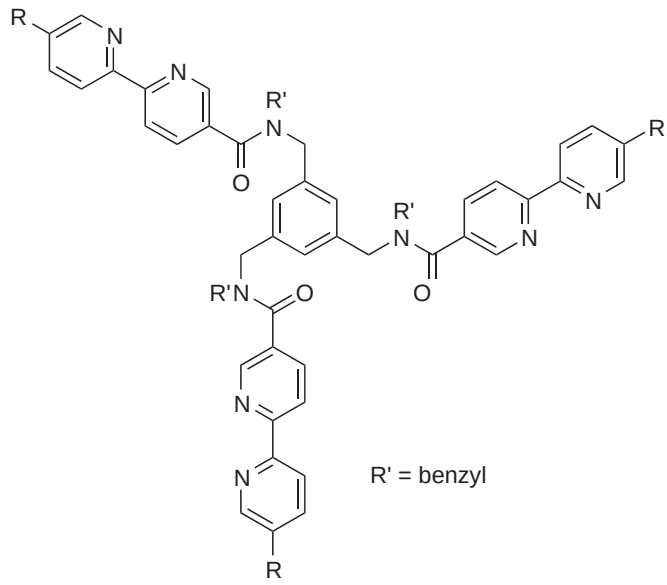
Ligand H_3(**191**) possesses three *N,N′*-domains (pyridine N and triazole N(1)) and is ideally suited to act as a triply bridging ligand between three $M(bpy)_2^{2+}$ units. Coordination is accompanied by deprotonation of the bridge, thereby reducing the overall charge on the trinuclear complexes $[\{Ru(bpy)_2\}_3(\mathbf{191})]^{3+}$, $[\{Os(bpy)_2\}_3(\mathbf{191})]^{3+}$, $[\{Ru(bpy)_2\}_2\{Os(bpy)_2\}(\mathbf{191})]^{3+}$, and $[\{Ru(bpy)_2\}\{Os(bpy)_2\}_2(\mathbf{191})]^{3+}$. Electrochemical data for these complexes indicate that the metal centers do not interact. Differences in properties as a function of protonation state of the bridging ligand have been discussed.[745] The assembly of a hexanuclear complex with a ligand related to H_3(**191**) is described later in the section. The flexibility of ligand (**192**) allows it to form a tris(chelate) complex $[Ru(\mathbf{192})]^{2+}$ or bridge three Ru^{II} centers in $[\{Ru(bpy)_2\}_3(\mathbf{192})]^{6+}$. Related complexes in which one or two bpy sites in (**192**) remain vacant have also been prepared, and the photophysical and electrochemical properties of all three members of this family of complexes



(**190**)



H$_3$(191)



(**192**) R = CO_2Et
(**193**) R = H

have been examined. It is observed that in $[Ru(bpy)_2(\mathbf{192})]^{2+}$, there is efficient intramolecular energy transfer between the two non-coordinated arms of ligand (**192**) and the $Ru(bpy)_2{}^{2+}$-chromophore.[746] Ligand (**193**) and related star ligands in which one or two C_6H_4 spacers are placed between the C_6 core and the amide group have been used in the synthesis of Ru, Ru_2, Ru_3, Ru_2Os, and Os_3-complexes of the general type $[\{M(bpy)_2\}_3L]^{6+}$ where L = (**193**) or related star ligand. All the complexes exhibit intense, ligand-based absorptions in the UV region and MLCT bands in the visible region. Luminescence data for the heterometallic species indicate that there is electronic energy transfer from Ru to Os-containing domains. Trends in the photophysical properties as a function of the core structure of the bridging ligand are discussed.[747]

The synthesis and properties of $[\{Os(bpy)_2\}_3(\mu\text{-}\mathbf{181})]^{3+}$ have been reported; the formal oxidation state of the Os centers is +3.[725] In contrast, $[\{Ru(bpy)_2\}_3(\mu\text{-}\mathbf{181})]^{3+}$ contains Ru^{II} with the bridging ligand possessing three semiquinone domains. The complex undergoes three reversible ligand-centered oxidations taking it ultimately to $[\{Ru(bpy)_2\}_3(\mu\text{-}\mathbf{181})]^{6+}$ with (**181**) in a tris(quinone) form. The wavelength of the intense NIR absorption (MLCT) that the complex exhibits varies with oxidation state.[748]

In Section 5.5.3.1.4, we described carboxylic acid or carboxylate-functionalized bpy ligands used in the exploration of efficient photosensitizers for use in TiO_2-based solar cells. The trinuclear complex $[\{4,4'\text{-}(CO_2)_2\}_2Ru\{(\mu\text{-}NC)Ru(bpy)_2(CN)\}_2]$ has been prepared in a study of potential "sensitizer antennas". The complex adsorbs on to the TiO_2 surface by means of the carboxyl groups, and emission and excitation spectra of the system indicate that light energy absorbed by the antenna $Ru(bpy)_2(CN)_2$ units is transferred efficiently to the sensitizer domain.[749]

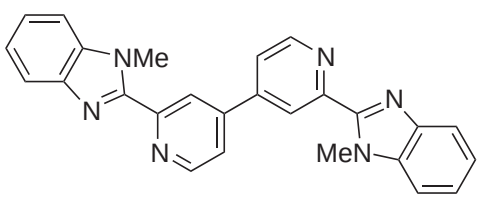
Heterometallic trimetallic complexes incorporating metals from groups other than group 8 include $[(bpy)_2Ru(\mu\text{-L})IrCl_2(\mu\text{-L})Ru(bpy)_2]^{5+}$ (L = 2,3-bis(2-pyridyl)quinoxaline or 2,3-bis(2-pyridyl)benzoquinoxaline, (**91**)).[750] Photolysis of $[(bpy)_2Ru(\mu\text{-}\mathbf{91})IrCl_2(\mu\text{-}\mathbf{91})Ru(bpy)_2]^{5+}$ in the presence of Me_2NH results in the formation of $[(bpy)_2Ru(\mu\text{-}\mathbf{91})IrCl_2(\mu\text{-}\mathbf{91})Ru(bpy)_2]^{3+}$, each ligand (**91**) having undergone a one-electron reduction. This is considered to be an effective "electron store".[751] $[(bpy)_2Ru(\mu\text{-L})IrCl_2(\mu\text{-L})Ru(bpy)_2]^{5+}$ where L = (**91**) or 2,3-bis(2-pyridyl)quinoxaline catalyzes the reduction of CO_2, the catalytically active center being the Ir^{III} core, the properties of which are tuned by the presence of the terminal $Ru(bpy)_2$ groups.[752] The related species $[(bpy)_2Ru(\mu\text{-bpm})M^{III}Cl_2(\mu\text{-bpm})Ru(bpy)_2]^{5+}$ (M = Ir or Rh) and $[(bpy)_2Ru(\mu\text{-2,3-dpp})Ir^{III}Cl_2(\mu\text{-2,3-dpp})Ru(bpy)_2]^{5+}$ have also been prepared and characterized.[750,753]

The dpp ligand has been utilized in the formation of tetranuclear species. The reaction of appropriate ratios of $[Ru(bpy)_2Cl_2]$ and $[Os(2,3\text{-dpp})_3]^{2+}$ (2,3-dpp = (**88**)) leads to the formation of

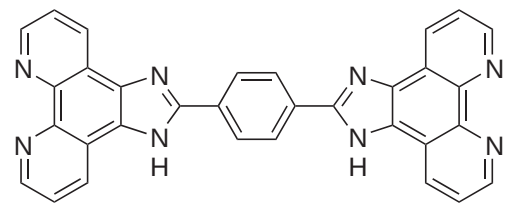
$[Os\{(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2\}_3]^{8+}$. The complex exhibits an antenna effect with energy transfer from the outer $Ru(bpy)_2$ chromophores to the Os^{II} center.[754] A series of di-, tri-, and tetranuclear complexes containing $Ru(bpy)_2^{2+}$ groups linked through bridging 2,3- or 2,5-dpp ligands has been reported, along with related mononuclear species. All the complexes luminesce in the 600–850 nm region; at 77 K (matrix), lifetimes are around 1 μs, and at 298 K (fluid solution), the lifetimes are ≈100 ns. Detailed discussions of spectroscopic and electrochemical properties of the complexes are given.[755] Heterometallic $RuRh_3$, $RuIr_3$, $OsRh_3$, and $OsIr_3$ complexes have been prepared that combine cyclometallated $Rh(ppy)_2^+$ or $Ir(ppy)_2^+$ (Hppy = 2-phenylpyridine) domains with a central $Ru(2,3\text{-}dpp)_3^{2+}$ or $Os(2,3\text{-}dpp)_3^{2+}$ core. The complexes are not stable in coordinating solvents, but studies can be carried out in CH_2Cl_2. Spectroscopic and electrochemical properties have been investigated.[756]

Ligands L of the type shown in structures (**140**) and (**142**) in which the spacer between the two bpy units is $(CH_2)_2$, $(CH_2)_5$ or $(CH_2)_{12}$, and ligand (**139**) have been used in the assembly of the complexes $[Fe\{LRu(bpy)_2\}_3]^{8+}$. Equilibrium constants (in the order of 10^{13} to 10^{15}) for the formation of the complexes have been determined to see how they vary with the length of the spacer in L. The emission of the complexes follows a double exponential decay, the components of which are L (rapid decay) and Ru^{II} centers (long decay).[757] In Section 5.5.3.1.4, we described $[(4,4'\text{-}Me_2bpy)_2Ru(\mu\text{-}\mathbf{139})Ru\{4,4'\text{-}(CO_2H)_2bpy\}_2]^{4+}$ and related complexes. As part of the same study, the tetranuclear complex $[\{4,4'\text{-}(CO_2H)_2bpy\}_2Ru(\mu\text{-}\mathbf{139})\}_3Ru]^{8+}$ has also been synthesized and characterized. The complex exhibits efficient intramolecular quenching of the emission of the $\{4,4'\text{-}(CO_2H)_2bpy\}_2Ru(\mathbf{139})^{2+}$ moiety.[758]

The tetranuclear complex $[(bpy)_2Ru(\mu\text{-bpt})Ru\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_2]^{7+}$ (Hbpt = the triazole derivative (**160**)) contains both electron-poor and electron-rich bridging ligands. The absorption spectrum of the complex shows ligand-centered and MLCT bands in the UV and visible regions, respectively. The luminescence lifetime (298 K) of 68 ns compares to values of 70 ns and 100 ns for $[Ru\{(\mu\text{-}2,3\text{-dpp})Ru(bpy)_2\}_3]^{8+}$ and $[(bpy)_2Ru(\mu\text{-bpt})Ru(bpy)_2\}_2]^{3+}$, respectively.[759] The tetranuclear complex $[Ru\{(\mu\text{-}\mathbf{194})Ru(bpy)_2\}_3]^{8+}$ can be converted into $[\{(bpy)_2Ru(\mu\text{-}\mathbf{194})\}_2Ru(\mu\text{-}\mathbf{194})\text{-}Ru(bpy)_2]^{6+}$ (in which two (**194**) ligands are in their one-electron reduced forms) by photolysis ($\lambda > 500$ nm) in the presence of dimeric *N*-benzyldihydronicotinamide, $(BNA)_2$. It is proposed that the mechanism of the process proceeds by photoinduced electron transfer from $(BNA)_2$ to the triplet excited state of the starting complex.[760] The complex $[Ru\{(\mu\text{-}\mathbf{195})Ru(bpy)_2\}_3]^{8+}$ has been assembled by reaction of $RuCl_3{\cdot}xH_2O$ with $[Ru(bpy)_2(\mathbf{195})]^{2+}$; the dinuclear complex $[(bpy)_2Ru(\mu\text{-}\mathbf{195})Ru(bpy)_2]^{4+}$ has also been prepared. Interaction between the Ru centers in both the di- and tetranuclear complexes is very weak. In addition to an investigation of the spectroscopic and electrochemical properties of these complexes, their NLO properties have been studied; each species exhibits both NLO absorption and self-focusing effects.[761] The syntheses and properties of $Ru(bpy)_2^{2+}$-containing complexes in which the bridging ligand is the 1,3-benzene substituted analog of (**195**) have also been reported.[762] In aqueous MeOH, $[(bpy)_2Ru(\mu\text{-}\mathbf{195})Ru(bpy)_2]^{4+}$ acts as an "off-on-off" luminescent pH sensor as a result of changes in the protonation state of the ligand.[763]



(**194**)

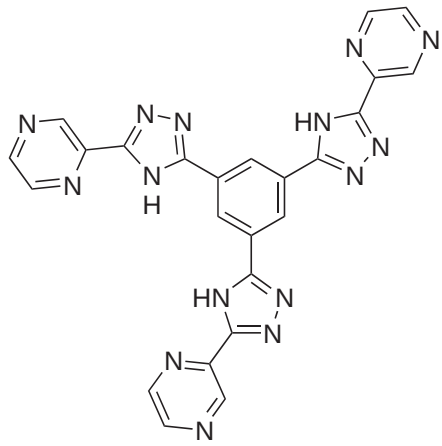


(**195**)

The synthesis, UV–vis spectroscopic and electrochemical properties of the heterometallic complex $[Ru\{(\mu\text{-dpq})PtCl_2\}_3]^{2+}$ (dpq = 2,3-bis(2-pyridyl)quinoxaline) have been described.[764]

Ligand $H_3(\mathbf{196})$ is closely related to $H_3(\mathbf{191})$ described earlier in this section. The hexanuclear complex $[\{Ru(bpy)_2\}_3\{Ru(bpy)_2Cl\}_3(\mathbf{196})]^{6+}$ has been assembled around $(\mathbf{196})^{3-}$. The $Ru(bpy)_2^{2+}$ units are coordinated by the triazole N(1) and pyrazine N(2) atoms, while each pyrazine N(4) donor binds an $Ru(bpy)_2Cl^+$ group. These latter groups dissociate when the complex is photolysed. Spectroscopic and electrochemical properties of and the effects on these properties of the protonation state of $[\{Ru(bpy)_2\}_3\{Ru(bpy)_2Cl\}_3(\mathbf{196})]^{6+}$ have been studied.[765] For the ligand HL = 3,6-bis(2-pyridyl)pyridazine, the reaction of $[Ru(bpy)_2(HL)]^{2+}$ with $RhCl_3$ leads to the formation of the hexanuclear species $[\{(bpy)_2Ru(\mu\text{-L})\}_2Rh(\mu\text{-Cl})_2Rh\{(\mu\text{-L})Ru(bpy)_2\}_2]^{8+}$ in

which L^- acts as a *C,N*-donor to Rh^{III}. The complex exhibits absorptions in the UV and visible regions and a phosphorescence band at 298 K ($\lambda_{max} = 657$ nm, $\tau = 925$ ns) and at 77 K ($\lambda_{max} = 632$ nm, $\tau = 5.5$ μs).[766]



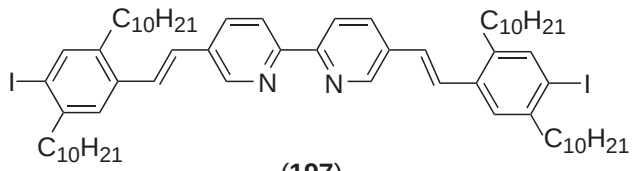
H_3 (196)

We progress now to heptanuclear complexes. The reaction of $RuCl_3 \cdot xH_2O$ with [Ru(bpy)-(2,3-dpp)$_2$]$^{2+}$ (2,3-dpp = (**88**)) in EtOH at reflux yields [Ru{(μ-2,3-dpp)Ru(bpy)(2,3-dpp)}$_3$]$^{8+}$, treatment of which with [Ru(bpy)$_2$Cl$_2$] leads to the formation of the heptanuclear [Ru{(μ-2,3-dpp)Ru(bpy)(μ-2,3-dpp)Ru(bpy)$_2$}$_3$]$^{14+}$. The spectroscopic properties of [Ru{(μ-2,3-dpp) Ru(bpy)(2,3-dpp)}$_3$]$^{8+}$ and [Ru{(μ-2,3-dpp)Ru(bpy)(μ-2,3-dpp)Ru(bpy)$_2$}$_3$]$^{14+}$ have been compared; increasing the nuclearity leads to a slight increase in the luminescence lifetime.[767] An investigation of the photophysical properties of [Ru(μ-**101**)$_3${Ru(phen)$_2$}$_6$]$^{14+}$ (**101** = hat) has been carried out; excitation at 590 nm gives an ^{3}MLCT state with a decay time of 1.9 ns.[768] Decanuclear complexes containing M(bpy)$_2^{2+}$ units (M = Ru, Os) are represented by [M{(μ-L)-M′{(μ-L)M″L′$_2$}$_2$}$_3$]$^{20+}$ where L = 2,3-dpp (**88**) and L′ = bpy or biq.[769,770]

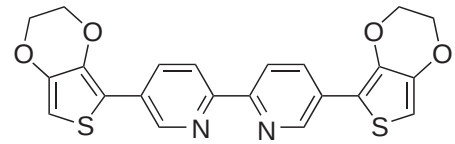
We conclude this section with a look at some polymeric systems. Vos *et al.* have investigated the photophysical and electrochemical properties of [Ru(bpy)$_2$(PVP)$_{10}$]Cl$_2$/[Os(bpy)$_2$(PVP)$_{10}$ Cl]Cl, [Ru(bpy)$_2$(PVI)$_{10}$]Cl$_2$/[Os(bpy)$_2$(PVI)$_{10}$Cl]Cl, [Os(bpy)$_2$(PVP)$_{10}$Cl]Cl/[Ru(bpy)$_2$(PVP)$_{10}$Cl]Cl, [Os(bpy)$_2$(PVI)$_{10}$Cl]Cl/[Ru(bpy)$_2$(PVI)$_{10}$Cl]Cl, [Os(bpy)$_2$(PVP)$_{10}$]Cl$_2$/[Ru(bpy)$_2$(PVP)$_{10}$]Cl$_2$, [Os-(bpy)$_2$(PVI)$_{10}$]Cl$_2$/[Ru(bpy)$_2$(PVI)$_{10}$]Cl$_2$ where PVP = poly(4-vinylpyridine) and PVI = poly (*N*-vinylimidazole). The polymers have been characterized by use of UV–vis and emission spectroscopies. It is concluded that the excited state and redox properties of the Ru and Os centers are retained on incorporation into the polymers.[771] The bpy derivative (**197**) has been incorporated into the complexes [Ru(**197**)L$_2$] where HL is one of a series of β-diketones or 8-hydroxyquinoline. Heck coupling has then been used to combine the complexes into polymers, aromatic spacers being used between Ru^{II}-centered complexes. The photoconductive properties of the polymers have been reported; the identity of HL has a significant influence on their redox and optical properties.[772] Polyconjugated polymers have been produced by the anodic coupling of [Ru(**198**)$_3$]$^{2+}$ and the analogous Fe^{II} complex. Polymerization is accompanied by ligand abstraction, resulting in bis(bpy)-type units. The properties of the polymer films have been discussed.[773] Soluble polymers containing Ru(bpy)$_3^{2+}$ or Os(bpy)$_3^{2+}$ units connected by poly(3-octylthiophene) spacers have been studied and it has been concluded that there is a strong interaction between the Ru^{II}-centered complex units and the π-conjugated polythiophenes. Differences between the Ru and Os-containing polymers have been observed, e.g., ordering of energy levels leading to differences in luminescence behavior.[774]

5.5.3.1.6 Stereochemical aspects of [M(bpy)$_3$]$^{2+}$ and related complexes

In this section, we consider systems in which chiral properties have been the focus of attention. Examples[115,282,391,530,531,603,649,703,705,706] have already been mentioned, and earlier sections should also be consulted. The synthesis and photophysical properties of dinuclear complexes with



(**197**)



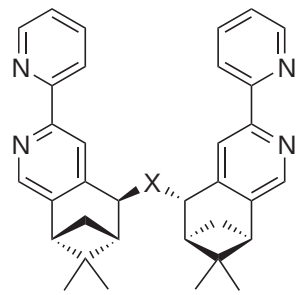
(**198**)

predetermined chirality have been overviewed.[775] Magnetic CD spectroscopic data (4.2 K) for $[Ru(bpy)_3]^{2+}$, $[Os(bpy)_3]^{2+}$, $[Ru(phen)_3]^{2+}$, and $[Os(phen)_3]^{2+}$ have been reported.[776]

When a CH_2Cl_2 solution of enantiomeric $[Ru(bpy)_3]Cl_2$ is illuminated with visible light, optically active $[Ru(bpy)_2Cl_2]$ is obtained. Mechanisms are proposed to explain the observed retention and inversion of configuration and dependence of optical purity of the product on the light intensity.[777] The crystal structures of racemic and resolved $[Ru(bpy)_3][ClO_4]_2$ have been determined, and the absorption spectra of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ in different crystalline hosts have been reported.[778] The structure of $[Ru(bpy)_3]_2[Co(CN)_6]Cl{\cdot}8H_2O$ is described as possessing two "pseudo-racemic" crystallographically independent cations. The structure consists of layers of Λ-$[Ru(bpy)_3]^{2+}$ cations and H_2O molecules, layers containing $[Co(CN)_6]^{3-}$ and Cl^- anions and H_2O molecules, and layers of Δ-$[Ru(bpy)_3]^{2+}$ cations and H_2O molecules.[779] The solution ^1H NMR spectrum of $[Ru(bpy)_2(1,1'\text{-biiq})]^{2+}$ (1,1′-biiq = 1,1′-biisoquinoline) shows the presence of a 3:1 mixture of diastereomers, but crystallization over one week gives selectively the diastereomer with a λ-conformation of the chelate ring involving 1,1′-biiq and a Δ-configuration at the Ru^{II} center. The mixture of diastereomers is re-established once the crystals are redissolved.[780] The electronic and CD spectra of reduced Δ-$[Ru(bpy)_3]^{2+}$ and Δ-$[Os(bpy)_3]^{2+}$ have been investigated; the data provide evidence that the electrons added in the one-, two- and three-electron reduction steps are localized on separate bpy ligands. Luminescence spectra for the three-electron reduced species have also been described.[781]

By using the mononuclear precursors Δ- or Λ-$[Ru(bpy)_2(CO)_2]^{2+}$ or Δ- or Λ-$[Ru(phen)_2(CO)_2]^{2+}$ (i.e., predetermined chirality) coupled with chromatographic separation methods, *meso*- and *rac*-$[(bpy)_2Ru(\mu\text{-hat})Ru(bpy)_2]^{4+}$ and *meso*- and *rac*-$[(phen)_2Ru(\mu\text{-hat})Ru(phen)_2]^{4+}$ (hat = (**101**)) as well as the enantiomers of the *rac*-forms have been isolated. The methodology has been extended to isolate diastereoisomers of $[\{RuL_2\}_3(\mu\text{-hat})]^{6+}$ (L = bpy, phen).[782]

The term "chiragen" has been introduced to describe a tetradentate ligand with a bridging unit linking two chiral 4,5-pinene-2,2′-bpy domains, e.g., (**199**). Δ- and Λ-[Ru(**199**)Cl_2] have been prepared and used as enantiomerically pure building blocks in higher nuclearity complexes.[783] Chir-optical absorption and luminescence spectra have been reported for Δ-[Os(4,4′-Me_2bpy){**199**(X = $(CH_2)_6$)}]$^{2+}$, in which the overall structural chirality of the complex depends on the chirality of the chiragen ligand.[784] Complex formation involving chiragen ligands (**199**) in which X = nothing, $(CH_2)_3$ or CH_2(5,5′-bpy)CH_2 have also been studied.[785]



X = bridging unit, e.g. $(CH_2)_5$, $(CH_2)_6$, xylyl

(**199**)

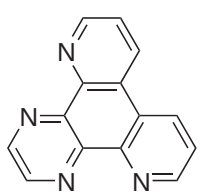
The preparations of Δ/Λ-, Δ- and Λ-$[Ru(bpy)_2(1R,2R\text{-chxn})]^{2+}$ (chxn = 1*R*,2*R* -(–)-1,2-diaminocyclohexane), *rac*-, Δ- and Λ-$[Ru(bpy)_2(chxdiim)]^{2+}$ (chxdiim = 1,2-diiminocyclohexane), and

rac- and Δ-$[Ru(bpy)_2L]^{2+}$ (L = *N,N*′-dimethylethylenediimine) have been reported. The extent of retention of configuration upon reduction (using $NaBD_4$) of the Ru^{II}-bound chxdiim, or oxidation (using Ce^{4+}) of the coordinated diamine ligands has been examined.[786] By making use of the stereocontrolled formation of reactive intermediates involving (*R*)-(+)- or (*S*)-(–)-methyl 4-tolyl sulfoxide, a "one-pot" asymmetric synthesis to Ru^{II} tris(bpy) complexes has been achieved; this method avoids the need for separation of individual enantiomers.[787] The stepwise syntheses of $[Ru(4,4'\text{-}X_2bpy)_3]^{2+}$ (X = Me, chiral ester, chiral amide) from $RuCl_3 \cdot xH_2O$, with the products resolved into pure Δ- or Λ-enantiomers or diastereomers, have been described.[788] General routes (starting from Ru^{II} dicarbonyl precursors) to the dinuclear polypyridyl (L, L′ and L″) complexes $[L_2Ru(\mu\text{-}L')RuL''_2]^{4+}$ and $[L_2Ru(\mu\text{-}L')OsL''_2]^{4+}$ and the chromatographic separation and characterization of diastereoisomeric pairs of complexes have been reported.[789] The separation, ^1H NMR spectroscopic, and photophysical properties of the Δ,Δ-, Λ,Λ-, Δ, Λ- and Λ,Λ-stereoisomers of $[(bpy)_2Ru(\mu\text{-bpt})Ru(bpy)_2]^{3+}$ where Hbpt is the triazole derivative (**160**), have been described with the aim of studying relationships between stereochemistry and photophysical behavior of these and related species.[790]

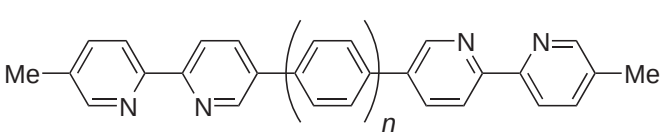
We have already mentioned several examples of the chromatographic separation of stereoisomers. Cation-exchange methods have been successfully applied to both mono- and dinuclear Ru^{II} polypyridyl systems,[538,791–793] and a general chromatographic technique for the resolution of tris-homoleptic $[RuL_3]^{2+}$ complexes (L = bpy, phen, 4,4′-Me_2bpy, hat (**101**) and bpm) has been described with the absolute configurations of the products being confirmed by using CD spectroscopy. The technique has been extended to heteroleptic complexes.[794] A novel method of resolving $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_2(\mathbf{200})]^{2+}$ has involved the use of double-stranded DNA immobilized on a column of hydroxyapatite.[795] Capilliary electrophoresis has been applied to the separation of the enantiomers of $[ML_3]^{2+}$ (L = phen or bpy; M = Fe, Ru, Ni).[796]

Development of synthetic routes with stereoisomeric control is an important goal, and several examples have already been described. Ligand (**201**) is an extended analog of hat (**101**) and has been used as a central building block in the disk-like, π-conjugated ΔΔΔ- and ΛΛΛ-$[\{Ru(phen)_2\}_3(\mathbf{201})]^{6+}$. The precursors are enantiomerically pure Δ- and Λ-$[Ru(phen)_2(py)_2]Cl_2$ which react with retention of configuration.[797] π-Conjugated rods with chiral components are represented by ΔΔ- and ΛΛ-$[(phen)_2Ru(\mu\text{-}\mathbf{202})Ru(phen)_2]^{4+}$, formed when enantiomerically pure Ru^{II} precursors are used.[798] The chiral building blocks Δ- and Λ-$[Ru(bpy)_2(py)_2]^{2+}$ have been used in the synthesis of chiral anion receptors; an alternative approach is the application of cation exchange chromatography.[799]

Within the area of molecular magnets, oxalate-bridged 3D networks of the type $X^+[M^{III}M^{II}(C_2O_4)_3]^-$ are important, and of significance is the introduction of chiral cations X^+. Examples have included enantiomers of $[Ru(bpy)_2L]^+$ where HL = 2-phenylpyridine or 8-hydroxyquinoline, which are able to act as chiral templates in the construction of 3D polymeric networks.[800]

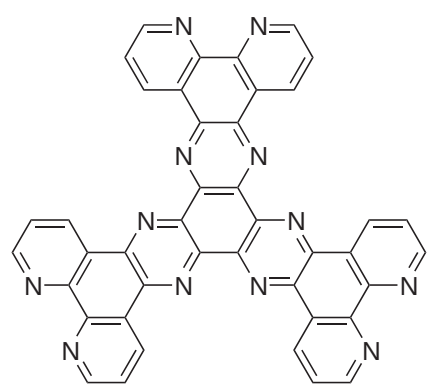


(**200**)



n = 0, 1

(**202**)



(**201**)

5.5.3.1.7 Complexes containing 1,10-phenanthroline or related ligands

Examples of complexes containing phen ligands have already appeared in this chapter,[44,182,246,320,340,417,519–521,528,621,673,680,699,736,743,744,768,776,782,796–798] in most cases where they are being considered along with analogous bpy-containing compounds. This section deals with mononuclear and some dinuclear complexes containing phen ligands.

The complex $[RuCl_2(PPh_3)_2(phen)]$ is among a number of complexes $[RuCl_2(PPh_3)_2L_2]$ (L = py or substituted py, or L_2 = phen, bpy or substituted bpy) that have been prepared and characterized. The crystal structure of $[RuCl_2(PPh_3)_2(phen)]$ has been determined.[801] Routes to $[Ru(phen)_3][ClO_4]_2$ and $[Ru(phen)_3][BPh_4]_2$ starting from Ru^{II} and Ru^{III} halo dmso complexes, and to several salts of $[Ru^{III}(phen)_2Br_2]^+$ have been reported.[802] Nucleophilic displacement of MeCN by Cl^-, CN^-, or py in enantiomerically pure Δ- or Λ-*cis*-$[Ru(phen)_2(MeCN)_2]^{2+}$ gives a route to optically active *cis*-$[Ru(phen)_2X_2]^{n+}$ (X = Cl, CN; $n = 0$; X = py, $n = 2$) and avoids the need for resolution of their enantiomers.[803] Solvent effects on the absorption and emission spectroscopic properties of *cis*-$[Ru(phen)_2(CN)_2]$ have been studied, and the properties correlated with the Gutmann solvent acceptor number.[804] There is an anomalous temperature-dependence on the rates of reductive and oxidative quenching by aromatic amines and nitroaromatic compounds of the excited *cis*-$[Ru(phen)_2(CN)_2]$ in MeCN solution; reasons for the behavior are discussed.[805] The results of an investigation of the photoinduced electron-transfer reactions of $[Ru(phen)_2(CN)_2]$ with [Ru(β-diketonate)$_3$] complexes have been reported, and comparisons made between several organic quencher systems;[806] solvent effects have also been investigated.[807]

The synthesis, characterization, and reactivity of *cis*-$[Ru(phen)_2(CO)(CHO)]^+$ have been described,[808] and comparisons have been made with the bpy analog.[416] Derivatives that have been prepared from $[Ru(phen)_2(CO)(CHO)]^+$ include $[Ru(phen)_2(CO)(CO_2H)]^+$ and $[(phen)_2Ru(\mu\text{-}CO_2)Ru(bpy)_2(CO)]^{2+}$.[808] Starting from the corresponding *N*-benzylglycinato complex, controlled-potential anodic oxidation has been used to prepare $[Ru(phen)_2L]^+$ in which L^- is the α-iminoacidato ligand. The crystal structure of $[Ru(phen)_2L][PF_6]$ has been determined and reveals π-stacking between the benzyl substituent of L^- and phen rings. ^1H NMR nOe data indicate that these intermolecular interactions persist in solution.[809]

A number of papers deal with aspects of $[Ru(phen)_3]^{2+}$. In the solid state, $[Ru(phen)_3][PF_6]_2$ consists of racemic layers of cations, between which the anions reside. This contrasts with the structure of $[Ru(bpy)_3][PF_6]_2$ which possesses homochiral layers.[810] Racemic layers of $[Ru(phen)_3]^{2+}$ cations are observed in the perchlorate salt.[811] The structure of Λ-$[Ru(phen)_3][PF_6]_2$ has been determined.[812] Data for 335 M(phen), 159 M(phen)$_2$, and 33 M(phen)$_3$ complexes from the Cambridge Structural Database have been analyzed and show that offset face-to-face interphen interactions are more common that edge-to-face interactions.[813]

The time-resolved resonance Raman spectrum of $[Ru(phen)_3]^{2+}$ has been interpreted and the results compared with those previously reported; the present interpretation indicates localization in the lowest MLCT state for $[Ru(phen)_3]^{2+}$, as observed for the excited state of $[Ru(bpy)_3]^{2+}$.[814] This result is in contrast to a previously reported delocalized model which has also been questioned in the light of the results of electroabsorption studies.[815] Time-resolved IR spectroscopic data (1,300–1,700 cm^{-1}) for the MLCT states of *$[Ru(phen)_3]^{2+}$ also provide evidence for the localization of the excited electron onto one of the phen ligands on a 100 ns timescale. Data for *$[Os(phen)_2(Ph_2AsCH_2CH_2AsPh_2)]^{2+}$ are also discussed.[816] The photoinduced electron transfer from *$[Ru(phen)_3]^{2+}$ to $[M(phen)_3]^{n+}$ (M = Co, Ni, Rh, Cr; $n = 2$, 3) has been investigated.[817] It has been shown that in $[Ru(phen)_3]_2[Cr(CN)_6]Cl{\cdot}2Me_2CO{\cdot}14H_2O$ (crystals of which were grown by a diffusion method), the rate of energy transfer from the ^{3}MLCT state of $[Ru(phen)_3]^{2+}$ to the E_{2g} state of $[Cr(CN)_6]^{3-}$ is much slower than that from the corresponding excited state of $[Ru(bpy)_3]^{2+}$ in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\cdot}8H_2O$;[818] (see related discussion in Section 5.5.3.1.2).[340] The results of temperature-dependent luminescence decay measurements, both in liquid and solid environments, have been discussed.[819] The excited-state lifetime of $[Ru(5\text{-pyrenylphen})_3]^{2+}$ (5-pyrenylphen = 5-pyrenyl-1,10-phenanthroline) has been determined to be 148 ± 8 μs.[820]

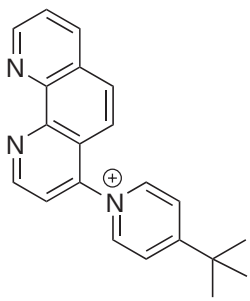
A series of papers report the results of DFT calculations on $[Ru(phen)_3]^{2+}$ and related complexes containing 5,6-,4,7-disubstituted phen ligands and on $[M(tap)_3]^{2+}$ (M = Fe, Ru, Os; tap = (**102**)).[821–823]

We now consider mononuclear complexes of the type $[Ru(phen)_2L]^{2+}$ (L ≠ phen). Complexes of general formula $[Ru(phen)_2(pyridyltriazole)]^{2+}$ have been prepared and characterized; comparisons with related series of complexes containing 4,4′-Me_2bpy or bpy in place of phen have shown differences in the isomers formed.[824] The effects on the structure of $[Ru(phen)_3]^{2+}$ of exchanging one phen ligand for the sterically hindered 2,9-Me_2phen have been investigated.[825] Sterically

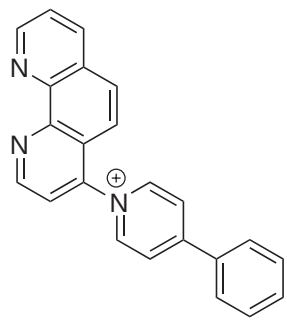
demanding ligands (L) such as 2,9-Ph_2phen, 6,6′-Ph_2bpy and 6,6′-Me_2bpy are expelled and replaced by two equivalents of MeCN when MeCN solutions of $[Ru(phen)_2L]^{2+}$ are irradiated with visible light.[826] Similar results have been obtained when L is a sterically demanding aromatic diimine ligand; the process can be thermally reversed.[827]

The preparation and structure of [Ru(phen)$_2$(1,5,6,10-tetraazaphenanthrene)]Cl_2 have been reported; ^{1}H NMR spectroscopic data provide insight into the hydrophilic properties of the complex.[828] The bpy-containing complexes $[Ru(bpy)_2(\mathbf{92})]^{2+}$ and $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{92})]^{4+}$ ((**92**) = dipyrido(2,3-*a*;2′,3″-*h*)phenazine) were described earlier in the chapter.[512] The analogous $[Ru(phen)_2(\mathbf{92})]^{2+}$ and $[\{Ru(phen)_2\}_2(\mu\text{-}\mathbf{92})]^{4+}$ have also been prepared and characterized, as has $[\{(phen)_2Ru(\mu\text{-}\mathbf{92})\}_3Ru]^{8+}$. The electronic spectra exhibit intense MLCT bands in the visible region; the electrochemical properties of the complexes have been investigated and for $[\{(phen)_2Ru(\mu\text{-}\mathbf{92})\}_3Ru]^{8+}$, two sets of reduction waves centered on ligand (**92**) are separated by those assigned to phen reductions.[829]

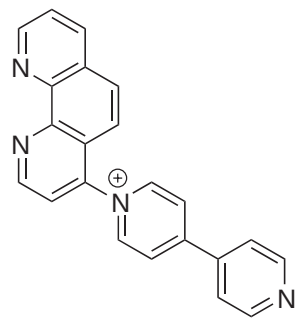
Complexes of type $[Ru(phen)_2L]^{2+}$ in which L is a functionalized phen ligand include those in which L = (**203**)–(**205**); related bpy-containing complexes have also been studied. The pyridinium groups are not efficient quenchers, and the excited states of $[Ru(phen)_2(\mathbf{203})]^{2+}$, $[Ru(phen)_2(\mathbf{204})]^{2+}$ and $[Ru(phen)_2(\mathbf{205})]^{2+}$ exhibit luminescent quantum efficiencies similar to that of $*[Ru(phen)_3]^{2+}$.[830] The photophysical properties of mono- and dinuclear Ru^{II} and Os^{II} complexes containing the phen-based ligands (**206**) and (**207**) have been investigated; in the dinuclear Ru–Os complexes in which (**206**) and (**207**) are the bridging ligands, intramolecular triplet energy transfer occurs from Ru^{II} to Os^{II}-unit.[831] The phen derivative (**208**) and the complex $[Ru(bpy)_2(\mathbf{208})]^{2+}$ have been prepared and characterized; $[Ru(bpy)_2(\mathbf{208})]^{2+}$ binds Cu^{I} in the pendent *N,N′,N″*-coordination site. The product of the reaction of Cu^{II} with $[Ru(bpy)_2(\mathbf{208})]^{2+}$ exhibits photophysical properties that are influenced by the presence of NO, but the material is too labile to make it a potential NO sensor.[832]



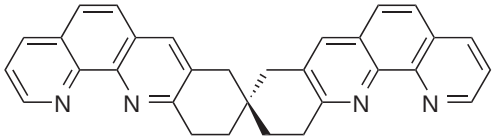
(**203**)



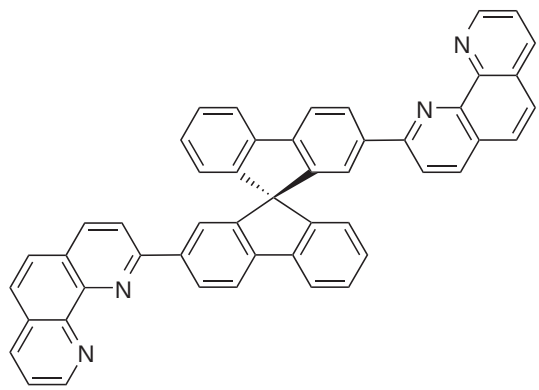
(**204**)



(**205**)

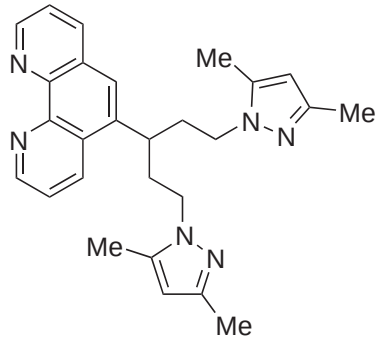


(**206**)

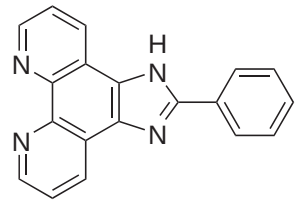


(**207**)

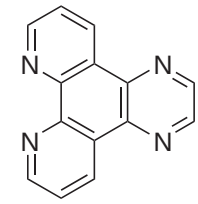
Electronic spectroscopic and electrochemical data for $[Ru(bpy)_2(\mathbf{98})]^{2+}$ ((**98**) = dipyrido[3,2-a:2′,3′-c]phenazine) are consistent with the presence of two electronically separate units, one behaving like $[Ru(bpy)_3]^{2+}$ and the other resembling a phenazine-like acceptor.[524] Spectroscopic



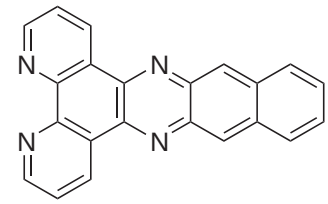
(**208**)



(**209**)



(**210**)

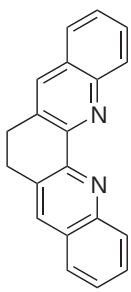


(**211**)

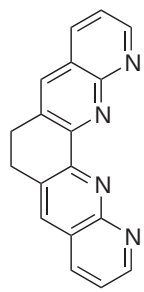
and electrochemical data for $[Ru(\mathbf{98})_3]^{2+}$, $[Ru(\mathbf{98})(bpy)_2]^{2+}$, and $[Os(\mathbf{98})(phen)_2]^{2+}$ indicate that the lowest-lying π^*-orbital of ligand (**98**) is effectively localized on the phenazine unit; consequences of this on the properties of the complexes are discussed.[833] The electrochemical and NLO properties of the complexes $[Ru(\mathbf{208})_2L]^{2+}$ where L = (**98**), (**210**), or (**211**) have been described; extending the π system in L affects the NLO behavior;[834] (see also structures (**95**)–(**97**) and discussion).[523]

Reaction between 5-Brphen and 3-pyrene boronic acid gives the corresponding pyrene-derivatized phen ligand (5-pyrphen). The complexes $[Ru(bpy)_2(5\text{-pyrphen})]^{2+}$ and $[Ru(5\text{-pyrphen})_3]^{2+}$ exhibit MLCT absorptions at ≈450 nm and a pyrene-based absorption close to 340 nm; these data and molecular modeling studies are consistent with there being little electronic interaction between the Ru^{II}-centered fragment and the pyrene chromophore.[835] Light-harvesting systems based on a $Ru(phen)_3^{2+}$ core carrying three pendant piperidinyl-1,8-naphthalimide[836] or coumarin dye molecules[837] have been developed, and enhanced room-temperature MLCT emission lifetimes have been observed.

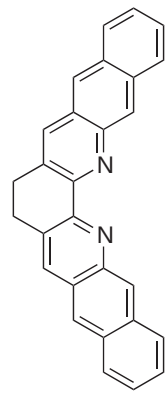
The complexes $[RuL(bpy)_2]^{2+}$ (L = 2,2′-bi-1,8-naphthyridine), $[Ru(\mathbf{212})(bpy)_2]^{2+}$ and $[Ru(\mathbf{213})(bpy)_2]^{2+}$ exhibit changes in their electronic spectra on electrochemical reduction that are consistent with the extra electron being localized in the non-bpy ligand, and resonance Raman spectra support these conclusions.[838] The series of complexes $[RuL(bpy)_2]^{2+}$ and $[RuL_3]^{2+}$ where L = (**212**), (**213**), (**214**), or (**215**) has been studied, with attention paid to the use of microwave irradiation to overcome synthetic problems associated with steric crowding in the homoleptic complexes.[839] In the complexes $[Ru(bpy)_2(\mathbf{216})]^{2+}$ and $[Ru(phen)_2(\mathbf{216})]^{2+}$, ligand (**216**) (considered an "S-tpy" analog) presents a phen-like donor set to the metal center, leaving one *N*-donor non-coordinated; this is confirmed in the crystal structure of $[Ru(bpy)_2(\mathbf{216}, R = {}^{i}Pr)][PF_6]_2$. The related "U-tpy" ligand binds as a tridentate ligand and is a true analog of tpy.[840]



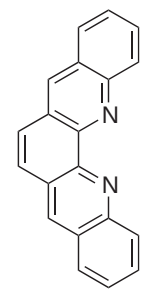
(**212**)



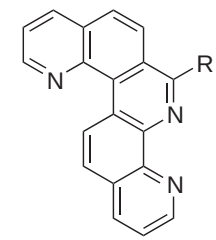
(**213**)



(**214**)



(**215**)

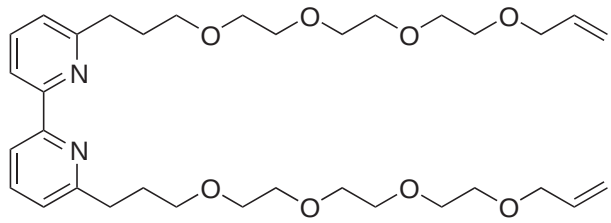


R = H, ^{i}Pr, Ph

(**216**)

Functionalized phen ligands include 4,7-$(CO_2H)_2$phen, which has been incorporated into the photosensitizers *cis*-[Ru{4,7-$(CO_2H)_2$phen}$_2X_2$] (X = Cl, CN, SCN) and carboxylate analogs. For X = SCN, the complex exhibits a more intense and broader MLCT absorption than is observed for *cis*-[Ru{4,4′-$(CO_2H)_2$bpy}$_2(NCS)_2$] and, like the latter, the 4,7-$(CO_2H)_2$phen ruthenium(II) derivatives function as efficient photosensitizers for use in TiO_2-based solar cells.[841] Electronic absorption spectra and the photoluminescence and electrochemiluminescence of Ru^{II} complexes containing 5-(3-carboxylic acid propionamido)-1,10-phenanthroline and 5-(4-carboxylic acid butanamido)-1,10-phenanthroline,[842] and the electrogenerated chemiluminescence from the electron-transfer reaction between the reduced and oxidized forms of $[Ru(4,7\text{-}Ph_2phen)_3]^{2+}$ have been investigated.[843] The reaction of $[Ru(bpy)_2Cl_2]$ with 5,6-$(NH_2)_2$phen results in the formation of $[(bpy)_2Ru(\mu\text{-L})Ru(bpy)_2]^{4+}$ in which L is phen-5,6-diimine. The mononuclear complex $[Ru(bpy)_2\{5,6\text{-}(NH_2)_2phen\}]^{2+}$ in which 5,6-$(NH_2)_2$phen binds through the phen domain has also been prepared and characterized. The spectroscopic, luminescence, and electrochemical properties of $[Ru(bpy)_2\{5,6\text{-}(NH_2)_2phen\}]^{2+}$ are similar to those of $[Ru(bpy)_3]^{2+}$.[844]

Ring closure of the diene in $[Ru(phen)_2(\mathbf{217})]^{2+}$ using Grubb's catalyst generates a macrocyclic complex, the photochemical behavior of which has been studied in MeCN solution. Irradiation at >300 nm leads to the expulsion of $[Ru(phen)_2(MeCN)_2]^{2+}$, and quantitative regeneration of the macrocyclic complex can be achieved by heating in ethylene glycol.[845]



(**217**)

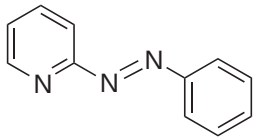
The ligand hat (**101**) acts as a bridging ligand in $[(phen)_2Ru(\mu\text{-hat})Ru(phen)_2]^{4+}$. Flash photolysis of the latter with hydroquinone gives rise to two transients, the first at ≈500 nm being $[(phen)_2Ru(\mu\text{-hat}^{\cdot-})Ru(phen)_2]^{3+}$; details of the processes involved are discussed.[845] The photophysical properties of $[(phen)_2(\mu\text{-}\mathbf{167})Ru(phen)_2]^{4+}$ ((**167**) = tetrapyridophenazine derivative) have been studied, and the interconversion dynamics of two MLCT excited states localized on the bridging ligand (**167**) have been experimentally observed.[846]

Bis(phenanthroline) ligands, L, in which the two phen groups are linked by one or two phenyl spacers have been incorporated into complexes of type $[(bpy)_2Ru(\mu\text{-L})Ru(bpy)_2]^{4+}$ in which L presents a phen binding site to each Ru^{II} center. Mononuclear complexes $[Ru(bpy)_2L']^{2+}$, where L′ = 3-Phphen or 2,9-Ph_2phen, have also been prepared and characterized. Representative structural data reveal interligand π–π stacking interactions, and the effects of these interactions on the photophysical properties of the complexes are discussed.[847] 5,5′-Bis(1,10-phenanthroline) (bisphen) has been used as a bridging ligand in several homodimetallic complexes including $[(bpy)_2Ru(\mu\text{-bisphen})Ru(bpy)_2]^{4+}$, $[(bpy)_2Os(\mu\text{-bisphen})Os(bpy)_2]^{4+}$, and $[(4,4'\text{-}Me_2bpy)_2Os(\mu\text{-bisphen})Os(4,4'\text{-}Me_2bpy)_2]^{4+}$. The bridging bisphen ligand is generated by coupling coordinated 5-Clphen ligands, and possesses a nonplanar structure. The latter results in the two halves of each complex being electronically isolated from one another.[848]

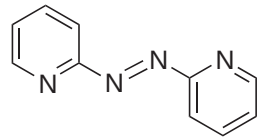
5.5.3.1.8 Mononuclear complexes containing didentate N,N-donor ligands other than bpy or phen

The coordination chemistry of 2-phenylazopyridine (**218**) and related ligands attracts significant attention. The reaction between (**218**) and $[Os(PPh_3)_3Br_2]$ yields $[Os(PPh_3)_2(\mathbf{218})Br_2]$ in which the Br^- ligands are mutually *cis*, and the PPh_3 ligands are *trans* to each other. Ligand (**218**) acts as an *N,N*-chelate, the mode adopted in many of the complexes discussed in this section. Ligand replacement in $[Os(PPh_3)_2(\mathbf{218})Br_2]$ and the properties of the complexes have been studied.[849] The reactions of $[OsBr_6]^{2-}$ with 2-phenylamino or 2-(4-methylphenyl)amino derivatives of (**218**) (HL) produce mixtures of Os^{II} products that include $[OsBr_2(\mathbf{218})_2]$, [OsBrL(HL)], [OsBrL(**218**)], and $[OsBr_2(HL)(\mathbf{218})]$.[850] The crystal structures of *mer*-$[Ru(\mathbf{219})_3][PF_6]_2$ and $[Ru(\mathbf{219})_2Cl_2]$ (*cis* Cl,

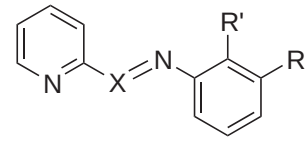
trans-pyridine donors) have been determined,[851] and the *fac* and *mer* isomers of $[Ru(\mathbf{219})_3]^{2+}$ and two diastereomers of $[Ru(\mathbf{219})_2(bpy)]^{2+}$ have been isolated using HPLC, and EPR spectroscopic data for the singly reduced species have been analyzed.[852] A general strategy for the synthesis of $[Ru(\mathbf{218})_3]^{2+}$ has been included in a study of routes to tris(bpy), tris(phen), and tris(**218**) complexes of Ru^{II} and Rh^{III}.[279] A comparison has been made between the photoinduced oxidative and reductive electron-transfer reactions of excited $[Ru(\mathbf{218})_3]^{2+}$ and $[Ru(imin)_3]^{2+}$ (imin = 2-(*N*-methylformimidoyl)pyridine) with selected organic quenchers, and those of $[Ru(bpy)_3]^{2+}$, $[Ru(4,4'\text{-}Me_2bpy)_2(CN)_2]$, $[Ru(5,5'\text{-}Me_2bpy)_2(CN)_2]$, and $[Ru(phen)_2(CN)_2]$.[853] An investigation of the absorption spectroscopic, MLCT excited-state, and electrochemical properties of $[Ru(imin)_n(bpy)_{3-n}]^{2+}$ ($n = 0$–3) has been carried out,[854] and the luminescent complex $[Ru(imin)_2(CN)_2]$ has been prepared and its properties compared with those of $[Ru(bpy)_2(CN)_2]$ and $[Ru(phen)_2(CN)_2]$.[855] Studies of complexes of type $[Ru(\mathbf{218})_2L_2]$ have been made for $L^- = CNS^-$,[856] and NO_3^-.[857] The reactions of $[Os(bpy)_2Br_2]$ with 2-(arylazo)phenol ligands (HL with various substituents) yield $[Os(bpy)_2L]^+$; structural data for a representative derivative confirm an *N,O*-chelation mode for L^-. The complexes can be oxidized chemically or electrochemically and the Os^{III} analogs isolated as perchlorate salts.[858] Silver(I)-assisted trans-metallation has been used in the synthesis of $[RuL_nL'_{3-n}]^{2+}$ where L = *N*-arylpyridine-2-aldimine and L′ = (**220**); reactivity studies include hydrolysis of coordinated L to picolinate.[859] The preparation and crystal structure of *trans*-$[Ru(\mathbf{221})(PPh_3)Br_2]$ have been described; a comparison is made between its reactivity towards various didentate chelates and that of *cis*-$[Ru(\mathbf{221})(PPh_3)Cl_2]$.[860] Reactions of $[Ru_2Cl_2(CS)_2(PPh_3)_4(\mu\text{-}Cl)_2]$ with (**218**)-**R** where (**218**)-**R** is a substituted derivative of ligand (**218**), the R group being H, Me, or Cl in the *o*, *m*, or *p*-position of the phenyl ring, lead to the formation of the mononuclear complexes $[RuCl_2(\mathbf{218}\text{-}\mathbf{R})_2]$ in which the Cl^- ligands are mutually *cis*.[861]



(**218**)



(**219**)



(**220**) X = N; R = Me; R' = H
(**221**) X = CH; R = H; R' = SMe

Ruthenium(III) chloride reacts with 1-methyl-2-(arylazo)imidazoles and 1-benzyl-2-(arylazo)-imidazoles (L) to give complexes of type $[RuL_2Cl_2]$. Green and blue isomers have been obtained, with *trans-cis-cis* and *cis-trans-cis* arrangements of Cl, N(imidazole) and N(azo) donor sets; the green isomer converts to the blue form on heating.[862] *cis-trans-cis*-$[RuL_2Cl_2]$ (L = 1-alkyl-2-(arylazo)imidazole) reacts with $AgNO_3$ and bpy, or with $[Ag(bpy)_2]^+$ to give $[Ru(bpy)L_2]^{2+}$ (isolated as perchlorates); ^1H NMR spectra are consistent with the presence of two isomers for each complex in solution. The complexes are emitters at 77 K, with quantum yields in the range 0.011–0.025.[863] Studies of complexes in the family $[RuL(bpy)_2]$ (L = 1-alkyl-2-(arylazo)imidazole) have also been carried out.[864] 2-(Arylazo)pyrimidines (L) react with $RuCl_3 \cdot xH_2O$ to give *trans-cis-cis*-, *cis-trans-cis*- and *cis-cis-cis*-$[RuL_2Cl_2]$ that can be separated by chromatography; IR, NMR, and electronic spectroscopic, electrochemical, and crystallographic data are presented.[865]

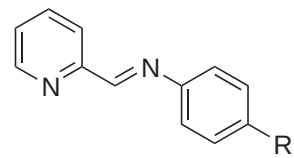
The reactions of ligand (**218**), 2-(*p*-chlorophenylazo)pyridine or 1-methyl-2-(*p*-chlorophenylazo)-imidazole with $[Ru(H)(X)(CO)(PPh_3)_3]$ (X = Cl, Br) yield azo anion radical-containing paramagnetic complexes of type $[Ru(L^{\cdot-})(X)(CO)(PPh_3)_2]$.[866,867] $[Os(\mathbf{218}^{\cdot-})Br(CO)(PPh_3)_2]$ and minor amounts of $[Os(\mathbf{218})H(CO)(PPh_3)_2]Br$ are produced in the reaction of $[Os(H)(Br)(CO)(PPh_3)_3]$ with (**218**). The complex containing the radical azo anion becomes the only product if (**219**) replaces (**218**).[868] Reaction of excess (**219**) with $[Ru(H)_2(CO)(PPh_3)_3]$ leads to $[Ru(\mathbf{219}^{\cdot-})_2(CO)(PPh_3)]$ and $[Ru(\mathbf{219}^{\cdot-})(H)(CO)(PPh_3)_2]$; only the corresponding hydride complex was obtained if (**219**) were replaced by 2-(*p*-chlorophenylazo)pyridine. Structural data are presented, and electrochemical results show that the complexes exhibit radical redox couples with $E_{1/2}$ values (vs. SCE) in the range −0.5 V to +0.10 V.[869]

The synthesis and characterization of $[Ru_2(\mu\text{-}pz')_2(\mathbf{220})_4]^{2+}$ (pz′ = conjugate base of pyrazole) have been reported.[870] The complexes $[M(\mathbf{218})_2(H_2biim)]^{2+}$ (M = Ru, Os; biim = 2,2′-biimidazole) deprotonate on the H_2biim ligand giving $[M(\mathbf{218})_2(Hbiim)]^+$ and $[M(\mathbf{218})_2(biim)]$. Using the "complexes-as-ligands" approach, $[M(\mathbf{218})_2(biim)]$ has been used as a building block in reactions with $[ML_2X_2]^{n+}$ (M = Ru, Os; L = (**218**), bpy; X = Cl, Br and $n = 0$; X = MeCN and $n = 2$) to give dimetallic species containing $biim^{2-}$ bridging units.[871] Trinuclear Ru_3, $RuOs_2$, Ru_2Os, and

Os_3-containing complexes have been prepared by the reactions of two equivalents of $[M(\mathbf{218})_2(biim)]$ (M = Ru, Os) with $[M(PPh_3)_3X_2]$ (M = Ru, Os).[872] When $[M(\mathbf{218})_2(H_2biim)]^{2+}$ (M = Ru, Os) in MeOH reacts with ammonical $AgNO_3$, the products are $[\{M(\mathbf{218})_2(biim)\}_2Ag_2]^{2+}$. Structural data for $[\{Ru(\mathbf{218})_2(biim)\}_2Ag_2][ClO_4]_2 \cdot H_2O$ reveal a short Ag—Ag distance (2.8899(19) Å).[873]

The synthesis and characterization of complexes of type $[RuL(\mathbf{220})_2]$ where H_2L = catechol (H_2cat), 4-^{t}BuH_2cat, 3,5-^{t}B$u_2H_2$cat, or 3,4,5,6-Cl_2H_2cat, have been described. Oxidation using Ce^{IV} yields paramagnetic complexes with L in the semiquinone form. Crystallographic data for $[\{Ru(cat)(\mathbf{220})_2\}_2(H_2O)] \cdot CH_2Cl_2$ confirm that hydrogen bonding between H_2O and catecholate O atoms supports dimers in the solid state. Electrochemical and electronic spectroscopic data are reported.[874] The quinolinolate (HL = 8-hydroxyquinoline) complex $[Ru(\mathbf{220})_2L]^+$ has been isolated as the perchlorate salt, and its properties compared with those of $[Ru(bpy)_2L]^+$;[875] osmium (II) analogs of these complexes have also been studied.[876]

The reactions between RuX_3 (X = Cl, Br) and ligands (**222**) in boiling EtOH give *cis* and *trans*-isomers of $[RuX_2(\mathbf{222})_2]$; spectroscopic and electrochemical data for the complexes are presented.[877] The reduction of *trans*-$[RuX_2(HL)L]$ (HL = RC(N═OH)N═NAr; X = Cl, Br) leads to the ruthenium(II) complex $[RuX_2(HL)L]^-$ which can be reoxidized by Ce^{4+}. Treatment of $[RuX_2(HL)L]^-$ with PPh_3 gives $[RuX(PPh_3)(HL)L]$ and $[Ru(PPh_3)_2(HL)L]^+$.[878] Oxidation of geometrical isomers of $[RuCl_2(\mathbf{222})_2]$ by Cl_2 gives the corresponding Ru^{III} complexes (isolated as perchlorate salts) with retention of stereochemistry.[879]

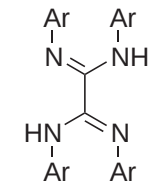


(**222**) R = H, Me, Cl

The energies and relative intensities of the lowest-energy electronic transitions in the UV–vis spectra of the complexes $[Ru(X)(R)(CO)_2L^{N,N}]$ (X = Cl, Br, I, CF_3SO_3; R = alkyl; $L^{N,N}$ = *N,N′*-diisopropyl-1,4-diaza-1,3-butadiene, bpy, pyridine-2-carbaldehyde-*N*-isopropylimine) show a significant dependency on X and R.[880] The excited states of these complexes have been investigated by using time-resolved absorption, resonance Raman, and IR spectroscopies,[881] and syntheses and spectroscopic properties and representative structural data have been reported for *trans,cis* and *cis,cis*-$[Ru(I)(Me)(CO)_2L^{N,N}]$.[882] The reaction of $[RuCl_2(HL)_2]$ (HL = 2,6-$Me_2C_6H_3$N═CHCH═N-2,6-$Me_2C_6H_3$) with potassium in THF produces isomers of $[RuL_2]$ in which L^- contains a metallated 2-Me group. The reduction of $[RuCl_2(HL)_2]$ with 3–4 molar equivalents of potassium results in the formation of $K_2[RuL_2]$ and a deprotonated derivative, the crystal structure of which has been determined, confirming that one ligand coordinates to Ru(0) through an *N,N′,C*-donor set.[883]

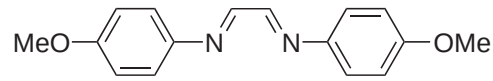
The mononuclear complexes $[Ru(bpy)_2(H_2\mathbf{223})]^{2+}$ and $[Ru(4,4'\text{-}Me_2bpy)_2(H_2\mathbf{223})]^{2+}$, and diastereoisomers of the bridged complex $[(bpy)_2Ru(\mu\text{-}\mathbf{223}, Ar = Ph)Ru(bpy)_2]^{2+}$ have been prepared and characterized. On going from $[Ru(bpy)_3]^{2+}$ to these complexes, the absorption maxima shift to lower energies; there is significant electronic interaction between the metal centers in $[(bpy)_2Ru(\mu\text{-}\mathbf{223}, Ar = Ph)Ru(bpy)_2]^{2+}$.[884] A study of the complexes $[M(CO)_2(SnR_3)_2L]$ in which M = Ru or Os, R = Me or Ph, and L = 4,4′-bpy, ^{i}PrN═CHCH═N^{i}Pr, (**224**) or (**225**), has focused on the variation in the excited-state properties among this series of complexes. All the complexes are photostable in a glass at 80 K and exhibit long excited-state lifetimes.[885]

The reactions between PhN═C(R)NHPh (R = various) and $[M(H)_2(CO)(PPh_3)_3]$, $[MH(Cl)(CO)(PPh_3)_3]$, or $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ (M = Ru, Os) lead to the formation of amidinato complexes which include $[RuCl(PhNCRNPh)(CO)(PPh_3)_2]$, $[Ru(O_2CCF_3)(PhNCRNPh)(CO)(PPh_3)_2]$, and $[OsH(PhNCRNPh)(CO)(PPh_3)_2]$.[886] $[M(H)_2(CO)(PPh_3)_3]$ (M = Ru, Os) reacts with $(PhHN)_2C$═NH to yield $[M(H)\{PhNC(NH_2)NPh\}(CO)(PPh_3)_2]$. In contrast, the product of the reaction of $[M(O_2CCF_3)_2(CO)(PPh_3)_2]$ (M = Ru, Os) with $(PhHN)_2C$═NH contains a didentate diphenylguanidinate anion and a monodentate diphenylguanidine.[887] The reactions of 1,3-diaryltriazenes (HL with Ph, tolyl, methoxyphenyl, and chlorophenyl substituents) with $[RuCl_2(PPh_3)_3]$ generate $[RuL_2(PPh_3)_2]$, which can be oxidized to the corresponding Ru^{III} complexes. Representative crystal structures have been determined, and

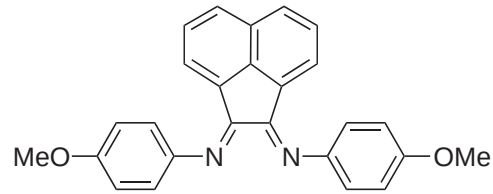


Ar = Ph, tolyl

H_2(223)



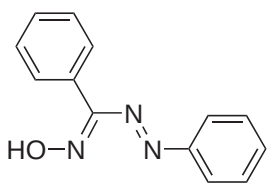
(224)



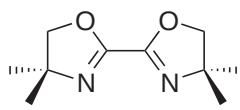
(225)

inter-ligand interactions have been addressed using molecular modeling studies.[888] The complex $[RuL_2(CO)(PPh_3)]$ has been prepared by the reaction of triphenylguanidine (HL) with $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$ and has been structurally characterized; the CO and PPh_3 ligands are mutually *cis*.[889] When a mixture of $[RuCl_2(PPh_3)_3]$ and mesityl azide is photolysed and subsequent phosphine exchange is carried out, the tetrazenido complex $[RuCl_2(PMe_3)_2$-(MesN=NN=NMes)] is obtained. In contrast, the thermal reaction of mesityl azide with $[RuCl_2(H)_2(P^iPr_3)_2]$ results in the formation of a triazenophosphorane complex.[890]

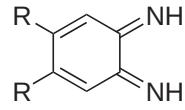
A comparison has been made of the structural parameters and hydrogen bonding in $[Ru^{II}Cl_2L(HL)]^-$ and $[Ru^{III}Cl_2L(HL)]$ where HL = (**226**),[891] and the crystal structure of tris (dimethylglyoxime)ruthenium(II) dichloride has been determined.[892]



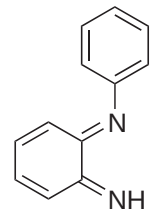
(226)



(227)



(228) R = H
(229) R = Cl
(230) R = OMe



(231)

The bisoxaline (**227**) acts as an *N,N′*-chelate in the Ru^{II} and Ru^{III} complexes $[RuCl_2(\mathbf{227})_2]$ and $[RuCl_3(\mathbf{227})(dmf)]$, both of which are useful starting materials for the synthesis of a range of compounds.[45]

The five-coordinate complex $[Ru(\mathbf{228})(PPh_3)_3]$ is assigned as a Ru^{II} diamide. Its reactivity has been investigated including the addition of ethene or styrene and reactions with diphosphines; in each, ligand (**228**) remains unchanged.[893] The crystal structure of $[RuCl_2(PPh_3)_2(\mathbf{228})]$ has been determined.[894] The complexes $[Ru(NH_3)_4L]^{n+}$ where L = (**228**), (**229**), or (**230**) and $n = 2$ or 3, are considered to possess extensively delocalized systems; spectroscopic properties and the results of ZINDO calculations are discussed, and it is found that the lowest energy, intense absorption in the visible region of the Ru^{III} complex is MLCT rather than LMCT in character.[895] In a novel methodology, the oxidative dimerization of arylamines has been used to prepare the *N*-aryl-1,2-benzoquinone diimine (L, e.g., **231**) complexes $[Ru(acac)_2L]$ starting from $[Ru(acac)_3]$.[896,897] With $RuCl_3 \cdot xH_2O$ as precursor, and the same reaction conditions using $PhNH_2$ as the arylamine, the product is $[RuCl_2(PhNH_2)_2L]$, i.e., substitution accompanies oxidative dimerization.[896] Related osmium chemistry has also been reported in which $[OsBr_2L_2]$ complexes are prepared from $[OsBr_6]^{2-}$ and $ArNH_2$.[898,899] Oxidative dimerization is also observed in the reactions of $[RuCl_2(ArNH_2)_2L]$ with aqueous H_2O_2 to produce isomers of $[RuCl_2L_2]$; the crystal structure of *trans*,*cis*-$[RuCl_2(\mathbf{231})_2]$ (*trans*-NH groups and the *cis*-NPh groups) has been determined.[900]

The ligand di-2-pyridyl sulfide (dps) acts as an *N,N′*-chelate in the complex *trans*-$[Ru(dps)_2(MeCN)_2]^{2+}$, formed from $[Ru(dps\text{-}N,N')_2(dps\text{-}N,S)]^{2+}$ in MeCN. The crystal structure of $[Ru(dps)_2(MeCN)_2][BF_4]_2 \cdot H_2O$ has been elucidated.[901] Reaction of $[RuCl_2(CO)_2]_n$ with

4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (L) gives two isomers of $[RuCl_2(CO)_2L]$, both of which have been structurally characterized. The coordination modes of L are *N*(py),*N*(triazole) in one isomer, and *N*(py),*N*(amino) in the other isomer. For the bromo and iodo complexes, preference for particular isomers is observed: *N*(py),*N*(triazole) coordination in $[RuI_2(CO)_2L]$, and *N*(py),*N*(amino) coordination in $[RuBr_2(CO)_2L]$.[902]

5.5.3.1.9 Mononuclear complexes of type $[M(bpy)L_4]^{n+}$ (L = monodentate ligand)

A study of the electronic transitions in $[Ru(NH_3)_4(bpy)]^{2+}$ has shown that the two longest-wavelength absorptions are red shifted as the Gutmann donor number of the solvent increases. These observations have been discussed in the light of results of calculations performed at the INDO/S level.[903] Resonance Raman and absorption spectroscopic data have been used to probe the solvatochromatic behavior of the electronic transitions of $[Ru(NH_3)_4(bpy)]^{2+}$, arising from hydrogen bonding between complex and solvent (MeOH, dmso).[904] The extent of metal–ligand orbital mixing in $[Ru(NH_3)_4(bpy)]^{2+}$ and $[Ru(NH_3)_4(phen)]^{2+}$ has been assessed by using an electrochemical variational technique. The dπ electrons appear to be mainly localized at the metal center, although some dπ(Ru)-π*(L) (L = bpy, phen) is observed. The results contrast with those obtained using MLCT oscillator strength measurements.[905]

The excited-state properties of $[Ru(CN)_4(bpy)]^{2-}$ have been investigated to provide a model for $[Ru(bpy)_3]^{2+}$ in which there is a localized excitation involving one bpy ligand[906] (see discussions in Section 5.5.3.1.2). $[Ru(CN)_4(bpy)]^{2-}$ can be conveniently prepared by the photolysis ($\lambda = 254$ nm) of $[Ru(CN)_6]^{4-}$ with bpy. The complex is a room-temperature emitter; the emission energy is strongly dependent on solvent and physical state, and lifetimes (298 K) have been measured as 101 ns in H_2O, 25 ns in EtOH and $\approx$4 ns in dmf.[907] The luminescence quantum yields of the lowest-energy d-π* states of $[Ru(CN)_4(bpy)]^{2-}$ and $[Ru(CN)_4(4,4'\text{-}Me_2bpy)]^{2-}$ (aqueous solution, 298 K) are $(8 \pm 1) \times 10^{-3}$ and $(7 \pm 1) \times 10^{-3}$ respectively, and the emission lifetimes are reported to be 125 and 115 ns respectively.[908] EPR spectroscopic data have been reported for electrochemically reduced $[Ru(CN)_4(bpy)]^{2-}$, $[Ru(CN)_4(bpm)]^{2-}$, and $[Ru(CN)_4(bpz)]^{2-}$; the hyperfine coupling constants indicate that the electron spin density is localized in the π*-orbitals.[909]

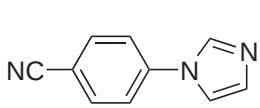
The complexes $[OsBr_2(PPh_3)_2(bpy)]$, $[OsBr_2(PPh_3)_2(4,4'\text{-}Me_2bpy)]$, and $[OsBr_2(PPh_3)_2(phen)]$ have been prepared and spectroscopically and electrochemically characterized. The complexes exhibit intense MLCT transitions in the visible region.[910]

Reactions and properties of $[RuCl_2(CO)_2(bpy)]$ and related complexes have been well explored. Halide exchange can be achieved by using HBr and HI at 160–200 °C, i.e., *cis*(CO),*trans*(Cl)-$[RuCl_2(CO)_2(bpy)]$ is converted to *cis*(CO),*trans*(X)-$[RuX_2(CO)_2(bpy)]$ (X = Br or I); no analogous fluoride complex could be obtained by a parallel route. The complexes can be converted to $[RuX_3(NO)(bpy)]$ by using HNO_3 in aqueous HX, and the formation of nitrido-bridged complexes including $[(H_2O)Br_2(bpy)Ru(\mu\text{-}N)RuBr_3(bpy)]$ and $[Cl_3(bpy)Ru(\mu\text{-}N)Ru(bpy)Cl_3]^-$ has also been described.[911,912] Aqueous HX (X = Cl, Br, I) has been used as a source of halide for the formation of $[RuX_2(CO)_2(4,4'\text{-}Me_2bpy)]$; for X = Cl and Br, selective routes to the *cis*(X) or *trans*(X) isomers were achieved by X = I, only the *trans*(I) isomer was isolated.[913] Starting from $[RuCl_2(CO)_2(4,4'\text{-}Me_2bpy)]$, reaction in the oxidizing environment of aqueous HCl/HNO_3 at 240 °C leads to the formation of $[RuCl_3(NO)\{4,4'\text{-}(CO_2H)_2bpy\}]$; when the precursor is $[RuCl_2(CO)_2(6,6'\text{-}Me_2bpy)]$, the bpy ligand is expelled and the ruthenium-containing product is $[RuCl_5(NO)]^{2-}$.[914] The sterically hindered bpy ligands 4,4′-^{t}Bu$_2$bpy, 6,6′-Me$_2$-4,4′-^{t}Bu$_2$bpy, and 6,6′-Ph$_2$-4,4′-^{t}Bu$_2$bpy (L) have been introduced into complexes of type $[RuCl_2(CO)_2L]$. For L = 6,6′-Ph$_2$-4,4′-^{t}Bu$_2$bpy, the steric demands of the ligand are sufficient to result in the formation of the *cis*(CO),*cis*(Cl) isomer, whereas for the less bulky bpy ligands, the *cis*(CO),*trans*(Cl) isomer is obtained in each case. A *cis*(CO),*cis*(Cl) isomer is also obtained for the related complex $[RuCl_2(CO)_2(2,9\text{-}Ph_2phen)]$.[915] Photochemical ligand substitution reactions of $[RuCl_2(CO)_2(bpy)]$[916,917] and $[RuCl_2(CO)_2(4,4'\text{-}Me_2bpy)]$ in MeCN and CH_2Cl_2 lead to the formation of products that include $[RuCl_2(CO)(MeCN)(bpy)]$, *mer*-$[RuCl(MeCN)_3(bpy)]^+$, and *fac*-$[RuCl(MeCN)_3(4,4'\text{-}Me_2bpy)]^+$, the structures of which have been determined.[916] An overview of the preparation, characterization, and properties of conductive polymers $[Ru(CO)_2L]_n$ (L = bpy or derivatives thereof) provides a useful summary of this area.[918] Initial work suggested that only the *cis*(CO),*trans*(Cl) isomer of $[RuCl_2(CO)_2(bpy)]$ undergoes electropolymerization to give $[Ru(CO)_2(bpy)]_n$, but this conclusion has been updated to include the electropolymerization of the *cis*(CO),*cis*(Cl) isomer.[919] Polymer films of $[Ru(CO)_2L]_n$ can also be generated

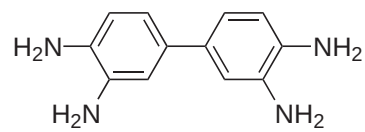
electrochemically from $[Ru_2(CO)_4(bpy)_2(MeCN)_2]^{2+}$.[920] The effects of the electron-withdrawing and donating properties of groups X on the vibrational and absorption spectroscopic properties of $[RuCl_2(CO)_2(4,4'\text{-}X_2bpy)]$ have been analyzed.[921] The syntheses and crystal structures of *trans*(X)-$[RuX_2(CO)_2\{4,4'\text{-}(CO_2H)_2bpy\}]$ (X = Br, I) have been reported. In MeCN, the complexes undergo photochemical reactions losing CO and forming *cis*(X)-$[RuX_2(CO)(MeCN)\{4,4'\text{-}(CO_2H)_2bpy\}]$. The complex $[RuI_2(CO)_2\{4,4'\text{-}(CO_2H)_2bpy\}]$ exhibits a temperature-dependent luminescence spectrum (77–116 K).[922]

5.5.3.1.10 Dinuclear complexes (M = Ru or Os) containing $M(NH_3)_5$ or related units

There is some overlap between the content of this section and some species discussed in Section 5.5.3.1.12, but the emphasis here is on dimetal(II) species containing terminal $M(NH_3)_5$ or related groups. Complexes with *N*-heterocyclic bridges are well represented. An electronic model for donor–acceptor systems has been discussed with respect to the complexes $[(NH_3)_5Ru(\mu\text{-pyz})Ru(NH_3)_5]^{n+}$ and $[(NH_3)_5Ru(\mu\text{-}4,4'\text{-bpy})Ru(NH_3)_5]^{n+}$ ($n = 4$, 5, 6), and provides an explanation for the optical properties of the complexes and their dependence on the oxidation states of the Ru centers.[923] The work is extended to include the effects of crown-ether encapsulation on the position of the near-IR-vis bands of the complexes,[924] and to the study of the trinuclear complexes $[\{(NH_3)_5Ru(\mu\text{-pyz})\}_2Ru(NH_3)_4]^{n+}$ ($n = 6$, 7, 8, 9).[925] The preparations and electrochemical properties of $[(NH_3)_4LRu(\mu\text{-pyz})Ru(NH_3)_4(dmso)]^{4+}$ (L = NH_3, py, PhCN, dmso) have been reported, and the rates of conversion between isomeric intermediate states have been investigated.[926] The 2,2′-bipyrimidine-bridged complex $[(NH_3)_4Ru(\mu\text{-bpm})Ru(bpy)_2]^{4+}$ has been synthesized and characterized.[927] Ligand (**232**) provides both cyano and imidazole binding domains and has been incorporated into $[(NH_3)_4Ru(\mu\text{-}\mathbf{232})Ru(bpy)_2]^{4+}$. Controlled oxidation of this complex gives a mixed valence ($Ru^{II}Ru^{III}$) species in which the Ru^{III} center is bound by the imidazole end of the bridging ligand; $[(NH_3)_4Ru(\mu\text{-}\mathbf{232})Ru(bpy)_2]^{5+}$ exhibits significant coupling between the two metal centers.[928] The complex $[(NH_3)_4Ru(\mu\text{-L})Ru(bpy)_2]^{4+}$ in which L is 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, exhibits intense electronic MLCT transitions at 850, 603, and 370 nm, compared to bands at 560 and 479 nm for the mononuclear complex $[(NH_3)_4Ru(L)]^{2+}$. Electrochemical data are consistent with substantial communication between the metal centers.[929] Mono- and dinuclear complexes involving the dipyridophenazine ligand (**92**) have been prepared; the electronic spectroscopic and electrochemical properties of $[(NH_3)_4Ru(\mathbf{92})]^{2+}$ and $[(NH_3)_4Ru(\mu\text{-}\mathbf{92})Ru(NH_3)_4]^{4+}$ have been investigated.[930]



(**232**)



(**233**)

There is evidence for extensive delocalization of electron density between the Ru^{II} centers in $[(NH_3)_5Ru(\mu\text{-L})Ru(NH_3)_5]^{4+}$ where L = 4,4′-dithiodipyridine,[931] and an overview of a range of Fe, Ru, and Os-containing complexes containing 4,4′-dithiodipyridine or bis(4-pyridine) sulfide provides a useful summary of the properties of these species.[932]

Ligand (**233**) contains two 1,2-phenylenediamine domains that can be independently oxidized, and this is observed in the complex $[(NH_3)_4Ru(\mu\text{-}\mathbf{233})Ru(NH_3)_4]^{4+}$ which undergoes two, two-electron ligand-oxidation processes; further oxidation generates Ru^{III}-containing species.[933]

5.5.3.1.11 Heterometallic (M = Ru or Os, M′ ≠ Ru or Os) dinuclear and polynuclear complexes

In this section, we consider heterometallic complexes in which the heterometal is one other than Ru or Os. The organization of the section is according to the type of bridge (if any) between the metal centers.

An Ru—Mn bond is present in the complexes $[(CO)_5MnRu(Me)(CO)_2L]$ where L is *N*,*N*′-diisopropyl-1,4-diaza-1,3-butadiene, or pyridine-2-carbaldehyde-*N*-isopropylimine; crystallographic

data confirm the structure. Each complex exhibits a strong, solvatochromic absorption in the visible region, assigned to an $Ru(d\pi) \rightarrow L(\pi)$ transition. Resonance Raman spectroscopic data are also presented.[934]

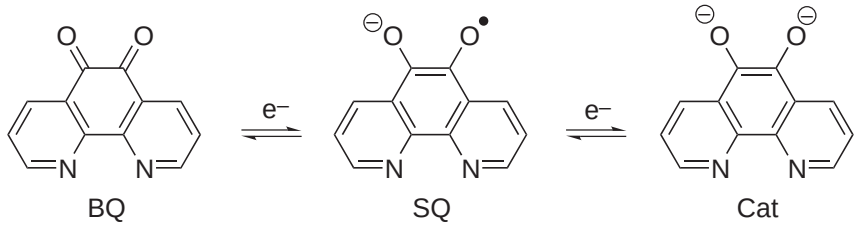
Among a series of complexes with sulfur-containing ligands (e.g., WS_4^{2-}, $MoS_4(ethanedithiolate)_2^{2-}$, S_5^{2-}) is the trinuclear species $[(bpy)_2RuS_2WS_2Ru(bpy)_2]^{2+}$ which has been structurally characterized.[935]

Cyano-bridged heterometallics are represented by $[(bpy)_2(CN)Ru(\mu\text{-}CN)Rh(NH_3)_5]^{3+}$, $[(bpy)_2(CN)Ru(\mu\text{-}CN)Rh(NH_3)_4I]^{2+}$, $[(bpy)_2(CN)Ru(\mu\text{-}CN)Rh(NH_3)_4Br]^{2+}$, $[(bpy)_2(CN)Ru(\mu\text{-}CN)Rh(NH_3)_4(CN)]^{2+}$, $[(bpy)_2Ru\{(\mu\text{-}CN)Cr(NH_3)_5\}_2]^{6+}$, and $[(bpy)_2(CN)Ru(\mu\text{-}CN)Cr(NH_3)_5]^{3+}$ and a study has been made of the excited-state relaxation pathways in these species.[936] The cyano-bridged complexes $[(bpy)(PPh_3)Cu(\mu\text{-}CN)Ru(bpy)_2Cl]^+$, $[(phen)(PPh_3)Cu(\mu\text{-}CN)Ru\ (bpy)_2Cl]^+$, and $[(PPh_3)_2Cu(\mu\text{-}CN)Ru(bpy)_2Cl]^+$ have been prepared and characterized.[937]

Heterometallic complexes involving N-heterocyclic bridges form a large group. The crystal structure of $[(bpy)(CO)_3Re(\mu\text{-}4,4'\text{-}bpy)RuCl\{1,2\text{-}(Me_2As)_2C_6H_4\}_2][PF_6]_2$ has been determined.[938] For L = 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane, the complexes $[(bpy)_2Ru(\mu\text{-}L)Re(CO)_3(py)]^{3+}$, $[Ru(bpy)_2L]^{2+}$, and $[Re(CO)_3(py)L]^+$ have been synthesized and their emission properties have been studied. Emission was observed from the Re center in the mononuclear complex, but not in the heterometallic complex; the excitation energy absorbed by Re is transferred efficiently to the Ru center.[939,940] Spectroscopic and electrochemical studies of the complexes $[(bpy)_2Ru(\mu\text{-}bpm)Re(CO)_3Cl]^{2+}$, $[(bpy)_2Ru(\mu\text{-}bpm)Mo(CO)_4]^{2+}$, and $[(bpy)_2Ru(\mu\text{-}bpm)Cu(PPh_3)_2]^{3+}$ have shown that the Ru-centered occupied *d*-orbitals undergo little change on introducing the heterometal (compared to the all Ru species). Changes in the absorption spectra as the function of the heterometal fragment are discussed.[941] Reactions of $[Ru(bpy)_2L]^{2+}$ (L = 2,3-dpp, 2,3-bpq, 6,7-Me_2-2,3-bpq) with $[Cu(PPh_3)_4]^+$ lead to the formation of $[(bpy)_2Ru\ (\mu\text{-}L)Cu(PPh_3)_2]^{3+}$, and the crystal structures of the 2,3-dpp and 6,7-Me_2-2,3-bpq derivatives have been determined. Coordination to the group 11 metal fragment causes little stabilization of the π^*-orbital of the bridging ligand, and resonance Raman spectroscopic data are consistent with an assignment of the dominant transition in the visible region as $Ru(d\pi) \rightarrow L(\pi^*)$ charge transfer.[942] The syntheses and characterization of the luminescent complexes $[(bpy)_2Ru(\mu\text{-}2,3\text{-}dpp)MX_2]^{2+}$ (M = Pd, X = Cl; M = Pt, $X_2 = Cl_2$, ClMe, Me_2, Ph_2, $(4\text{-}MeOC_6H_4)_2$ or $(4\text{-}FC_6H_4)_2$), $[(bpy)_2Ru(\mu\text{-}bpm)MX_2]^{2+}$ (M = Pd, X = Cl; M = Pt, $X_2 = Cl_2$, ClMe, Ph_2, $(2\text{-}MeC_6H_4)_2$, $(4\text{-}MeOC_6H_4)_2$ or $(4\text{-}FC_6H_4)_2$), and $[(bpy)_2Ru(\mu\text{-}2,3\text{-}bpq)Pt(4\text{-}MeOC_6H_4)_2]^{2+}$ have been described. The crystal structure of $[(bpy)_2Ru(\mu\text{-}2,3\text{-}dpp)PdCl_2]^{2+}$ confirms that the bridging ligand acts as an *N,N′*-chelate to each metal center.[943] In these types of complexes, good σ donation from the bridging ligand to the Pd^{2+} or Pt^{2+} center is essential to their formation. A pyridine unit is a better donor to the group 10 metal than a pyrazine or pyrimidine group, and the dpp ligand is particularly suited for bridging between $Ru(bpy)_2^{2+}$ and MX_2 (M = Pd or Pt) fragments.[944] Dimetallic complexes have resulted from the photolysis of a mixture of mononuclear precursors: reaction of $[Ru(bpy)_2(2,3\text{-}dpp)]^{2+}$ with $[PtCl_6]^{2-}$, $[PdCl_6]^{2-}$, or $[RhCl_6]^{3-}$ generates $[(bpy)_2Ru(\mu\text{-}2,3\text{-}dpp)MCl_4]^{2+}$. It is suggested that the reaction proceeds by excited-state acid–base chemistry rather than energy transfer or electron transfer quenching.[945,946]

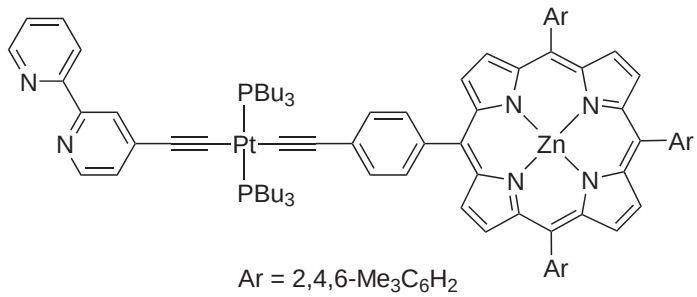
Deprotonation of $[Ru(pypzH)_3]^{2+}$ (pypzH = 3-(pyridin-2-yl)pyrazole) to give $[Ru(pypz)_3]^-$ followed by reaction with $CuClO_4 \cdot 6H_2O$ (or Cu^{II}) in MeOH yields $[Ru(pypz\text{-}Cu^{I}\text{-}pypz)_2Ru]^+$ (i.e., pz domains of $pypz^-$ coordinate to Cu^{I}) which possesses a triple-stranded helical structure.[947]

The ligand 1,10-phenanthroline-5,6-dione (BQ form in Equation (5)) reacts with $[Pt(PPh_3)_4]$ under oxidative conditions to give $[(Ph_3P)_2Pt(L\text{-}O,O')]$ leaving a phen-like *N,N′*-donor set free for further coordination chemistry. Thus, complexes such as $[(Ph_3P)_2Pt(\mu\text{-}L)Ru(PPh_3)_2Cl_2]$ can be prepared; the crystal structure of the latter confirms a planar $P_2Pt(\mu\text{-}L)RuCl_2$ unit with *trans*-PPh_3 ligands bound to Ru^{II}. This complex undergoes two ligand-based reductions (Equation (5)).[948] Abstraction of Cl^- from $[(Ph_3P)_2Pt(\mu\text{-}L)Ru\ (PPh_3)_2Cl_2]$ in the presence of a two-electron donor produces cationic complexes in which changes in the energies of the metal orbitals as a function of the incoming donor influences the redox chemistry of the system.[949] 1,10-phenanthroline-5,6-dione has been used in the series of complexes $[(^tBu_2bpy)_{3-n}Ru\{(\mu\text{-}L)Pt(^tBu_2bpy)\}_n]^{2+}$ (n = 1–3); at 77 K, emission from the Pt center is observed as a result of direct irradiation of the Pt unit or excitation of the Ru center, giving evidence for Ru–Pt energy transfer. $[(^tBu_2bpy)_2Ru(\mu\text{-}tppz)Pt(tdt)]^{2+}$ (H_2tdt = toluene-3,4-dithiol) has also been prepared and characterized; there are similarities between the spectroscopic properties of $[(^tBu_2bpy)_2Ru\text{-}(\mu\text{-}tppz)Pt(tdt)]^{2+}$ and $[(^tBu_2bpy)_{3-n}Ru\{(\mu\text{-}L)Pt(^tBu_2bpy)\}_n]^{2+}$.[950]

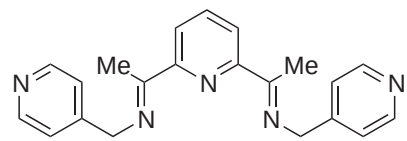


(5)

The heterometallic system $[(bpy)_2Ru(\mathbf{234})]^{2+}$ exhibits several intramolecular energy-transfer processes: (i) ultrafast singlet-to-singlet transfer, (ii) fast triplet-to-singlet transfer and (iii) singlet-to-triplet transfer. Excitation into the $Ru(bpy)_3^{2+}$ domain is followed by rapid energy transfer to the triplet state of the Zn(porphyrin) fragment. There is no evidence for intramolecular electron transfer between the $Ru(bpy)_3^{2+}$ and Zn(porphyrin) units.[951]



(**234**)



(**235**)

The pentametal species $[Fe\{(Cl(bpy)_2Ru)_2(\mu\text{-}\mathbf{235})\}_2]^{6+}$ has been prepared. It contains an octahedral Fe^{II} center coordinated by two *N,N′,N″*-donors of ligand (**235**), each of which carries two pyridyl-coordinated $RuCl(bpy)_2^{2+}$ fragments. The complex exhibits MLCT bands at 584 and 486 nm, characteristic of the FeN_6 and $Ru(bpy)_2^{2+}$ chromophores, and emits at 614 nm at 77 K; the latter is assigned to emission from the lowest-energy ^{3}MLCT state of the Ru-centered group. Electrochemical properties of the complex have been investigated.[952] The $Ru(bpy)_3^{2+}$ domain has been attached to $M\{(3,5\text{-}Me_2pz)_3BH\}Cl(NO)$ units (M = Mo, W) by functionalization of one bpy ligand in the 4-position with a phenolate capable of acting as a donor to Mo or W. The electronic spectroscopic and electrochemical properties of the heterometallic complexes indicate a small degree of electronic communication between the metal centers. Luminescence data show that there is quenching of the ^{3}MLCT excited state of the Ru-centered fragment; it is proposed that this occurs by an energy-transfer mechanism.[953,954]

The phosphine/cumulene-bridged complexes $[(bpy)_2M\{\mu\text{-}L)M(bpy)_2]^{4+}$ (L = $(Ph_2P)_2C{=}C{=}C{=}C(PPh_2)_2$; M—M = Ru—Ru, Ru—Os, Os—Os) have been isolated as the PF_6^- salts, and their properties compared with those of analogous species with shorter C_n spacers. Redox properties depend strongly on the length of the spacer, electron donation from bridge to metal varying with *n*. In the Ru–Os system, efficient energy transfer from Ru to Os is observed.[955] Studies have been extended to rhenium-containing systems.[956]

5.5.3.1.12 *Mixed-valence dinuclear complexes*

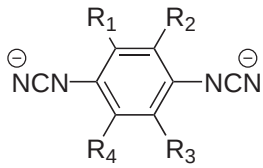
Mixed-valence di- and polynuclear complexes have been of wide interest ever since the discovery of the Creutz–Taube ion[957,958] and progress in the field has been reviewed.[959–964] In this section, we consider representative mixed-valence complexes which are organized according to the type of bridging ligand.

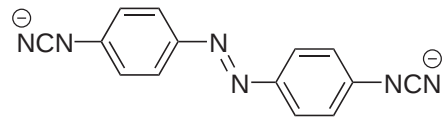
Cyano-bridged complexes include both di- and polynuclear systems. Spectroelectrochemical studies of the oxidized and reduced forms of $[(bpy)_2(CN)Ru(\mu\text{-}CN)Ru(CN)(bpy)_2]^+$ have been carried out. This cation and its reduced form exhibit UV–vis spectra that are consistent with the chromophores being identical. Experimental evidence indicates that the one-electron oxidation product is valence-delocalized.[965] Reaction of $[Ru(NH_3)_5(H_2O)]^{3+}$ and $[Os(CN)_6]^{4-}$ leads to the

mixed-valence complex $[(NH_3)_5Ru(\mu\text{-}NC)Os(CN)_5]^-$. This exhibits an intervalence band at 830 nm assigned to CT from Os^{II} to Ru^{III}. IR and Raman spectroscopic data are discussed.[966] Reaction of $[Ru(edta)(H_2O)]^-$ with $[M(CN)_6]^{4-}$ (M = Fe, Ru, Os) yields $[(NC)_5M^{II}(\mu\text{-}CN)Ru^{III}(edta)]^{5-}$. An intense absorption in the range 600–1,000 nm depending on M is associated with an intervalence transition from M^{II} to Ru^{III}. The Hush model indicates that the complexes are valence-trapped species, with some coupling between the metal centers. When the concentration of $[Ru(edta)(H_2O)]^-$ is increased in the syntheses, higher-nuclearity complexes can be obtained.[967] The kinetics of the formation of $[(NH_3)_5Ru(\mu\text{-}NC)Os(CN)_5]^-$ and $[(NC)_5M^{II}(\mu\text{-}CN)Ru^{III}(edta)]^{5-}$ (M = Fe, Ru, Os) have been investigated.[966,967] The complex $[(NH_3)_5Ru^{III}(\mu\text{-}NC)Fe^{II}(CN)_5]^-$ has been studied in detail,[968] and an electrochemical variational method (applied also to mononuclear systems such as $[Ru(NH_3)_4(bpy)]^{2+}$ and $[Ru(NH_3)_4(phen)]^{2+}$)[905] has been used to assess electronic coupling and donor–acceptor orbital mixing in $[(NH_3)_5Ru^{III}(\mu\text{-}NC)Fe^{II}(CN)_5]^-$.[968] The formation of $[(bpy)_2(py)Ru^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5]^{4+}$ and $[(bpy)_2(py)Ru^{II}(\mu\text{-}CN)Fe^{III}(CN)_5]^-$ is accompanied by a blue shift in the lowest-energy MLCT band. The luminescence of $[Ru(bpy)_2(py)(CN)]^+$ is completely quenched on going to $[(bpy)_2(py)Ru^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5]^{4+}$.[969] The resonance Raman spectroscopic method can be used to gain insight into vibrational barriers to intramolecular electron transfer, associated electronic transitions, and the extent of electronic coupling between metal centers in mixed-valence compounds.[970] The technique has been applied to the cyano-bridged species $[(bpy)_2(NC)Os^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5]^{3+}$, $[(bpy)_2Ru^{II}\{(\mu\text{-}CN)Ru^{III}(NH_3)_5\}_2]^{6+}$, $[(bpy)_2Os^{II}\{(\mu\text{-}CN)Ru^{III}(NH_3)_5\}_2]^{6+}$, and $[(phen)_2(CO)_3Re^{I}(\mu\text{-}CN)Ru^{III}(NH_3)_5]^{3+}$.[970] The combination, via a cyano bridge, of the electron-acceptor unit $Ru(NH_3)_5^{3+}$ and $[(bpy)_2(NC)Ru^{II}(\mu\text{-}CN)\{(bpy)_2Ru^{II}(\mu\text{-}NC)\}_nRu^{II}(bpy)_2(CN)]^{(n+1)+}$ ($n = 0$, 1) leads to mixed-valence complexes in which the lowest-energy $Ru(bpy)_2^{2+}$ chromophore is that adjacent-but-one to the Ru^{III}-containing group. Complete quenching of the excited states of the poly-$Ru(bpy)_2^{2+}$ system is observed and, thus, it is concluded that there is efficient electron transfer along the molecule to the $Ru(NH_3)_5^{3+}$ acceptor.[971] The complex $[(NH_3)_5Ru^{III}(\mu\text{-}NC)Ru^{II}(CN)_4(\mu\text{-}CN)Co^{III}(NH_3)_5]^{2+}$ exhibits UV–vis absorptions at 647 and 372 nm assigned to $Ru^{II} \rightarrow Ru^{III}$ and $Ru^{II} \rightarrow Co^{III}$ metal-to-metal CT transitions. The photoredox chemistry of the complex has been detailed.[972]

1,4-Dicyanamidobenzene dianion (**236**) and related ligands which are both σ- and π-donating, have been used as bridges in a number of mixed-valence dinuclear species. UV-vis/near IR spectroscopic and electrochemical data for $[(NH_3)_5Ru(\mu\text{-}\mathbf{237})Ru(NH_3)_5]^{3+}$ are consistent with there being only weak inter-metal coupling; it is proposed that coupling by the low-energy LMCT system is symmetry forbidden and that by the high-energy LMCT system is not energetically favorable.[973] The metal–metal coupling in $[(NH_3)_5Ru(\mu\text{-}\mathbf{236})Ru(NH_3)_5]^{3+}$ and $[(NH_3)_5Ru(\mu\text{-}\mathbf{238})Ru(NH_3)_5]^{3+}$ is strongly dependent on the solvent. This is explained in terms of donor–acceptor interactions between solvent and the ammine protons which weaken the Ru^{III}–cyanamide π-bond, thus decoupling the Ru^{III} center from the superexchange pathway.[974,975] The degree of metal–metal coupling in $[(NH_3)_5Ru(\mu\text{-}L)Ru(NH_3)_5]^{3+}$ where L = (**236**), (**237**), (**238**), or (**239**) has been assessed and it was concluded that the Creutz–Newton–Sutin model gives a good fit to experimental observations.[976] The Ru^{III} complexes $[(NH_3)_4(py)Ru(\mu\text{-}L)Ru(NH_3)_4(py)]^{4+}$ where L^{2-} = (**236**)–(**239**) have been prepared and characterized, and structural data for $[(NH_3)_4(py)Ru(\mu\text{-}\mathbf{236})Ru(NH_3)_4(py)]^{4+}$ confirm an essentially planar bridging unit. The extent of metal–metal coupling in the mixed-valence derivatives $[(NH_3)_4(py)Ru(\mu\text{-}L)Ru(NH_3)_4(py)]^{3+}$ (L = (**236**)–(**239**)) has been compared with that in $[(NH_3)_5Ru(\mu\text{-}L)\ Ru(NH_3)_5]^{3+}$.[977] The $Ru^{III}Ru^{III}$ complexes $[(NH_3)_3(bpy)Ru(\mu\text{-}L)Ru(NH_3)_3(bpy)]^{4+}$ (L = (**236**), (**238**), or (**239**)) possess a *mer* arrangement at each Ru^{III} center. Their $Ru^{III}Ru^{II}$ derivatives show strong metal–metal coupling and possess comproportionation constants in the order L = (**238**) > (**236**) > (**239**), consistent with a hole-transfer superexchange mechanism.[978] The solvent dependence of the cyanamide stretching frequencies of the complexes $[(NH_3)_5Ru(\mu\text{-}L)Ru(NH_3)_5]^{3+}$, *trans*,*trans*-$[(NH_3)_4(py)Ru(\mu\text{-}L)Ru(NH_3)_4(py)]^{3+}$, and *mer*,*mer*-$[(NH_3)_3(bpy)Ru(\mu\text{-}L)Ru(NH_3)_3(bpy)]^{3+}$ (L = (**236**) and various derivatives of (**236**)) has been investigated, and the data provide information on the effects of outer-sphere perturbation on the mixed-valence state.[979] The $Ru^{II}Ru^{II}$ complex $[(tpy)(bpy)Ru(\mu\text{-}\mathbf{240})Ru(tpy(bpy)]^{4+}$ has been prepared and characterized and its crystal structure determined. One-electron oxidation yields the $Ru^{II}Ru^{III}$ species which shows class III behavior. It exhibits an intervalence band at 1920 nm. Experimental data indicate that bridging ligand (**240**) can facilitate metal–metal coupling via hole-transfer and electron-transfer superexchange mechanisms.[980]

The reaction of $[Ru(NH_3)_5(3\text{-}NCpy)]^{2+}$ or $[Ru(NH_3)_5(4\text{-}NCpy)]^{2+}$ with $[Fe(CN)_5(H_2O)]^{3-}$ yields $[(NH_3)_5Ru(\mu\text{-}NCpy)Fe(CN)_5]^-$, hydrolysis of which generates the mixed-valence complexes





(**236**) $R_1 = R_2 = R_3 = R_4 = H$

(**237**) $R_1 = R_2 = R_3 = R_4 = Cl$

(**238**) $R_1 = R_3 = H$; $R_2 = R_4 = Me$

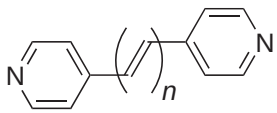
(**239**) $R_1 = R_3 = H$; $R_2 = R_4 = Cl$

(**240**)

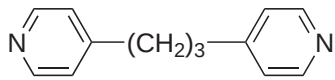
$[(NH_3)_5Ru(\mu\text{-}3\text{-}CONHpy)Fe(CN)_5]^-$ and $[(NH_3)_5Ru(\mu\text{-}4\text{-}CONHpy)Fe(CN)_5]^-$. These are valence-trapped species containing Fe^{II} and Ru^{III}; $[(NH_3)_5Ru(\mu\text{-}4\text{-}CONHpy)Fe(CN)_5]^-$ exhibits an intervalence band at 645 nm. The kinetics for the formation and dissociation of these complexes have been investigated.[981] IR and UV–vis spectroscopic data indicate that the pyridine-N donor is bonded to the Ru^{II} center in $[Ru(bpy)_2(py)(4\text{-}NCpy)]^{2+}$, and this mode is retained in the dinuclear complex $[(bpy)_2(py)Ru(\mu\text{-}py\text{-}4\text{-}CN)Ru(NH_3)_5]^{4+}$. Oxidation of the latter gives $[(bpy)_2(py)Ru^{II}(\mu\text{-}py\text{-}4\text{-}CN)Ru^{III}(NH_3)_5]^{5+}$ and the process is accompanied by the disappearance of the lowest-energy MLCT absorption in the UV–vis spectrum.[982] In weakly basic solvents, the stable isomer of $[(bpy)_2ClRu(\mu\text{-}py\text{-}4\text{-}CN)Ru(NH_3)_4(py)]^{4+}$ is *trans*-$[(bpy)_2ClRu^{III}(\mu\text{-}py\text{-}4\text{-}CN)Ru^{II}(NH_3)_4(py)]^{4+}$, whereas in stronger Lewis bases the isomer that is observed is *trans*-$[(bpy)_2ClRu^{II}(\mu\text{-}py\text{-}4\text{-}CN)Ru^{III}(NH_3)_4(py)]^{4+}$. This redox isomerization is supported by several lines of experimental data, and can also be facilitated by interaction of the ammine ligands with polyethers or macrocyclic ligands such as dibenzo-36-crown-12.[983] The complexes $[(NH_3)_5Ru^{II}(\mu\text{-}py\text{-}4\text{-}CO_2)Ru^{III}(NH_3)_5]^{4+}$ and $[(NH_3)_5Ru^{II}(\mu\text{-}py\text{-}4\text{-}CONH)\ Ru^{III}(NH_3)_5]^{4+}$ have been prepared and show intervalence CT bands at 720 and 761 nm respectively (at pH 4.8). The electronic spectra are solvent dependent. The bridging ligands permit coupling between the ruthenium centers.[984] Cerium(IV) oxidation of $[(tpy)(bpy)Ru^{II}(\mu\text{-}py\text{-}4\text{-}CN)Ru^{II}(NH_3)_5]^{4+}$ leads to the corresponding $Ru^{II}Ru^{III}$ complex; this exhibits no MMCT bands in the visible region of the spectrum.[985]

We move now to mixed-valence complexes containing pyrazine (pyz, the prototypical Creutz–Taube bridging ligand) and other *N*-heterocyclic bridges. Resonance Raman spectroscopic data in the extended near-IR region provide evidence for a three-site mechanism for valence delocalization in $[(NH_3)_5Ru(\mu\text{-}pyz)Ru(NH_3)_5]^{5+}$.[986] The effects of interactions between the $Ru(NH_3)_5^{n+}$ groups in $[(NH_3)_5Ru(\mu\text{-}pyz)Ru(NH_3)_5]^{5+}$ and crown ether ligands have been analyzed; double $Ru(NH_3)_5^{n+}$-crown encapsulation results in small energy shifts in the visible and near-IR regions of the electronic spectrum of the complex. These can be interpreted in terms of a three-site (Ru-bridge-Ru) model.[987] The solvent dependence of association between the $Ru(NH_3)_5^{3+}$ unit in $[(bpy)_2ClRu^{II}(\mu\text{-}pyz)Ru^{III}(NH_3)_5]^{4+}$ and crown ethers has been investigated and results show that for dicyclohexano-24-crown-8, the largest association constants are when the solvent is of low Lewis basicity.[988] DFT methods have been applied to $[(NH_3)_5Ru(\mu\text{-}pyz)Ru(NH_3)_5]^{5+}$ to provide a description of the low-lying excited states; the results of vibronic coupling calculations along the symmetric and anti-symmetric Ru–pyz–Ru stretching modes are reported.[989] The complexes $[(Hedta)Ru^{III}(\mu\text{-}L)Fe^{II}(CN)_5]^{3-}$ (L = pyz, 4,4′-bpy, 3,3′-Me_2-4,4′-bpy, (**241**) (with $n = 1$, and (**242**)) have been prepared and characterized, and the kinetics of the formation investigated using stopped-flow techniques. In their ground states, each complex exhibits a weak Ru–Fe interaction.[990] The properties of $[(NH_3)_5Ru(\mu\text{-}\mathbf{243})Ru(NH_3)_5]^{5+}$ have been compared to those of $[(NH_3)_5Ru(\mu\text{-}pyz)Ru(NH_3)_5]^{5+}$. The former complex exhibits an unexpectedly weak absorption arising from the intervalence transition; UV–vis, near-IR, and EPR spectroscopic data are presented.[991] Reaction of $[Fe(CN)_5(H_2O)]^{3-}$ and $[Ru(NH_3)_5L]^{2+}$ results in the formation of $[(NH_3)_5Ru^{III}(\mu\text{-}L)Fe^{II}(CN)_5]^-$ (HL = im) which is a valence-trapped species.[992] $[M(CN)_5(H_2O)]^{3-}$ (M = Fe, Ru) reacts with $[Ru(NH_3)_5L]^{2+}$ (L = 4,4′-dithiodipyridine) to give $[(NH_3)_5Ru^{II}(\mu\text{-}L)M^{II}(CN)_5]^-$ that can be oxidized to the $Ru^{III}M^{II}$ species; the bridging ligand permits significant delocalization of electronic charge between the metal centers.[993] The electronic spectra of $[(NH_3)_5Ru(\mu\text{-}\mathbf{241})Ru(NH_3)_5]^{5+}$ ($n = 0$, 1, 2 in ligand (**241**)) have been compared; the spectra were deconvoluted into $\pi \rightarrow \pi^*$, M → L, L → M, and intervalence transitions. The inter-ruthenium

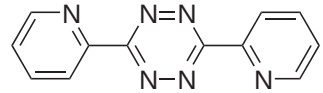
coupling shows a near-exponential bridge dependence.[994] The influence of solvent on the intervalence CT absorption energy of $[(NH_3)_5Ru(\mu\text{-pyz})Ru(NH_3)_5]^{5+}$ has been discussed; with the exception of the solvent being hmpa, the solvent data are in agreement with predictions based on the Marcus–Hush model.[995] The variation in coupling of the metal centers in the series of complexes $[(bpy)_2Ru^{III}(\mu\text{-L})Ru^{II}\{4,4'\text{-}(CO_2Et)_2bpy\}_2]^{5+}$ in which the bridging ligand L comprises two 2-(2′-pyridyl)benzimidazolyl units linked by spacers $(CH_2)_n$ ($n = 1$–5 or 10) or $CH_2C_6H_4CH_2$ has been investigated; the separation between Ru centers ranges from 10 Å to 22 Å.[996]



(241)



(242)



(243)

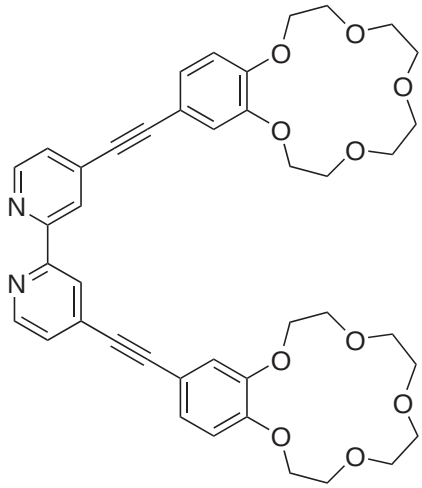
Mixed-valence complexes terminated in other than ammine and cyano ligands include $[([9]aneS_3)ClRu(\mu\text{-}243)RuCl([9]aneS_3)]^{3+}$ which exhibits a strong intermetallic interaction consistent with a Robin–Day class III (delocalized) species.[997] The synthesis of the $Ru^{II}Ru^{III}$ complex $[\{P(OMe)_3\}_2(MeCN)Ru(\mu\text{-}S_2)(\mu\text{-}NH_2NH_2)Ru\{P(OMe)_3\}_2(MeCN)]^{3+}$ has been reported.[998] Oxidation of the $M^{II}M^{II}$ (M = Ru or Os) complexes $[\{4'\text{-}(4\text{-}MeC_6H_4\}tpy)M(\mu\text{-L})M\{4'\text{-}(4\text{-}MeC_6H_4\}tpy)]^{2+}$ (H_2L = 3,3′,5,5′-tetrapyridylbiphenyl) yields the corresponding $M^{II}M^{III}$ complexes. The near-IR spectrum of each complex shows an intense intervalence band, and there is strong intermetallic coupling across the bis-cyclometallated bridging ligand.[999] Chemical oxidation using peroxydisulfate of $[(tpy)(bpy)Ru^{II}(\mu\text{-L})Ru^{II}(NH_3)_5]^{n+}$ gives $[(tpy)(bpy)Ru^{II}(\mu\text{-L})Ru^{III}(NH_3)_5]^{(n+1)+}$ (L = CN, $n = 3$ and 4; L = pyz, 4,4′-bpy, 4-NCpy, *trans*-1,2-(4-pyridyl) ethene, $n = 4$ and 5); the kinetics of the oxidations were studied using stopped-flow techniques.[1000]

5.5.3.1.13 *Complexes containing M(bpy) units coupled to macrocyclic or calix[4]arene recognition domains*

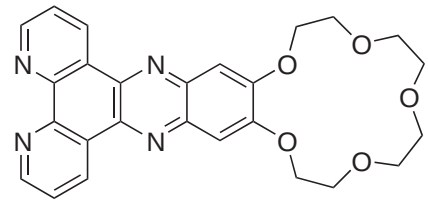
In this section, complexes that contain macrocyclic or calix[4]arene recognition domains coupled to bpy ligands are considered. In addition, discussions of calix[4]arene-containing complexes are extended to include a number of species that are of interest other than for anion or cation recognition. Compounds are organized according to the type of species that they bind.

Complexes of the type $[Ru(bpy)_2(\mathbf{244})]^{2+}$ and $[Ru(\mathbf{244})_3]^{2+}$ have been prepared; the complexes can bind two and six Na^+ ions respectively and the PF_6^- salts of the Na^+ complexes have been isolated. Related complexes containing bpy ligands bearing *trans*-vinyl-linked crown ethers (e.g., ligand (**109**)) have also been prepared and electropolymerized to give poly-$[RuL_3]^{2+}$-modified electrodes. Electronic absorption and fluorescence-emission spectroscopic data illustrate that the complexes in solution and the polymeric films recognize group 1 and 2 metal ions.[1001,1002] Binding of alkali and alkaline earth M^{n+} ions is also observed for $[RuL_3]^{2+}$ where L = 6,6′-oligoethyleneglycol-3,3′-bipyridazine,[1003] and Li^+ and Na^+ ions are recognized by the crown ether domain of the complex $[Ru(bpy)_2L]^{2+}$ where L is a bpy-3,3′-crown ether ligand.[1004] $[Ru(bpy)_2(\mathbf{245})]^{2+}$ also binds M^+ ions; this is one of a series of polypyridine complexes carrying crown ether units that has been prepared and characterized with emphasis on photophysical and electrochemical properties.[1005] A number of calix[4]arene receptors have been reported and in the case of $[Ru(bpy)_2(\mathbf{246})]^{2+}$ and $[\{Ru(bpy)_2\}_2(\mathbf{246})]^{4+}$, Ba^{2+} is bound by the calix[4]arene diquinone in its cone conformation. Molecular mechanics calculations have been used to model the Ba^{2+} binding site.[1006]

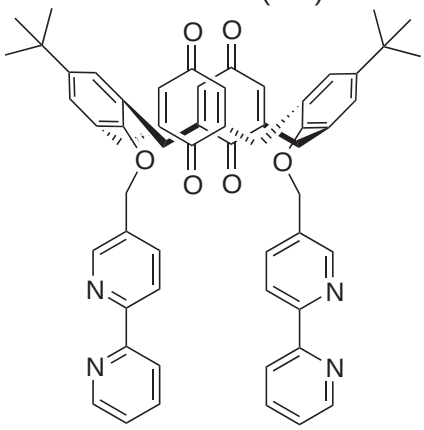
Nickel(II) ions are bound by the pendant cyclam unit in $[Ru(bpy)_2(\mathbf{247})]^{2+}$. The synthesis and characterization of $[Ru(bpy)_2(\mathbf{247})Ni]^{4+}$ has been reported; NMR spectroscopic and crystallographic data show that there is a close contact between the H^5 atom of the substituted bpy ring and the Ni^{2+} ion held within the cyclam macrocycle.[1007] A related Cu^{2+} derivative has also been described; coordination to the Cu^{2+} ion leads to fluorescence quenching of the $Ru(bpy)_3^{2+}$ unit.[1008] Ligand (**248**) has been incorporated into the complex $[Ru(bpy)_2(\mathbf{248})]^{2+}$ and the photochemical properties, and cation and anion binding of the complex have been described.[1009] The cryptand-functionalized bpy ligand (**249**) coordinates three peripheral $Ru(bpy)_2^{2+}$ units while the cryptand cavity hosts two Zn^{2+} ions. The related complex $[(\mathbf{250})\{Ru(bpy)_2\}_3Cu^I_2]^{8+}$ has also been isolated, again with peripheral $Ru(bpy)_2^{2+}$ groups and a cavity hosting two late *d*-block metal



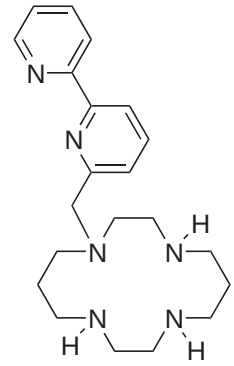
(**244**)



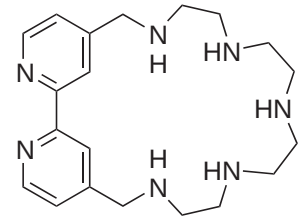
(**245**)



(**246**)

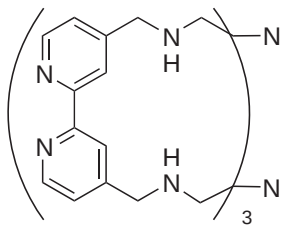


(**247**)

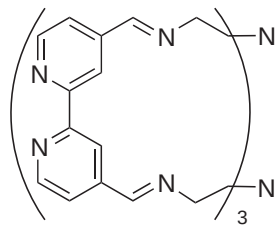


(**248**)

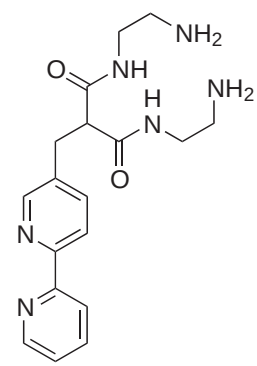
ions.[1010] The water-soluble complex $[Ru(bpy)_2(\mathbf{251})]^{2+}$ binds Cu^{2+} and Ni^{2+} with concomitant deprotonation of the amide NH groups; coordination of Cu^{2+} and Ni^{2+} is accompanied by quenching of the $Ru(bpy)_3^{2+}$ fluorescence and thus the complex can act as a sensor for these metal ions.[573]



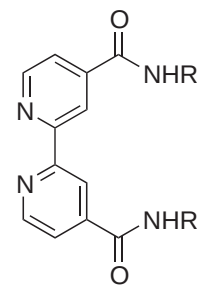
(**249**)



(**250**)



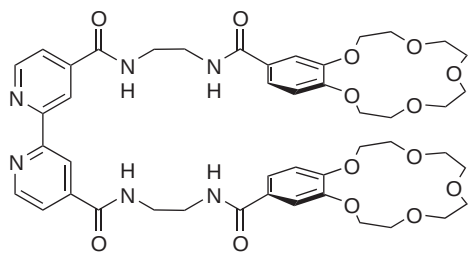
(**251**)



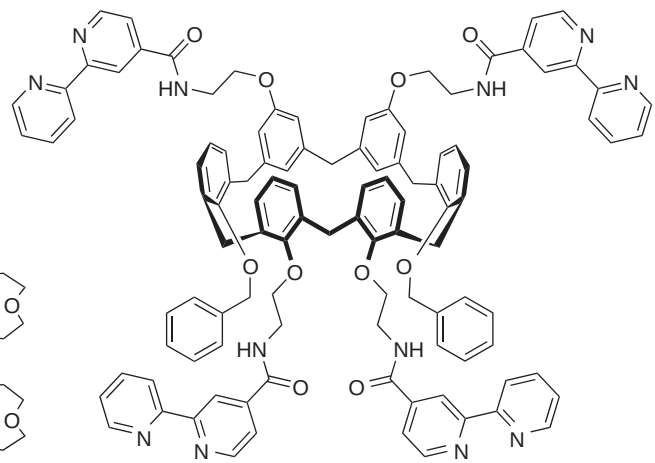
(**252**)

Anion sensing by complexes involving macrocyclic and calix[4]arene domains has been reviewed.[1011] The receptors $[Ru(bpy)_2(\mathbf{252})]^{2+}$ (in (**252**), R = Ph, 2-HOC_6H_4, 3-HOC_6H_4, 4-HOC_6H_4, ^{t}Bu, or 4-^{t}BuC_6H_4) bind Cl^-, Br^-, and I^-; hydrogen-bonded interactions that contribute to this process are discussed. All the complexes show the same anion selectivity: $Cl^- > Br^- > I^-$.[1012] The crystal structure of $[Ru(bpy)_2\{(\mathbf{252}),R = 3,4\text{-}(MeO)_2C_6H_3\}Cl]^+$ confirms the importance of hydrogen bonding to the binding of the Cl^- anion in the bis(amide) cavity.[1013] Calix[4]arenes have been attached to ligand (**252**) (i.e., replacing the two R groups), and once again, the role of hydrogen bonding in anion binding has been assessed from structural data for $[Ru(bpy)_2((\mathbf{252}), R_2 = \text{calix[4]arene})(H_2PO_4)]^+$.[1013] 5,5′-Bis(amide)-substituted bpy ligands (L) related to the 4,4′-derivatives (**252**) have also been incorporated into receptors of type $[Ru(bpy)_2L]^{2+}$. These species exhibit spectral and electrochemical recognition of Cl^-, and spectral recognition of Br^- in polar solvents.[1014] Complexes of the type $[Ru(bpy)_2L]^{4+}$ and $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2]^{6+}$ containing bipyridyl pyridinium ligands L have been prepared as receptors, but show no selectivity preference for Cl^- vs. Br^-.[1015] The anion selectivity properties of ditopic receptors such as $[Ru(bpy)_2(\mathbf{253})]^{2+}$ can be tuned by binding K^+ in the bis-macrocyclic ether cavity. With no K^+ present, the complexes bind $H_2PO_4^-$ in preference to Cl^-, but this selectivity is reversed in the presence of K^+.[1016]

A number of $[Ru(bpy)_2L]^{2+}$ complexes in which L is a bpy ligand functionalized with a calix[4]arene (or derivative)[1017–1020] or resorcinarene[1021] receptor site have been reported. For example, the complex $[Ru(bpy)_2L]^{2+}$ in which L is related to (**253**) but with a calix[4]diquinone replacing the two benzocrown ethers, binds Cl^-, $MeCO_2^-$, and $H_2PO_4^-$, but shows selectivity for $MeCO_2^-$. The complex senses $MeCO_2^-$ by means of a luminescent emission intensity retrieval effect.[1017] Although not focused on receptor design, the preparation and characterization of $[(\mathbf{254})\{Ru(bpy)_2\}_4]^{8+}$ is appropriately included in this discussion of calixarene-containing species. The $Ru(bpy)_2^{2+}$ groups are introduced using *cis*-Δ-$[Ru(bpy)_2(dmso)Cl]^+$ and virtually complete retention of absolute stereochemistry at each metal center is observed on calix[6]arene complex formation.[1022]



(**253**)

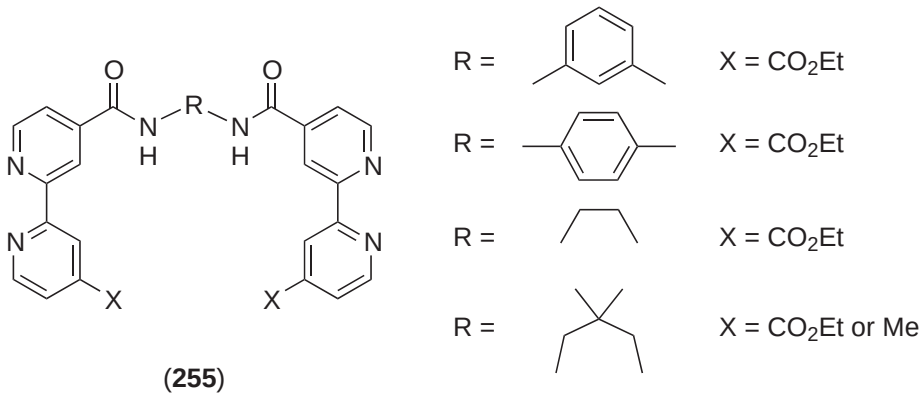


(**254**)

The receptor complexes $[(bpy)_2M(\mu\text{-}\mathbf{255})M(bpy)_2]^{4+}$ (M–M = Ru–Ru or Os–Os) show selectivity for $H_2PO_4^-$ over halide ions, and NMR titration data have been used to determine stability constants for the receptor:anion complexes. The nature of group R in ligand (**255**) has a critical effect on the strength of anion binding.[1023] A series of $[Ru(bpy)_2L]^{2+}$ complexes in which L is a polyaza-functionalized bpy ligand has been reported. These water-soluble complexes bind phosphate and ATP anions; quenching of the MLCT emission that accompanies anion binding is observed and means that the complexes can be used as sensors for phosphate and ATP.[1024]

5.5.3.1.14 Complexes containing 2,2′:6′,2″-terpyridine ligands and cyclometallated analogs

The discussion in this section is organized as follows: (i) mononuclear complexes containing non-functionalized tpy ligands, (ii) mononuclear complexes containing functionalized tpy ligands,



(**255**)

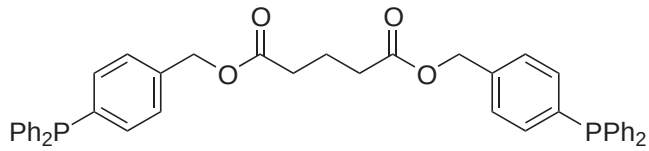
(iii) di- and polynuclear complexes, and (iv) tpy-like ligands (e.g., 6-phenyl-2,2′-bipyridine) which are cyclometallated upon complex formation.

A common precursor to Ru^{II} tpy chemistry is $[Ru^{III}(tpy)Cl_3]$, the crystal structure of which has been elucidated.[1025] Whereas the chemistry of $[M(bpy)_3]^{2+}$ is complicated by the complex being chiral, that of $[M(tpy)_2]^{2+}$ does not suffer from this problem. The crystal structures of perchlorate salts of $[Ru(tpy)_2]^{2+}$ and $[Os(tpy)_2]^{2+}$,[1026] and of $[Ru(tpy)_2][PF_6]_2{\cdot}2MeCN$[1027] have been determined, and vibrational spectroscopic data for $[Ru(tpy)_2]^{2+}$ have been reported.[1028] The tpy ligand exhibits didentate coordination in a number of complexes, and examples include *cis*-[Ru(tpy-*N,N′*)(bpy)(CO)$(CO_2H)]^+$,[1029] and *trans,cis*-$[RuX_2(CO)_2$(tpy-*N,N′*)] (X = Cl, Br, I);[1030] further examples are described later in the section.

The reductive cleavage of oxo dimers provides a convenient method of preparing $[Ru(tpy)(H_2O)_3]^{2+}$, which itself is a useful precursor to several $Ru(tpy)^{2+}$-containing species.[1025] Cyano complexes containing the $Ru(tpy)^{2+}$ group include $[Ru(tpy)(CN)_3]^-$, fully-assigned ^{13}C NMR spectroscopic data for which have been reported.[1031] In a study of $[Ru(tpy)(bpy)(CN)]^+$, it has been observed that the excited state produced on MLCT excitation decays in a process for which $k = 1.3 \times 10^8\ s^{-1}$.[1032] The phenylcyanamido complex $[Ru(tpy)(bpy)(4\text{-}IC_6H_4NCN)]^+$ has been prepared and characterized by spectroscopic, electrochemical, and crystallographic methods; one-electron oxidation produces a radical species resulting from phenylcyanamide-centered oxidation.[1033]

Ruthenium(II) tpy complexes that feature phosphine ligands include $[Ru(tpy)(PPh_3)_2H]^+$, the structure of the salicylate salt of which has been determined.[1034] $[RuCl(tpy)$(**256**)$]^+$ is a rare example of an undistorted, octahedral complex in which the bis(phosphine) ligand has its *P,P*-donors in a *trans* configuration. The synthetic route involves reaction between $[RuCl(tpy)(Ph_2PC_6H_4CH_2OH)_2]^+$ and $ClCO(CH_2)_3COCl$.[1035] Sodium azide reacts with $[Ru(tpy)(PPh_3)_2Cl]^+$ to give $[Ru(tpy)(PPh_3)_2(N_3)]^+$, isolated and structurally characterized as the perchlorate salt.[1036] Syntheses of the derivatives $[Ru(tpy)(PR_3)_2(NO_2)]^+$ and $[Ru(tpy)(PR_3)_2(NO)]^{3+}$ (R = Et, Pr, Bu, Ph, Bz) have also been described. Electrochemical data for $[Ru(tpy)(PR_3)_2(NO_2)]^+$ illustrate that the nature of the PR_3 ligand affects whether the cyclic voltammogram is reversible or irreversible.[1037] In an extension of this work, the complexes $[Ru(tpy)(PR_3)(PMe_3)(NO_2)]^+$ (R = Et, Pr, Ph, Bz) have been prepared and their electrochemistry investigated.[1038] The crystal structures of *trans*-$[Ru(tpy)(PPh_3)(PMe_3)(NO_2)][ClO_4]{\cdot}H_2O$,[1038] *trans*-$[Ru(tpy)(PPh_3)_2(NO_2)][PF_6]$,[1039] and *trans*-$[Ru(tpy)(PPr_3)_2(NO_2)][ClO_4]$[1040] have been determined. In the complex $[Ru(tpy)Cl(OH)(NO)][PF_6]$, the hydroxyl group is *trans* to the nitrosyl ligand, and the Ru—O bond suffers some shortening as a result of this arrangement.[1041] Another nitrosyl complex that has been studied is $[Ru(tpy)(acac)(NO)]^{2+}$. This is one of a series of complexes containing the $Ru(tpy)^{2+}$ unit that has been prepared and characterized, and these include [Ru(tpy)(acac)Cl], $[Ru(tpy)(acac)(H_2O)]^+$, $[Ru(tpy)(ox)(H_2O)]$, [Ru(tpy)(ox)(py)], $[Ru(tpy)(acac)(py)]^+$, and $[Ru(tpy)(acac)(NO_2)]$. The electrochemical properties of these species have been detailed.[1042]

We move now to complexes containing $Ru(tpy)(bpy)^{2+}$ fragments. $[Ru(tpy)(bpy)(H_2O)]^{2+}$ and related species in which bpy is replaced by, for example, 4,4′-Me_2bpy, phen, 2,9-Me_2phen, or 6,6′-Cl_2bpy, have been prepared. The aqua ligand may be substituted by MeCN and the kinetics of this process have been studied. The work has been extended to include MeCN-for-H_2O substitution in $[Ru(N\text{-}N)_2(H_2O)(PR_3)]^{2+}$ (N–N = bpy or bpy derivative) and data have been analyzed to



(**256**)

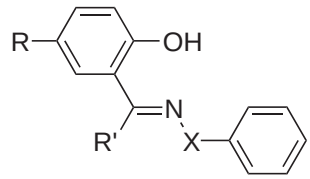
provide values of cone angles for the bpy ligands.[1043] The electrochemical properties of $[Ru(tpy)(bpy)(H_2O)]^{2+}$ are unaffected by changes in solvent from water to CH_2Cl_2 or acetone. Moreover, these properties are maintained on formation of poly(pyrrole-$[Ru(tpy)(bpy)(H_2O)]^{2+}$) films.[1044] The complexes $[Ru(tpy)L(CO)]^{2+}$ in which L = bpy, 4,4′-Me_2bpy, 4-(2-methylpropyl)bpy or phen have been synthesized by a photochemical route. The CO ligand is an active site for substitutions (e.g., with py, PPh_3, or Cl^-) and these reactions proceed with retention of stereochemistry.[1045] Irradiation of $[Ru(tpy)(bpy)(MeCN)]^{2+}$ in the MLCT region leads to ligand substitution by py, 4-Phpy, and 2-Mepy. Attempts to perform similar reactions with the Os^{II} analog were unsuccessful. The crystal structure of $[Ru(tpy)(bpy)(py)][PF_6]_2 \cdot Me_2CO$ reveals an asymmetrically bound bpy ligand, presumably as a result of steric crowding. These data have been used to understand difficulties encountered in preparing the 2-methylpyridine analog.[1046] In basic, aqueous solution, the MeCN ligand in $[Ru(tpy)(bpy)(MeCN)]^{2+}$ (the crystal structure of which has been determined)[1047] is converted to $MeCONH_2$, and the Ru^{II} product is $[Ru(tpy)(bpy)(OH)]^+$.[1048] The complex $[Ru(tpy)(4,4'\text{-}X_2bpy)H]^+$ (X = H, MeO) exhibits greater hydridic character than $[Ru(bpy)_2(L)H]^+$ (L = CO, PPh_3, $AsPh_3$); the kinetics of the reactions of $[Ru(tpy)(4,4'\text{-}X_2bpy)H]^+$ with CO_2 to give $[Ru(tpy)(4,4'\text{-}X_2bpy)(OCHO)]^+$ have been studied in various solvents and it is proposed that the rate-determining step involves nucleophilic attack of H^- on CO_2. Structural data for $[Ru(tpy)(bpy)(OCHO)][PF_6]$ are presented.[1049] The syntheses, spectroscopic, and electrochemical properties of $[Ru(tpy)(4,4\text{-}X_2bpy)(H_2O)]^{2+}$ (X = MeO, NO_2) have been described; for X = NO_2, the behavior of the complex is rationalized in terms of the presence of deprotonated species in solution.[1050] The crystal structure of $[Ru(tpy)(bpy)(pyz)][PF_6]_2$ shows the Ru^{II} center to be in a distorted octahedral environment, indicative of steric crowding of the ligands.[1051] For the complexes $[Ru^{II}(tpy)L(py)]^{n+}$ (L = bpy, 4,4′-Me_2bpy, 4-NO_2bpy, ox^{2-}, $acac^-$), electronic absorption and luminescence spectroscopic properties have been investigated and the results indicate that these species may be good triplet-energy acceptors when incorporated into organic and polymeric light-emitting devices.[1052]

6-Thienyl-2,2′-bipyridine (HL) forms $[Ru(tpy)(HL)]^{2+}$ or $[Ru(tpy)L]^+$ depending on conditions: the cyclometallated complex $[Ru(tpy)L]^+$ is converted to $[Ru(tpy)(HL)]^{2+}$ on treatment with acid, and the reverse process occurs in aqueous NaOH.[1053] Reaction between $[Ru(tpy)Cl_3]$ and 2,2′:6′,4″-terpyridine (HL) produces $[Ru(tpy)(HL)Cl]^+$ and $[Ru(tpy)(LH)]^{2+}$ in which LH represents the cyclometallated ligand (L^-) which has been protonated on the non-coordinated N atom. The reaction can be encouraged along one of the two pathways by changing the reaction conditions.[1054] In the complexes $[Ru(tpy)(bpy)_2]^{2+}$, $[Ru(tpy)(phen)_2]^{2+}$, and $[Ru(6\text{-}Brtpy)(bpy)_2]^{2+}$, tpy acts as a didentate ligand.[1055]

A $Ru(tpy)(bpy)^{2+}$-like coordination sphere is present in the complexes $[Ru(tpy)LCl]^+$ and $[Ru(tpy)L(H_2O)]^{2+}$ (L = 1,1′-biisoquinoline) isolated as ClO_4^- salts; in the solid state, the two isoquinoline rings in the former cation are mutually twisted by 37.4°. $[Ru(tpy)L(H_2O)]^{2+}$ exhibits two reversible/quasi-reversible oxidation Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} couples.[1056] The aqua complexes $[Ru(tpy)L(H_2O)]^{2+}$ where L = 3,6-bis(pyrid-2-yl)pyridazine, 3,6-bis(6-methylpyrid-2-yl) pyridazine, or 3,6-bis(6-chloropyrid-2-yl)pyridazine can be made by treating the corresponding chloro complexes with aqueous Ag^+; the H_2O ligand can be replaced by MeCN.[1057] For L = 2,3-bis(2,2′-bipyridin-6-yl)pyrazine, NMR spectroscopic studies of $[Ru(tpy)L]^{2+}$ and $[\{Ru(tpy)\}_2(\mu\text{-}L)]^{4+}$ have elucidated their fluxional behavior. Results for the solution species are compared with structural data obtained for $[\{Ru(tpy)\}_2(\mu\text{-}L)]^{4+}$.[1058] The solution fluxional properties of $[Ru(tpy)(CO)_2Cl_2]$ in which tpy is an *N,N*-chelate have also been investigated; the tpy ligand exchanges between equivalent didentate sites.[1030] The spectroscopic, electrochemical, and photophysical properties of $[Ru(tpy)LCl]^+$ and $[Ru(tpy)L(py)]^{2+}$ where L = 2,3-dpp, 2,3-bis(2-pyridyl)-quinoxaline (2,3-dpq) and 2,3-bis(2-pyridyl)benzoquinoxaline (2,3-dpb) have been described; the MLCT absorption shifts to lower energy for the complexes in the order 2,3-dpp > 2,3-dpq > 2,3-dpb, and going from the chloro to py complex for each L results in a blue shift for the MLCT band.[1059] The 2,2′-bipyrazine (L) complexes $[Ru(tpy)LCl]^+$ and $[Ru(tpy)L(H_2O)]^{2+}$ have been

characterized by spectroscopic and (for the chloro complex) X-ray diffraction methods. Over the pH range 0–11, $[Ru(tpy)L(H_2O)]^{2+}$ undergoes one reversible redox process, assigned to a single two-electron oxidation of Ru^{II}.[1060] In the solid-state structure of the PF_6^- salt of $[Ru(tpy)(biq)Cl]^+$, the latter contains a distorted octahedral Ru^{II} coordination sphere.[1061]

The complexes [Ru(tpy)LCl] (L^- is salicylaldiminate or 2-(arylazo)phenolate ion) exhibit intense MLCT absorptions and reversible Ru^{II}/Ru^{III} and irreversible Ru^{III}/Ru^{IV} redox processes plus a tpy reduction at −1.45 V (vs. SCE). Reaction of [Ru(tpy)LCl] with aqueous Ag^+ yields $[Ru(tpy)L(H_2O)]^+$.[1062] Reaction of $[Ru(tpy)Cl_3]$ with HL (HL = (**257**)) gives [Ru(tpy)L′Cl] in which L'^- is derived directly from (**257**) for X = CH, but for X = NH, the imine has undergone tautomerism to the azo form.[1063] The preparation, structure, and electrochemical properties of [Ru(tpy)(dipic)] (H_2dipic = dipicolinic acid) have been described as part of a study involving this and related $[Ru(bpy)_2L]^{n+}$ complexes.[1064]



R = H, X = CH_2, R' = H
R = H, X = CH_2, R' = Me
R = NO_2, X = CH_2, R' = H
R = H, X = NH, R' = H
R = H, X = NH, R' = Me
R = NO_2, X = NH, R' = H

(**257**)

The electrochemical properties of the quinone-containing complex $[Ru(tpy)(Q)(H_2O)]^{2+}$ (Q = 3,5-di-*tert*-butyl-1,2-benzoquinone) in the presence of base have been studied in detail and differences in the behavior of aqua and hydroxo complexes analyzed and applied to the conversion of the proton gradient to electricity.[1065]

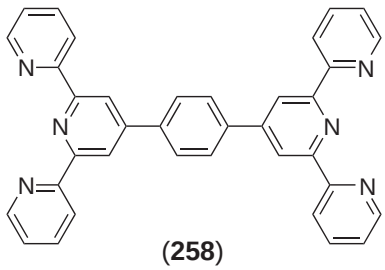
The reaction of $[Ru(tpy)Cl_3]$ with 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine, qpy, (or derivatives) leads to $[Ru(qpy\text{-}N,N',N'')(tpy\text{-}N,N',N'')]^{2+}$ (in which two of the five *N*-donors in qpy are non-coordinated) and $[(tpy)Ru(\mu\text{-}qpy)Ru(tpy)Cl]^{4+}$ in which the bridging ligand is didentate with respect to one metal center and tridentate with respect to the other.[1066]

In the next part of this section, we consider complexes containing functionalized tpy ligands; a general abbreviation, e.g., 4′-Rtpy, will be used to indicate a tpy ligand substituted in the, for example, 4′-position by an R group. As a general point, reaction to form $[Ru(4'\text{-}Xtpy)_2]^{2+}$ starting from $[Ru(4'\text{-}Xtpy)Cl_3]$ may be accompanied by the formation of minor amounts of $[Ru(4'\text{-}Xtpy\text{-}N,N',N'')(4'\text{-}Xtpy\text{-}N,N')Cl]^+$.[1067] The ^{1}H NMR spectroscopic and electrochemical properties of a range of $[Ru(4'\text{-}Xtpy)_2]^{2+}$ and $[Ru(4'\text{-}Xtpy)(4'\text{-}Ytpy)]^{2+}$ complexes (X or Y = NMe_2, Cl, OH, OEt, Ph) have been investigated; the general method of synthesis is via the intermediate complex $[Ru(4'\text{-}Xtpy)Cl_3]$. The redox properties of the complexes are correlated with a Hammett parameter (σ') that is defined for the pair of ligands taking $\sigma' = 0$ for the unsubstituted ligands in $[Ru(tpy)_2]^{2+}$. Two linear correlations are found for plots of σ' against $E^o(Ru^{II}/Ru^{III})$ (vs. Fc/Fc^+); complexes involving the 4′-Me_2Ntpy ligand fall on a separate correlation line from all other species and this is rationalized in terms of a conformational change of coordinated 4′-Me_2Ntpy on going from Ru^{II} to Ru^{III}.[1068] For X = Cl or $MeSO_2$ in $[Ru(4'\text{-}Xtpy)_2]^{2+}$, the complexes are luminescent in fluid solution at 298 K,[1069] and for substituents X and Y being H, $MeSO_2$, NMe_2, Cl, OH, Oet, or Ph, the complexes $[Ru(4'\text{-}Xtpy)(4'\text{-}Ytpy)]^{2+}$ are strongly luminescent (rigid matrix, 77 K) with lifetimes of 1–10 μs. The effects of the different substituents on the photophysical properties, and correlations between Ru^{II}/Ru^{III} redox potentials, the Hammett parameter σ' and the energy of the luminescent level are discussed.[1070] The excited-state properties of $[Ru(4'\text{-}Xtpy)_2]^{2+}$ for X = Ph, 4-MeC_6H_4, 4-HOC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4) have also been investigated; lowering the temperature (298 to 77 K) significantly increases the luminescence quantum yield.[1071]

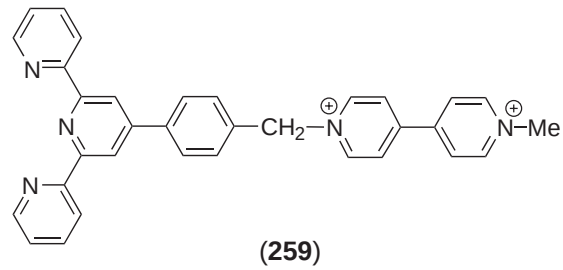
The complexes $[Ru(tpy)(4'\text{-}Rtpy)]^{2+}$ where R = $C_{19}H_{39}$ or $C_{31}H_{63}$ have been prepared, the ligands first being made by coupling 1-bromoalkanes to 4′-Metpy. $[Ru(tpy)(4'\text{-}C_{19}H_{39}tpy)]Cl_2$ exhibits lyotropic mesomorphism in water, while $[Ru(tpy)(4'\text{-}C_{31}H_{63}tpy)]$ shows the formation of a mesophase in ethylene glycol.[1072] The tri-*tert*-butyl-substituted ligand 4,4′,4″-^{t}Bu_3tpy has been prepared and incorporated into the complexes $[Ru(4,4',4''\text{-}{}^tBu_3tpy)(bpy)Cl]^+$, $[Ru(4,4',4''\text{-}{}^tBu_3tpy)(4,4'\text{-}{}^tBu_2bpy)Cl]^+$, $[Ru(4,4',4''\text{-}{}^tBu_3tpy)(bpy)(CF_3SO_3)]^+$, $[Ru(4,4',4''\text{-}{}^tBu_3tpy)LCl_2]$ (L = CO, PPh_3, PMe_3, PMe_2Ph, $P(OPh)_3$, $P(OMe)_3$). The introduction of the ^{t}Bu substituents has the advantage of increasing the solubility of the complexes.[1073–1075]

2,2′:6′,2″-Terpyridine ligands carrying aryl substituents have been widely studied and this includes the use of aryl spacers between two tpy ligands to construct potentially bridging ligands.

The reactions of $[CpRu(PPh_3)_2Cl]$ with 4′-Phtpy and ligand (**258**) yield $[CpRu(PPh_3)(4'\text{-Phtpy})]^+$ and $[\{CpRu(PPh_3)\}_2(\mu\text{-}4'\text{-Phtpy})]^{2+}$ in which each tpy-based ligand behaves as an *N,N′*-donor, leaving one pyridyl group non-coordinated.[1076] On going from $[Ru(tpy)_2]^{2+}$ to $[Ru(4,4'\text{-}Ph_2tpy)_2]^{2+}$ or $[Ru(4,4',4''\text{-}Ph_3tpy)_2]^{2+}$, the lifetime of the excited state of the complex increases; conjugation between Ph and the low-lying π^*-orbital of tpy occurs, stabilizing the emissive CT excited state relative to the thermally accessible ^{3}d–d excited state and thereby affecting the decay pathway.[1077] The electrochemical and photophysical properties of $[M(tpy)_2]^{2+}$, $[M\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}_2]^{2+}$, and $[M(4,4',4''\text{-}Ph_3tpy)_2]^{2+}$ (M = Ru, Os) have been compared; MLCT excited-state quenching measurements using different redox-active species have illustrated that, when irradiated with light, $[Ru(4,4',4''\text{-}Ph_3tpy)_2]^{2+}$ is a good electron-transfer agent.[1078] Along the series $[M\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}_2]^{2+}$ for M = Fe, Ru, or Os, the Os^{II} complex exhibits the most intense luminescence; the excited state of $[Os\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}_2]^{2+}$ reacts with MV^{2+} by electron transfer. The properties of $[Os\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}_2]^{2+}$ have been compared with those of $[Os\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}(\mathbf{259})]^{2+}$ and the quenching effects of the viologen group investigated.[1079] The complexes $[Ru\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}L(MeCN)]^{2+}$ (L = 1-(2-pyridyl)-3,5-dimethylpyrazole or 6,6′-Me_2bpy) undergo photosubstitution reactions involving the MeCN ligand.[1080]



(**258**)



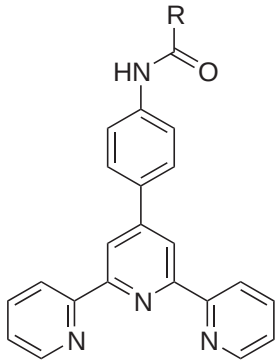
(**259**)

The properties of the complexes $[Ru(tpy)\{4'\text{-}(4\text{-}FC_6H_4)tpy\}]^{2+}$ and $[Ru\{4'\text{-}(4\text{-}FC_6H_4)tpy\}_2]^{2+}$ illustrate that the 4-FC_6H_4 substituent is electron-releasing.[1081] Laser-flash spectroscopy has been used to obtain the absorption spectrum of the ^{3}MLCT triplet state of $[Ru\{4'\text{-}(4\text{-}ClC_6H_4)tpy\}_2]^{2+}$; it is concluded that the excited electron is localized on one of the 4′-(4-ClC_6H_4)tpy ligands.[1082] Dimethylation of the complexes $[Ru(tpy)\{4'\text{-}(3,4\text{-}(MeO)_2C_6H_4)tpy\}]^{2+}$ and $[Ru\{4'\text{-}(3,4\text{-}(MeO)_2C_6H_4)tpy\}_2]^{2+}$ produces complexes with catechol coordination domains on the periphery of the complexes; these sites have been used to prepare di- and trinuclear species in which $Ru(bpy)_2^{2+}$ or $Pd(bpy)^{2+}$ units are coordinated by the *O,O′-donor* sites in the catecholate, benzosemiquinone, or benzoquinone oxidation levels.[1083]

The phosphine-functionalized tpy ligand 4′-Ph_2Ptpy has both hard and soft donor sites; the ligand is prone to oxidation to 4′-Ph_2P(O)tpy and this affects the method of preparation of $[Ru(4'\text{-}Ph_2Ptpy)_2]^{2+}$.[1084] The complex [RuL(4,4′-Me_2bpy)(NCS)] where L = 4-phosphonato-2,2′:6′,2″-terpyridine, shows two ground-state pK_a values at 6.0 and <4.0. The emission spectrum of the complex and the excited-state lifetimes are pH-dependent.[1085]

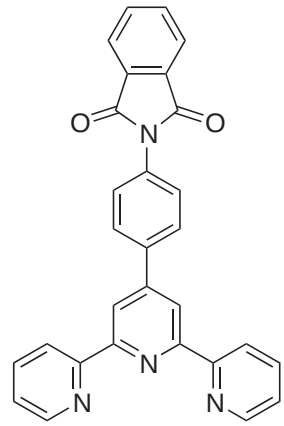
Amino and nitro-functionalized tpy ligands include 4′-NH_2tpy and 4′-NO_2tpy and these ligands have been incorporated into the complexes $[Ru(4'\text{-}NH_2tpy)_2]^{2+}$, $[Ru(4'\text{-}NO_2tpy)_2]^{2+}$, and $[Ru(4'\text{-}NH_2tpy)(4'\text{-}NO_2tpy)]^{2+}$ as well as Fe^{II} analogs.[1086,1087] The ligand 4′-(4-$NH_2C_6H_4$)tpy and its complexes can be functionalized further at the amine site to give, for example, $[Ru(tpy)L]^{2+}$ where L = (**260**) and (**261**). Related bridging ligands containing two tpy domains linked by functionalities derived from those in (**260**) and (**261**) have also been prepared and used to generate dinuclear complexes or mononuclear species with a pendent tpy group. The latter is a versatile entry point into the synthesis of higher-nuclearity complexes.[1088,1089] The complex $[Ru\{4'\text{-}(4\text{-}NH_2C_6H_4)tpy\}_2]^{2+}$ has also been prepared and characterized, and has been used as a building block in polymers of the type shown in (**262**) where the schematic about the Ru^{II} center represents the $Ru\{4'\text{-}(4\text{-}NC_6H_4)tpy\}_2$-unit derived from $[Ru\{4'\text{-}(4\text{-}NH_2C_6H_4)tpy\}_2]^{2+}$. The polymer films exhibit emission and electroluminescent properties.[1090]

The pendant py group in Ru^{II} and Os^{II} complexes containing 4′-(4-py)tpy reacts with electrophiles to generate complexes containing 4′-(4-Hpy)tpy$^+$ and 4′-(4-HMepy)tpy$^+$.[1091] A group of nanoscale rigid-rod complexes of axis dimension = 35.5 Å has been made in which the central metal is Ru^{II} or Os^{II} and the ligands are triarylpyridino-functionalized tpy and 4′-(4-$NMe_2C_6H_4$)tpy. Structural data for ligands and two complexes (evidencing a pronounced twist angle between photosensitizer and pyridinium ring of the acceptor) are presented in addition to solution NMR properties.[1092] A luminescent, rod-like Ru–Zn–Ru complex has been assembled by

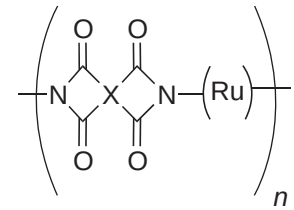


R = Me, Ph

(**260**)



(**261**)



X = various aromatic spacers

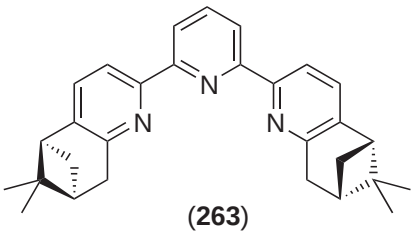
(**262**)

the interaction of $[Ru\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}L]^{2+}$ (L is related to ligand (**258**) but has no phenyl spacer) with Zn^{2+}; the photophysical properties of the Ru–Zn–Ru species are compared with those of the complex containing ligand (**258**).[1093] The syntheses and properties of triads containing a $[Ru(4'\text{-}Phtpy)_2]^{2+}$ core attached to Zn^{II} and Au^{III}-containing porphyrin groups have been summarized in reviews of systems with long-range photoinduced energy and electron transfer,[1094,1095] and relevant to this topic are systems involving an $[M(tpy)_2]^{2+}$ (M = Ru or Os) photosensitizer covalently linked to electron donor (e.g., phenothiazine) and acceptor (e.g., MV^{2+}) sites.[1096–1098] Reactions between $[M\{4'\text{-}(4\text{-}py)tpy\}_2]^{2+}$ (M = Ru, Os) and [Ru(ttp)(CO)(EtOH)] lead to linear systems of type Ru^{II}(porph)–$Ru^{II}(tpy)_2$–Ru^{II}(porph) in which intramolecular phosphorescence quenching is observed.[1099] The absorption spectra and luminescence properties of $[M\{4'\text{-}(9\text{-anthryl})tpy\}_2]^{2+}$ (M = Ru, Os, Zn) compared to those of $[M(tpy)_2]^{2+}$ have been presented.[1100]

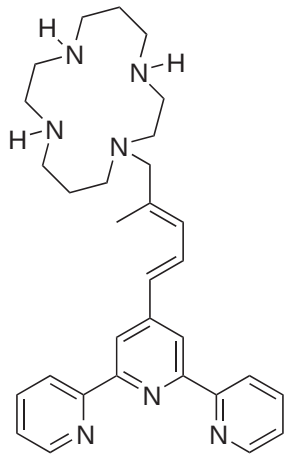
A tpy-functionalized β-cyclodextrin has been prepared. It bears one pendent tpy domain and reacts with $[Ru(tpy)Cl_3]$ or $[Ru\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}Cl_3]$ in the presence of *N*-ethylmorpholine to give complexes with a pendent $Ru(tpy)_2^{2+}$ or $Ru\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}_2$-unit. Their absorption and emission properties, which respond to guest binding, are described.[1101] In related work, a $Ru(bpy)_3^{2+}$ unit has been appended to α-cyclodextrin; a mixture of diastereoisomers was produced. Electron transfer within and outside the cyclodextrin cavity has been investigated.[1102] Bis(tpy) Ru^{II} complexes with an appended C_{60} cage on either one or both ligands have been prepared; ^{1}H NMR spectroscopic and electrochemical studies show that there is electronic interaction between the fullerene and Ru^{II} center.[1103] The $Ru(tpy)_2^{2+}$ center has been used as a central motif in the construction of a catenate. Each tpy ligand is functionalized so as to permit ring closure only on itself; the final catenate consists of two 38-membered rings.[1104] Enantiomerically pure ligands (**263**) and the [4,5:4″,5″]-fused analog (**263a**), have been synthesized along with the complexes $[RuL_2]^{2+}$, $[RuLCl_2]$, and $[RuLCl_3]$. In the Ru^{II} complexes, the ligands exhibit a helically distorted tpy unit.[1105]

Ligand (**264**) has been prepared and complexed with Ru^{II} to give [Ru(**264**)(4-Metpy)]$^{2+}$ which protonates on the cyclam N atoms to give a series of species up to $[Ru(H_3\mathbf{264})(4\text{-}Metpy)]^{5+}$. In aqueous solution, the system acts as a selective luminescent sensor for ATP (with respect to phosphate, sulfate, and chloride ions).[1106] Oxaaza macrocycles attached to the 4′-position of tpy either directly or with a spacer as in (**265**) have been synthesized; in addition, 1,10-diaza-18-crown-6 has been incorporated as a bridging unit between two tpy domains.[1107,1108] Ruthenium(II) complexes containing these ligands have been studied. Recrystallization of $[Ru(tpy)\{4'\text{-}(1,10\text{-diaza-18-crown-6})tpy\}]^{2+}$ from a solution containing traces of $NaBF_4$ lead to a complex (structurally characterized) in which the crown binds Na^+.[1107]

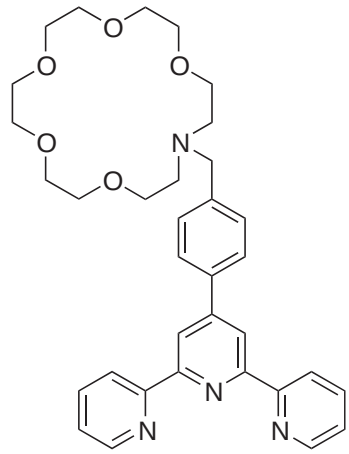
The next part of this section focuses on di- and polynuclear Ru^{II}/Os^{II} systems (organized according to the bridging ligands), and pertinent reviews covering multicomponent molecular arrays should be consulted.[1109,1110] The cyano-bridged complexes $[(bpy)(tpy)Ru(\mu\text{-}CN)Ru^{II/III}(NH_3)_5]^{n+}$ ($n = 3$ or 4) have been studied. Picosecond excitation of $[(bpy)(tpy)Ru(\mu\text{-}CN)Ru(NH_3)_5]^{3+}$ results in the observation of a transient intermediate which decays by an



(263)



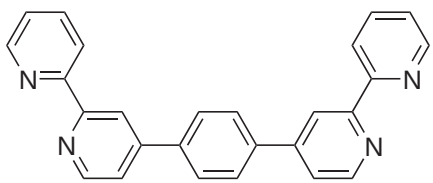
(264)



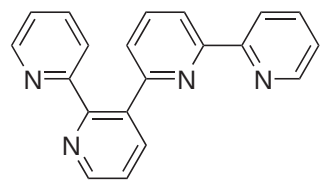
(265)

intramolecular electron-transfer process ($k = 3.8 \times 10^{10}\,s^{-1}$).[1032] The mixed-valence 1,4-dicyanamidobenzene (L) bridged complex $[(bpy)(tpy)Ru(\mu\text{-}L)Ru(bpy)(tpy)]^{3+}$ exhibits strong coupling and has an intervalence absorption at $\lambda = 1{,}090$ nm.[1111] The CO_2-bridged complex $[(MeCN)(CO)(tpy)Ru(\mu\text{-}CO_2)Ru(tpy)(CO)_2]^{2+}$ (in which the MeCN ligand can be replaced by CO) has been prepared from *cis*-$[Ru(tpy)(CO)_2Cl]^+$ and aqueous Na_2CO_3 in MeCN.[1112] The N_2-bridged complex $[(tpy)Cl_2Os(\mu\text{-}N_2)OsCl_2(tpy)]$ results from the reductive coupling of $[Os(tpy)Cl_2(N)]^+$. The crystal structure of $[(tpy)Cl_2Os(\mu\text{-}N_2)OsCl_2(tpy)]$ has been determined; for the bridging unit, N—N = 1.132(13) Å and Os—N—N bond angles are 171.5(9)° and 172.1(9)°.[1113]

The luminescence and excitation spectroscopic properties and transient absorption decays of $[(bpy)_2Ru(\mu\text{-}\mathbf{266})Ru(bpy)_2]^{4+}$, $[(tpy)(CN)Ru(\mu\text{-}\mathbf{266})Ru(CN)(tpy)]^{2+}$, and $[(bpy)_2Ru(\mu\text{-}\mathbf{266})Ru(CN)(tpy)]^{3+}$ in MeCN solution and low-temperature glasses indicate that efficient intramolecular energy transfer from the MLCT excited state of the $Ru(bpy)_2(\mathbf{266})^{2+}$ unit to the MLCT state of the $Ru(CN)(tpy)^+$ group occurs in $[(bpy)_2Ru(\mu\text{-}\mathbf{266})Ru(CN)(tpy)]^{3+}$.[1114] An unexpected cyclometallated complex $[(tpy)ClRu(\mu\text{-}L)Ru(tpy)]^{2+}$ where HL = (**267**) is obtained from the reaction of $[Ru(tpy)Cl_3]$ and HL in the presence of *N*-methylmorpholine; the L^- ligand acts as an *N,N, C*-donor to the $Ru(tpy)^{2+}$ unit and an *N,N*-donor to the $RuCl(tpy)^{2+}$ group.[1115]



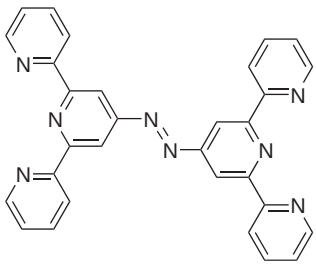
(266)



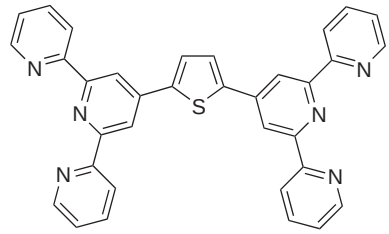
(267)

Bridging ligands involving two tpy domains coupled either directly or by various spacers feature in a significant number of complexes, some examples of which were cited earlier.[1093] The complexes $[(tpy)M(\mu\text{-}\mathbf{268})M(tpy)]^{4+}$ (M–M = Ru–Ru, Ru–Os, Os–Os) have been prepared and characterized; they show MLCT absorptions involving both tpy and ligand (**268**) and the data are consistent with ligand (**268**) possessing a lower-lying π^* level than tpy. Electrochemical reduction of $[(tpy)Os(\mu\text{-}\mathbf{268})Os(tpy)]^{4+}$ generates a species that luminesces at 298 K, contrasting with low-temperature luminescence of the reduced diruthenium complex.[1116] The electronic absorption spectra and luminescence spectra and lifetimes of $[(tpy)Ru(\mu\text{-}\mathbf{269})Ru(tpy)]^{4+}$, $[(tpy)Os(\mu\text{-}\mathbf{269})Os(tpy)]^{4+}$, $[(tpy)Ru(\mu\text{-}\mathbf{269})Os(tpy)]^{4+}$, $[(tpy)Ru(\mu\text{-}\mathbf{269})Ru(\mu\text{-}\mathbf{269})\ Ru(tpy)]^{6+}$, and $[(tpy)Ru(\mu\text{-}\mathbf{269})Os(\mu\text{-}\mathbf{269})Ru(tpy)]^{6+}$ have been reported. The results indicate significant interaction between the metal centers, and in the heterometallic species, Ru → Os energy transfer occurs. The luminescence lifetimes of $[(tpy)Ru(\mu\text{-}\mathbf{269})Os(tpy)]^{4+}$ and $[(tpy)Ru(\mu\text{-}\mathbf{269})Os(\mu\text{-}\mathbf{269})Ru(tpy)]^{6+}$

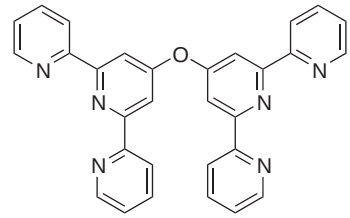
are 120 and 125 ns respectively (293 K).[1117,1118] Ligand (**270**) is synthesized by the condensation of 4′-Cltpy and 4′-HOtpy, or can be prepared in situ as a bridging ligand by reacting $[(tpy)Ru(4'\text{-}Cltpy)]^{2+}$ with $[(tpy)Ru(4'\text{-}HOtpy)]^{2+}$. The latter strategy has been extended to assemble, for example, $[Ru(\mathbf{270})_2]^{2+}$ starting from $[Ru(4'\text{-}Cltpy)_2]^{2+}$, and $[(4'\text{-}Xtpy)Ru(\mu\text{-}\mathbf{270})Ru(\mu\text{-}\mathbf{270})Ru(4'\text{-}Xtpy)]^{6+}$ (e.g., X = Cl). The work has been further extended to species of the type $[\{(4'\text{-}Cltpy)Ru(\mu\text{-}\mathbf{270})Ru\}_3(\mu\text{-}L)]^{12+}$ where L = 1,3,5-tris{4′-(2,2′:6′,2″-terpyridinyl)}benzene.[1119] This trinucleating ligand has also been used as the core in the complexes $[\{(4'\text{-}Xtpy)Ru\}_3(\mu\text{-}L)]^{6+}$ for X = H, Cl, OH, OEt, NMe_2, Ph, SMe, and MeO_2S.[1120] Ligand (**258**) and its analog with no phenyl spacer (**258a**) have been used to assemble the rigid, dinuclear complexes $[(4'\text{-}Xtpy)Ru(\mu\text{-}L)Ru(4'\text{-}Xtpy)]^{4+}$ (L = **258** or **258a**; X = H, Cl, OH, OEt, NMe_2, Ph, SMe, and MeO_2S).[1120] Heterometallic complexes $[(4'\text{-}Xtpy)Ru(\mu\text{-}L)Os(4'\text{-}Xtpy)]^{4+}$ (X = 4-MeC_6H_4 or MeO_2S) have also been studied for L containing 0, 1, or 2 phenyl spacers ($n = 1$ is **258**). The luminescence of the $Ru(tpy)_2^{2+}$ unit is quenched by the Os-centered group in each complex, and quenching is accompanied by sensitization of the Os-based luminescence.[1121,1122] In the related mononuclear species, $[\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}RuL]^{2+}$ which contains a non-coordinated tpy domain, the extent to which protonation of the latter site affects the luminescence properties of the complex have been discussed.[1123] The properties of $[\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}Ru(\mu\text{-}L')Os\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}]^{2+}$ containing bis(*N,C,N*)-donor bridging ligands L′ where H_2L = (**271**), have also been investigated;[1124] (see also ref. 1151). The photophysical properties of $[\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}Ru(\mu\text{-}L)Ru\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}]^{4+}$ (L = **258** or **258a**)[1125] may be compared with those of the heterometallic complexes $[\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}Ru(\mu\text{-}L)Rh\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}]^{5+}$.[1126,1127] Work in this area has been overviewed[1128] and includes comparisons of the properties of complexes with phenylene and bicyclo[2.2.2]octane spacers between the tpy domains in the bridging ligands in Ru–Os systems.[1129] The preparation and characterization of polymeric species using the bridging ligand 4,4″-bis(2,2′:6′,2″-terpyridine)-2′,5′-dihexyl-*p*-terphenyl between Ru^{II} centers have been reported.[1130]



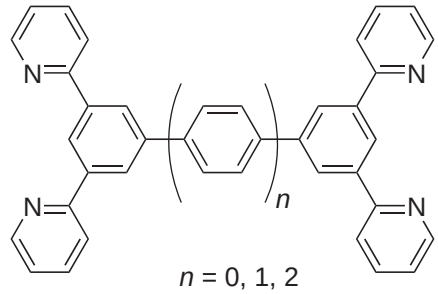
(**268**)



(**269**)



(**270**)

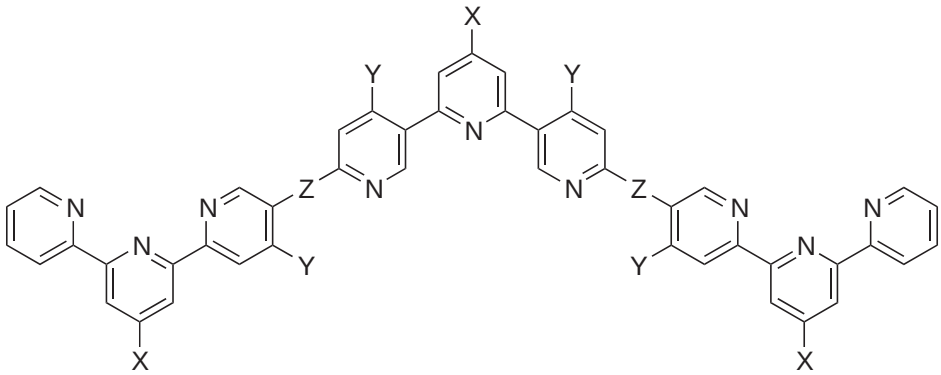


n = 0, 1, 2

(**271**)

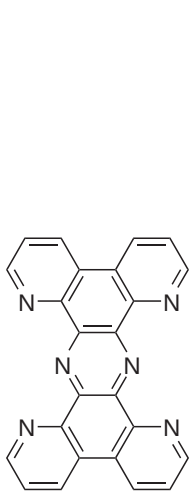
The complexes $[Ru_3(\mathbf{272})_2]^{6+}$ and $[Ru_3(\mathbf{273})_2]^{6+}$ contain three $Ru(tpy)_2^{2+}$ domains. The luminescence properties of $[Ru_3(\mathbf{272})_2]^{6+}$ are similar to those of $[Ru(tpy)_2]^{2+}$, whereas $[Ru_3(\mathbf{273})_2]^{6+}$ exhibits a room-temperature ^{3}MLCT emission ($\lambda = 690$ nm, $\tau = 11$ ns).[1131]

The ligand 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tpp) possesses two tpy-like binding sites, making it an ideal bridging ligand in $[(tpy)M(\mu\text{-}L)M(tpy)]^{4+}$ and related species. Using a building-block strategy, $[(tpy)M(\mu\text{-}tpp)RuCl_3]^{+}$ and $[(tpy)M(\mu\text{-}tpp)Ru(tpp)]^{4+}$ (M = Ru, Os) have been prepared; the complexes exhibit long-lived excited states. In the chloro complexes, the Ru^{II} center coordinated by Cl^- is easier to oxidize than M^{II}. The HOMO of $[(tpy)M(\mu\text{-}tpp)Ru(tpp)]^{4+}$ is M-based (M = Ru or Os); the lowest excited state is an MLCT state for L = tpp, and can be tuned to

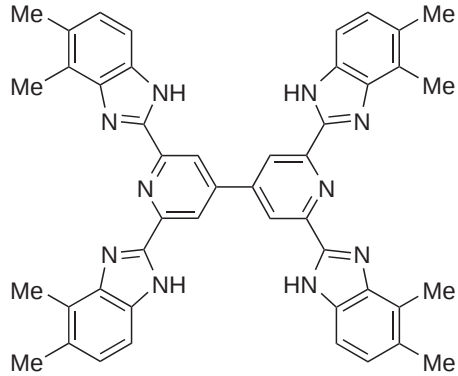


(**272**) X = H; Y = H; Z = CH_2CH_2
(**273**) X = CH_2CH_2OH; Y = Me; Z = CH=CH

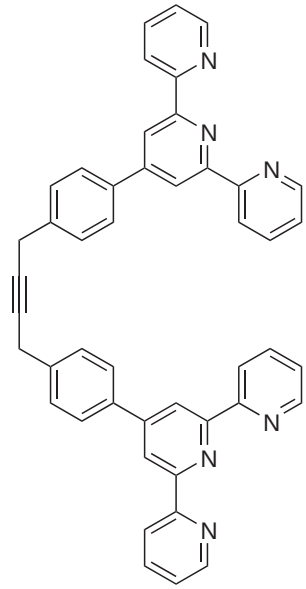
involve either Ru or Os centers depending on the local environment. The range of tpp-bridged dinuclear complexes that has been studied also includes $[(tpy)Ru(\mu\text{-}tpp)Ru(tpy)]^{4+}$, $[(tpy)Ru(\mu\text{-}tpp)Ru(MeCN)_3]^{4+}$, $[(tpy)Ru(\mu\text{-}tpp)Ru(dpq)Cl]^{4+}$ (dpq = 2,3-bis(2-pyridyl)benzoquinone), and $[(tpy)Ru(\mu\text{-}tpp)RhCl_3]^{2+}$.[1132–1135] In the latter complex, excitation into the Ru → tpp MLCT state is followed by electron transfer to the Rh center and quenching of the emission from the excited state.[1135] Like tpp, the phenazine-based ligand (**274**) exhibits two binding sites each resembling tpy. The electronic spectra of the complexes $[Ru\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}(\mathbf{274})]^{2+}$, $[\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}Ru(\mu\text{-}\mathbf{274})Ru\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}]^{4+}$, and $[\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}Ru(\mu\text{-}\mathbf{274})Ru(\mu\text{-}\mathbf{274})Ru\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}]^{6+}$ show low-energy Ru → tpp MLCT absorptions. In each case, the first one-electron reduction is centered on ligand (**274**). Electrochemical data for the metal-centered oxidation processes in the di- and trinuclear complexes indicate a strong degree of electronic coupling between the metal centers.[1136] Ligand (**275**) (H_4L in its fully protonated form) forms the complexes $[(tpy)Ru(\mu\text{-}H_4L)Ru(tpy)]^{4+}$ and $[(tpy)Ru(\mu\text{-}L)Ru(tpy)]$ which can be interconverted by changes in pH; the effects of protonation state on the spectroscopic and electrochemical properties of the species have been discussed.[1137]



(**274**)



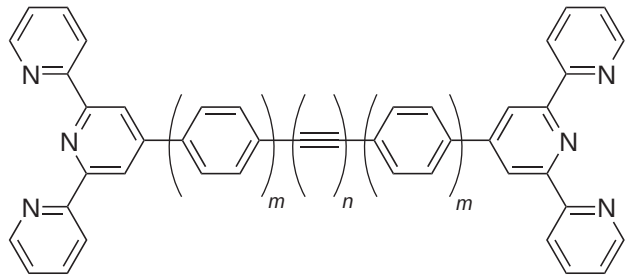
(**275**)



(**276**)

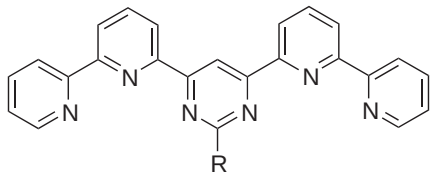
The complex $[(tpy)Ru(\mu\text{-}\mathbf{276})Ru(tpy)]^{4+}$ has been prepared and characterized both in solution and the solid state; structural data confirm a single-stranded helicate and reveal that the ethynyl bridge suffers from severe bending.[1138] Other alkyne-containing bridging ligands impose rigidity

on the system, e.g., two tpy domains linked at the 4′-positions by a $C{\equiv}CC_6H_4C{\equiv}C$ or $C{\equiv}C(bpy)C{\equiv}C$ spacer to give bridging ligands L. Compared to $[Ru(tpy)_2]^{2+}$, $[(tpy)Ru(\mu\text{-}L)\text{-}Ru(tpy)]^{4+}$ are strongly emissive with the luminescence maxima being red-shifted, and exhibit triplet lifetimes of around 100 ns.[1139] Triplet lifetimes for $[(tpy)Ru(\mu\text{-}L)Ru(tpy)]^{4+}$ where L = (**277**–(**280**)) range from 55 ns to 720 ns,[724] and fast energy transfer has been observed from Ru^{II} to Os^{II} in $[(tpy)Ru(\mu\text{-}\mathbf{278})Os(tpy)]^{4+}$.[1140] Alkyne spacers in polynuclear systems containing tpy or bpy coordination domains are fundamental to families of photoactive molecular wires and progress in the area has been reviewed.[1141,1142]

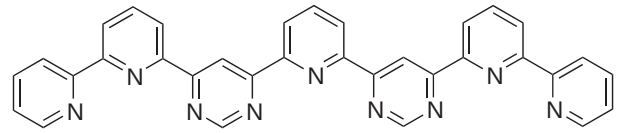


(**277**) $n = 1, m = 0$
(**278**) $n = 2, m = 0$
(**279**) $n = 1, m = 1$
(**280**) $n = 2, m = 1$

Polynuclear rack and grid complexes can be assembled using bis(tpy) domains, capitalizing on the fact that the two tpy donor sets in each $M(tpy)_2$ unit are orthogonal. Ligands (**281**) and (**282**) contain two and three tpy-like bonding domains and form the rack-type complexes $[(\mathbf{281})\{Ru(tpy)_2\}_2]^{4+}$ and $[(\mathbf{282})\{Ru(tpy)_2\}_3]^{6+}$. Solution NMR spectroscopic and the photophysical properties of these species have been reported; the complexes exhibit emission from the ^{3}MLCT state (τ in the range 40–80 ns) at 298 K in fluid solution and the properties can be varied by changing the R group (H, Me, Ph) in ligand (**281**).[1143–1145]



R = H, 9-anthryl, Me, Ph
(**281**)



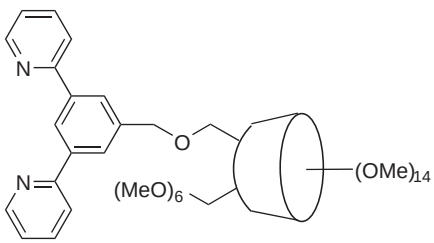
(**282**)

Oxidative coupling of $[Ru^{II}(tpy)\{2,6\text{-}(CH_2NMe_2)_2C_6H_3\}]^+$ leads to the formation of a diruthenium(III) complex that undergoes two-electron reduction to give $[(tpy)Ru^{II}\{\mu\text{-}2,6\text{-}(CH_2NMe_2)_2C_6H_3\}Ru^{II}(tpy)]^{2+}$ in which the bridging ligand presents an *N,C,N*′-donor set to each metal center. The central biphenylene unit is nonplanar in the solid state.[1146] 6-Phenyl-2,2′-bipyridine (HL) undergoes cyclometallation to provide an *N,N*′,*C*-donor set and this is observed in the complex $[Ru(tpy)L]^+$, which, in contrast to $[Ru(tpy)_2]^{2+}$, luminesces at 298 K in fluid solution. The lifetime of the ^{3}MLCT state is 60 ns (MeCN).[1147] The reaction of $[Ru(tpy)Cl_3]$ with 6-Phbpy (HL) is influenced by solvent. In glacial $MeCO_2H$, the product is $[Ru(tpy)(HL\text{-}N,N')Cl]^+$ while in aqueous solution, $[Ru(tpy)(L\text{-}N,N',C)]^+$ is formed. Both complexes are isolated from reactions carried out in MeOH or BuOH.[1148] "Back-to-back" bis(6-phenyl-2,2′-bipyridine) ligands, H_2L, in which the binding domains are either directly coupled through the 4′-positions of 6-Phbpy or are coupled through C_6H_4 or $C_6H_4C_6H_4$ spacers, along with an analogous tris(6-phenyl-2,2′-bipyridine) ligand, H_3L', have also been prepared. Their noncyclometallated and cyclometallated complexes $[Cl(tpy)Ru(\mu\text{-}H_2L)Ru(tpy)Cl]^{2+}$, $[\{Cl(tpy)Ru\}_3(\mu\text{-}H_3L')]^{3+}$, $[(tpy)Ru(\mu\text{-}L)Ru(tpy)Cl]^{2+}$, and $[\{(tpy)Ru\}_3(\mu\text{-}L')]^{3+}$ have been studied.[1149] 6-Phenyl-2,2′-bipyridine units have also been coupled through the 4-position of the phenyl rings to give H_2L. This ligand has the potential to act as an *N,N*′- or bis(*N,N*′)-donor or to undergo cyclometallation and coordinate through *N,N*′,*C*-, bis(*N,N*′,*C*), or (*N,N*′)(*N,N*′,*C*)-donor sets.[1150]

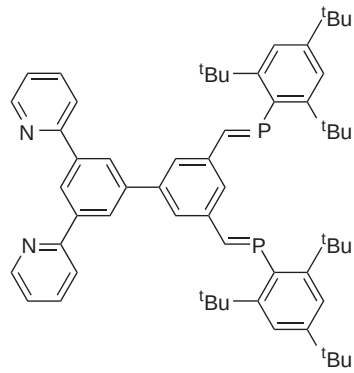
Di-(2-pyridyl)-1,3-benzene (HL) undergoes cyclometallation to act as an *N,C,N*′-donor in, for example, $[M(L)\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}]^{2+}$ (M = Ru, Os). The "back-to-back" bis-derivative of HL is ligand (**271**) with $n = 0$ (HL–LH), and has been used to form the cyclometallated complexes $[\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}M(\mu\text{-}L\text{-}L)M\{4'\text{-}(4\text{-}MeC_6H_4)tpy\}]^{4+}$ (M–M = Ru–Ru, Os–Os, Ru–Os at a separation of 11 Å), the luminescence and electrochemical properties of which have been described.[1151]

The same *N,C,N′*-donor set has been appended to the rim of a cyclodextrin, H(**283**), and used to prepare [Ru(tpy)(**283**)]$^{+}$, giving a route into luminescent cyclodextrins.[1152] It is also present in ligand H_2(**284**) which reacts with [Ru{4′-(4-MeC_6H_4)tpy}Cl_3] in the presence of $AgBF_4$, followed by [$PdCl_2$(PhCN)$_2$] to give the doubly cyclometallated complex [{4′-(4-MeC_6H_4)tpy}Ru-(μ-**284**)PdCl]$^{+}$.[1153]

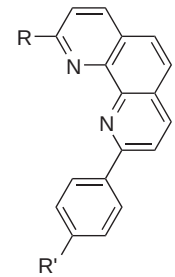
The orthogonal nature of the ligands in [Ru{4′-(4-MeC_6H_4)tpy}L]$^{+}$ where HL = H(**285**) or H(**286**) places these complexes among those containing cyclometallated-tpy analogs. The properties of these species have been compared; while [Ru{4′-(4-MeC_6H_4)tpy}(**286**)]$^{+}$ does not luminesce in MeCN at 298 K, the more sterically crowded [Ru{4′-(4-MeC_6H_4)tpy}(**285**)]$^{+}$ luminesces and has an excited-state lifetime of 95 ns.[1154] Changing the substituents in these ligands leads to variation in the excited-state lifetimes (70–106 ns).[1155] Cyclometallation involving pyrene units has proved difficult but has been achieved.[1156]



H(**283**)



H_2(**284**)



H(**285**) R = 4-MeC_6H_4; R′ = Me

H(**286**) R = H; R′ = OMe

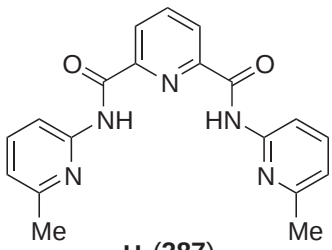
Monomethylation of tpy blocks one *N*-coordination site, and, depending on the reaction conditions, *N*-Metpy^{+} coordinates to Ru^{II} either as an *N,N′*- or *N,N′,C*-donor.[1158]

5.5.3.1.15 *Complexes containing ligands with N,N′,N″- or N,C,N′-donor sets excluding tpy and tripodal ligands*

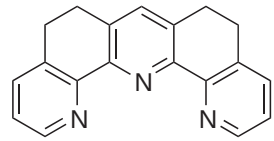
There is necessarily some overlap between the content of this and the previous sections. The theme in the present section is complexes containing *N,N′,N″*- or *N,C,N′*-donor ligands other than tpy and related species; tripodal ligands are covered in the next section.

2,6-Bis[(dimethylamino)methyl]pyridine (L) reacts with [$RuCl_2(PPh_3)_3$] to yield *mer,trans*-[$RuCl_2L(PPh_3)$] which is a useful precursor to a series of complexes containing ligand L, e.g., [$RuCl(L)(PPh_3)$]$^{+}$, [RuCl(MeCN)(L)(PPh_3)], [Ru(MeCN)$_2$(L)(PPh_3)]$^{2+}$, [$RuCl_2$(CO)(L)], and [$RuCl(CO)_2(L)$]$^{+}$. The work extends to cover related P,N,P complexes.[1157] The reaction of H_2(**287**) with [$RuCl_2(PPh_3)_3$] generates [$RuCl_2(PPh_3)$(**287**H_2)] in which the amide groups in H_2(**287**) are deprotonated and involved in coordination, and the pendent pyridine N atoms are protonated. [$RuCl_2(PPh_3)$(**287**H_2)] can be converted to nitrosyl, thiocyanate, or acetate derivatives.[1159] The ligand 4-(4-MeC_6H_4)-2,6-dipyrazinylpyridine (L) can present an *N,N′,N″*-donor set to Ru^{II} in a similar manner to tpy; [RuL_2]$^{2+}$ has been prepared and structurally characterized.[1160] Ligand (**288**) and its unsaturated dihydroacridine and acridine analogs also act as pseudo-tpy ligands in the homoleptic complexes [RuL_2]$^{2+}$.[1161] Ligand (**289**) has available both tpy- and bpy-like binding domains and both modes of coordination have been observed. Assignments of the ^{1}H NMR spectra of [Ru(tpy)(**289**)]$^{2+}$ and [Ru(tpy)(μ-**289**)Ru(bpy)$_2$]$^{4+}$ are aided by comparisons of the spectra with those of [Ru(tpy-d_{11})(μ-**289**)Ru(bpy-d_8)$_2$]$^{4+}$.[1162]

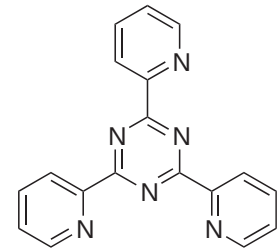
A range of Ru^{II} complexes incorporating tridentate bis(pyrazolyl)pyridine or related ligands has been reported. Six complexes of type [RuLL′]$^{2+}$ (L = L′ or L ≠ L′) in which L and L′ are ligands (**290**) have been prepared; the oxidation potentials for the Ru^{II}/Ru^{III} couple decrease as the number of Me substituents increases.[1163] The tridentate coordination mode of ligands (**291**) and (**292**) have been confirmed by structure determinations of [Ru(**291**)(NO_2)(PMe_3)][ClO_4][1164]



H_2(**287**)

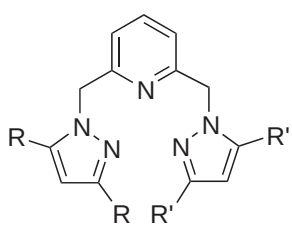


(**288**)



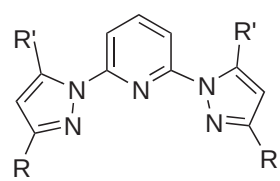
(**289**)

and [Ru(**291**)Cl(PPh_3)][ClO_4].[1165] In both complexes, the PPh_3 groups are mutually *trans*. The presence of the 1,3-substituted β-diketonate ligand L^- in [Ru(**291**)(L)X] and [Ru(**293**)(L)X]$^{n+}$, or the ligands containing the dimethyl analog of (**291**) and (**293**) (X = Cl or an N-heterocycle; $n = 0$, 1), lowers the Ru^{II}/Ru^{III} redox potential with respect to related polypyridyl complexes; variation in the substituents in the ligands allows the potential to be systematically altered.[1166] Spectroscopic, electrochemical, and representative structural data have been reported for [Ru(**293**)(bpy)Cl]$^+$, [Ru(**293**)(phen)Cl]$^+$, and [Ru(**293**)(4,4′-Me_2bpy)Cl]$^+$.[1167] Ligands (**294**) act, as expected, as tridentate donors in the complexes [Ru(**294**)$_2$]$^{2+}$ for which ^{1}H and ^{13}C NMR spectra have been fully assigned; electronic spectroscopic and redox behavior have been described.[1168] Replacing the pyrazol-1-yl group in (**291**) by oxazolin-2-yl or 4-iso-propyloxazolin-2-yl groups gives rise to novel ligands that have been used to prepare chiral and achiral Ru^{II} complexes.[1169] 2,6-Bis(benzimidazol-2-yl)pyridine and *N*-methyl derivatives form [RuL_2]$^{2+}$ complexes in which the ligands act as *N,N′,N″*-bis chelates. For L = 2,6-bis(benzimidazol-2-yl)pyridine, [RuL_2]$^{n+}$ for $n = 2$ or 3 behave as tetrabasic acids with pK_a values in the range 2.5–10.7.[1170] For the same L, the structure of [RuL(NO_2)(PPh_3)][ClO_4] has been determined; the bis(imidazolyl)pyridine Ru^{II} unit is planar but steric crowding forces the benzene rings of the ligand out of plane.[1171] 6-(Benzimidazol-2-yl)-2,2′-bipyridine, L′, forms [Ru(L′)$_2$]$^{2+}$; a study of the redox potential as a function of pH shows there to be two one-proton/one-electron transfer processes in the pH regions 1.39–2.58 and 5.92–7.97, and a two-proton/one-electron transfer in the pH range 2.58–5.92.[1172] A series of substituted 2,6-bis(4,5,6,7-tetrahydroindazol-3yl)pyridines has been prepared and combined with Ru^{II} to give homo- and heteroleptic complexes.[1173]

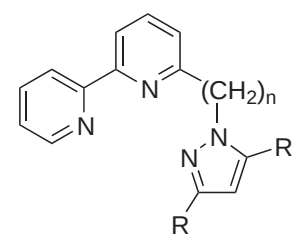


R = R' = H
R = H, R' = Me
R = R' = Me

(**290**)



(**291**) R = R' = H
(**292**) R = Ph; R' = H
(**293**) R = R' = Me



R = H; n = 0 or 1
R = Me; n = 0 or 1

(**294**)

The versatility of the quinolyl derivative (**295**) is exemplified in the complex [Ru(**295**-*N,N′*)(**295**-*N,N′,N″*)Cl]$^+$. The coordination behavior of (**295**) has been compared with those of (**296**) and (**297**) and factors influencing didentate vs. tridentate preferences have been examined.[1174] Perchlorate salts of [Ru(tpy)L)]$^{2+}$ and [RuL_2]$^{2+}$ where L = (**298**)–(**300**) have been synthesized and characterized, and their properties compared with those of [Ru(tpy)$_2$]$^{2+}$.[1175] Complexation of Ru^{II} with 2,6-bis(4′-phenyl-2′-quinolyl)pyridine (L) affords [RuL_2]$^{2+}$, spectroscopic properties of which have been discussed.[514] The bis(7′-methyl)-derivative of this ligand, L^{Me}, has also been prepared and incorporated into the complexes [$M(L^{Me})_2$]$^{2+}$, [$M(L^{Me})Cl_3$] (M = Ru, Os), and [Ru(L^{Me})(tppz)]$^{2+}$ where tppz = 2,3,5,6-tetra(2′-pyridyl)pyrazine. Related cyclometallated complexes have also been studied. All the complexes luminesce at 77 K and [$M(L^{Me})_2$]$^{2+}$ (M = Ru or Os), [Ru(L^{Me})(L′)]$^{2+}$, and two of the cyclometallated species are luminescent at room

temperature.[1176] In the complex $[Ru(tppz)(4,4'\text{-}Me_2bpy)Cl]^+$, the coordination environment about the Ru^{II} center is highly distorted, and the effects of this on ^1H NMR chemical shifts are noted.[1177] An investigation of the photophysical properties of $[Os(tppz)(PPh_3)_2X]^{n+}$ (X = Cl^- or MeCN, $n = 1$ or 2) and $[Os(tppz)L]^{2+}$ (L = tpy, tppz) reveals that these complexes possess relatively long-lived MLCT excited states; the presence of the tppz ligand makes these species suitable as building blocks in supramolecular assembly.[1178] Methylation of one of the non-coordinated pyridyl groups gives a viologen that can act as an electron acceptor.[1179] Examples of tppz acting as a bridging ligand include $[Cl(bpy)Ru(\mu\text{-}tppz)Ru(bpy)Cl]^{2+}$ and $[Cl(4,4'\text{-}Me_2bpy)Ru(\mu\text{-}tppz)Ru(4,4'\text{-}Me_2bpy)Cl]^{2+}$.[1180]

The ability of polypyridine ligands to partition themselves into *N,N′*- and *N,N′,N″*-binding domains has already been illustrated in the structure of $[(tpy)Ru(\mu\text{-}qpy)Ru(tpy)Cl]^{4+}$ (qpy = 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine).[1066] In $[Ru_2(qpy)_2Cl_2]^{2+}$, the two ligand strands form a double helical arrangement, placing one Ru^{II} center in an N_6-coordination sphere and the second in an N_4Cl_2 environment. The "prehelicate" $[Ru(qpy)_2]^{2+}$ contains four (two sets of two) non-coordinated *N*-donor atoms.[1181]

5.5.3.1.16 Complexes containing $[HBpz_3]^-$, $HCpz_3$ (pz = pyrazolyl), and related ligands

The chemistry of hydrotris(pyrazolyl)borate, $[HBpz_3]^-$, straddles the coordination–organometallic border. The coverage in this section is, therefore, selective but should give a useful entry into the field. A review covering the period 1993–1998 provides a survey of ruthenium complexes containing the $[HBpz_3]^-$ ligand.[1182] Unless otherwise specified, the $[HBpz_3]^-$ ligand in the complexes described below is tridentate, coordinating through three pyrazolyl N atoms.

The compound $[Ru(HBpz_3)(MeCN)_3][PF_6]$ can be made by treating $[Ru(HBpz_3)(cod)Cl]$ with $[NH_4][PF_6]$ in hot dmf/MeCN; the kinetics of MeCN exchange are compared with those for $[CpRu(MeCN)_3][PF_6]$.[1182] Reaction of $[Ru(HBpz_3)Cl(PPh_3)_2]$ with NaS_2CNMe_2 leads to the formation of $[Ru(HBpz_3)(Me_2NCS_2)(PPh_3)]$, the structure of which has been determined. Treatment of $[Ru(HBpz_3)Cl(PPh_3)_2]$ with $(4\text{-}MeC_6H_4S)_2$ in the presence of Zn yields the trinuclear complex $[\{(HBpz_3)(PPh_3)Ru(\mu\text{-}4\text{-}MeC_6H_4S)_2\}_2Zn]$; an alternative route to this species also yields $[(HBpz_3)(PPh_3)Ru(\mu\text{-}4\text{-}MeC_6H_4S)_2Zn(SC_6H_4\text{-}4\text{-}Me)(MeOH)]$.[1183] Abstraction of Cl^- from $[Ru(HBpz_3)(Me_2NCH_2CH_2NMe_2)Cl]$ in acetone or dmf (solv) generates $[Ru(HBpz_3)(Me_2NCH_2CH_2NMe_2)(solv)]^+$, which are shown to be useful intermediates in the formation of vinylidene complexes.[1184] Reactions of the $[Ru(HBpz_3)(Me_2NCH_2\ CH_2PPh_2)]^+$ unit have also been studied, including those giving N_2, H_2O, CO, MeCN, Me_2CO, and vinylidene complexes. Structural data for $[Ru(HBpz_3)(Me_2NCH_2CH_2PPh_2)(\eta^2\text{-}N_2)]^+$ reveal an N—N bond length equal to that in free N_2, indicating that the effects of σ-donation and π-back donation offset one another.[1185] The reaction of $[Ru(HBpz_3)Cl(PPh_3)(MeCN)]$ with $NaBH_4$ in RCH_2OH unexpectedly produce $[Ru(HBpz_3)(PPh_3)(CO)(R)]$.[1186] The synthesis and structure of $[Ru(HBpz_3)(PPh_3)(CO)(PMe_3)][PF_6]$ have been reported as part of a study of the reactions of $[Ru(HBpz_3)(PPh_3)(CO)X]$ (X = H, Cl).[1187] Reaction of $[Ru(HBpz_3)(PPh_3)_2Cl]$ with dppm, dppe, or dppf results in phosphine substitution and the formation of $[Ru(HBpz_3)(dppx)Cl]$; with neat ^tBuNC, $[Ru(HBpz_3)(PPh_3)_2Cl]$ reacts to give $[Ru(HBpz_3)(PPh_3)Cl(^tBuNC)]$ but the product depends on solvent and is $[Ru(HBpz_3)(PPh_3)(^tBuNC)]^+$ if the reaction is carried out in CH_2Cl_2/MeOH. A range of other reactions are reported,[1188] including that with NaS_2CNMe_2 described earlier.[1183] Substitution of the PPh_3 ligands in $[Ru(HBpz_3)(PPh_3)_2Cl]$ by 1,2-bis(diisopropylphosphino)ethane (dippe) followed by treatment with $NaBH_4$ yields $[Ru(HBpz_3)(dippe)H]$. This and the complex $[Ru(HBpz_3)(PPh_3)_2H]$ are both protonated by $HBF_4.OEt_2$ at low temperature to give cationic H_2 complexes.[1189,1190] The crystal structure of $[Ru(HBpz_3)(dippe)(H_2)][BF_4]$ has been determined,[1189] and both this and $[Ru(HBpz_3)(PPh_3)_2H]$ are reactive with respect to displacement of H_2 by, for example, CO, N_2, and thf.[1189,1190] Several routes to $[Ru(\eta^2\text{-}HBpz_3)(PPh_3)_2(CO)H]$ have been described. The η^2-$HBpz_3^-$ ligand in this complex can be converted to an η^3-bound form by heating, and the change is accompanied by loss of PPh_3. The synthesis of $[Ru(\eta^2\text{-}HBpz_3)(PPh_3)_2(CS)H]$ has also been achieved and again, the mode of coordination of $HBpz_3^-$ changes when the complex is heated.[1191] The synthesis and characterization of the dihydrogen/hydride complex $[Ru(HBpz_3)(H_2)H(PCy_3)_2]$ has been reported.[1192]

The 3,5-dimethylpyrazolyl derivative $[HB(3,5\text{-}Me_2pz)_3]^-$ reacts with $[RuH(Cl)(CO)L_3]$ (L = PPh_3 or $AsPh_3$) to give, rather surprisingly as a result of B—N cleavage, $[RuH(Cl)(CO)L_2(3,5\text{-}Me_2pzH)]$.[1193] Trifluoromethanesulfonic acid reacts with $[Ru\{HB\ (3,5\text{-}^iPr_2pz)_3\}H_5]$

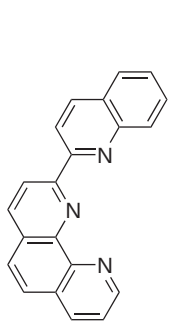
in thf to give $[Ru\{HB(3,5\text{-}^{i}Pr_2pz)_3\}(H_2O)_2(thf)][CF_3SO_3]$ which is reactive with respect to substitution of the labile thf and H_2O ligands and is, therefore, a useful synthon.[1194]

Although a didentate rather than a tripodal ligand, $[H_2Bpz_2]^-$ is mentioned in this section because of its relationship to $[HBpz_3]^-$. Examples of complexes involving $[H_2Bpz_2]^-$ are $[Ru(H_2Bpz_2)H(CO)(PPh_3)_2]$,[1195] $[Ru(H_2Bpz_2)H(CS)(PPh_3)_2]$,[1195] $[Ru(H_2Bpz_2)(COMe)(CO)(PMe_3)_2]$,[1196] and $[Ru(H_2Bpz_2)H(CO)(AsPh_3)_2]$.[1197] The coordination of dihydrobis(benzotriazolyl)-borate, $[H_2Bbt_2]^-$ to Ru^{II} has also been studied; complexes in the series $[Ru(H_2Bbt_2)(X)(CO)(PPh_3)_2]$ (e.g., X = H, Cl, Br, I, 4-MeC_6H_4) have been prepared and characterized.[1198]

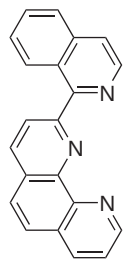
The reaction between $Tl[Bpz_4]$ and $[RuCl_2(PhCN)_4]$ in refluxing CH_2Cl_2 leads to the formation of $[Ru(Bpz_4)Cl(PhCN)_2]$, but when the solvent is changed to benzene, the product is $[Ru(Bpz_4)_2]$. Each $[Bpz_4]^-$ ligand acts as an *N,N′,N″*-donor.[1199] With $[Ru(Bpz_4)Cl(PhCN)_2]$ as the precursor, reactions with a range of ligands lead to products that include $[Ru(Bpz_4)Cl(L)(L')]$ (L = L′ = 4-picoline, MeCN, PEt_3, $P^{i}Pr_3$, or L = PhCN and L′ = PPh_3 or 2,4-lutidine), and $[Ru(Bpz_4)L_3]^+$ (L = MeCN, CO).[1200]

The ligand $HCpz_3$ is isoelectronic and shares a common coordination mode with $[HBpz_3]^-$. One of the simplest complexes of Ru^{II} to incorporate $HCpz_3$ is $[Ru(HCpz_3)(H_2O)_3]^{2+}$, the structure of which has been determined.[1201] The complexes $[Ru(HCpz_3)(H_2O)(4,4'\text{-}X_2bpy)]^{2+}$ (X = H, Me, NH_2, NO_2, and CO_2Et) that differ in the electron-withdrawing or accepting properties of X, make up a series in which the redox potentials are tuned by changing the substituent.[1202] The complexes $[Ru(HCpz_3)(bpy\text{-}PTZ)Cl]^+$, $[Ru(HCpz_3)(bpy\text{-}PTZ)(H_2O)]^{2+}$, $[Ru(HCpz_3)(bpy\text{-}PTZ)(py)]^{2+}$, and $[Ru(HCpz_3)(bpy\text{-}PTZ)(N\text{-}Me\text{-}4,4'\text{-}bpy)]^{3+}$ all contain an electron-donating phenothiazine unit (bpy-PTZ = 4-methyl-4′-(*N*-phenothiazylmethyl)-2,2′-bipyridine). The last complex in the series also contains the quencher *N*-Me-4,4′-bpy^+ (related to MV^+). A detailed study of the photochemical and photophysical properties of these complexes has been carried out.[1203] *cis*-$[Ru(\alpha\text{-diimine})_2(\eta^2\text{-}Bpz_4)]^+$, *cis*-$[Ru(\alpha\text{-diimine})_2(\eta^2\text{-}HCpz_3)]^{2+}$ (α-diimine = bpy, phen) and related complexes each exhibit an intense MLCT absorption associated with the $Ru(\alpha\text{-diimine})_2{}^{2+}$ unit; the complexes are room-temperature emitters. In $[Ru(\alpha\text{-diimine})_2(Bpz_4)]^+$, the two pendant pz groups permit $[Bpz_4]^-$ to act as a bridging ligand, for example in the formation of $[(bpy)_2Ru(\mu\text{-}Bpz_4)Ru(bpy)_2]^{3+}$.[1204]

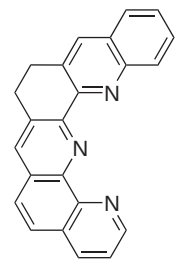
Complexes of the tripodal ligand tris(2-pyridylmethyl)amine are described in the next section. See also structure (**377**) and ref. 1709.



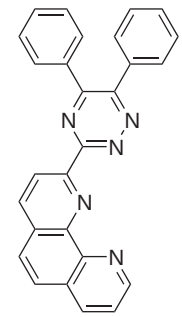
(**295**)



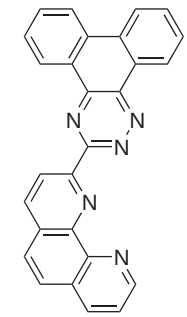
(**296**)



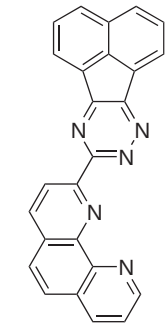
(**297**)



(**298**)



(**299**)

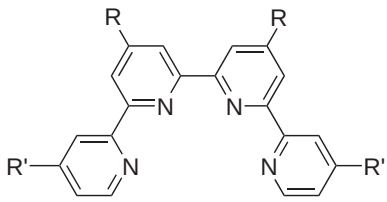


(**300**)

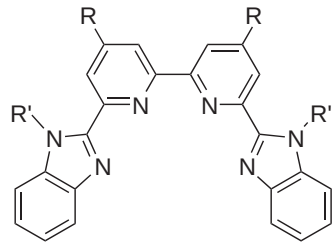
5.5.3.1.17 Complexes containing noncyclic ligands with N,N′,N″,N‴-donor sets

We have already discussed coordination chemistry of the two quaterpyridine ligands (**129**) and (**155**) which are effective at connecting two metal sites.[659–662] Now we consider tetradentate *N*-donor ligands that include derivatives of another isomer of quaterpyridine, (**301**). The complexes *trans*-[Ru(**302**)X_2], *trans*-[Ru(**303**)X_2], *trans*-[Ru(**304**)X_2], and *trans*-[Ru(**305**)X_2] (X = Cl, NCS) have been prepared and characterized; they exhibit MLCT bands in the visible and near-IR regions, and compared to the spectra of complexes with X = Cl, those with X = NCS are blue-shifted. The properties of the complexes indicate that they are suitable for use as sensitizers in TiO_2-based solar cells;[1205] (see also ref. 571 and following). Closely related to *trans*-[Ru(**305**)X_2] are the complexes *trans*-$[RuLX_2]$ where L = (**306**)–(**309**) and X = Cl, Br, or CN. Their absorption spectra exhibit strong MLCT bands between 450 and 600 nm. The Ru^{II}/Ru^{III} oxidation potential

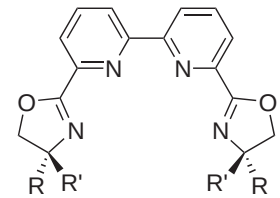
varies with X^- ($Cl^- < Br^- < CN^-$).[1206] 1,2-Bis(2,2′-bipyridin-6-yl)ethane, L, is similar to quaterpyridine (**301**) in that it possesses two bpy binding domains. It forms the complexes *trans*-$[RuL(MeCN)Cl]^+$ (structurally characterized as the PF_6^- salt), *trans*-$[RuL(MeCN)_2]^{2+}$, and *trans*-$[RuL(MeCN)(CN)_2]$. The cyano complex is a room-temperature emitter in fluid solution.[1207]



(**301**) R = R' = H
(**302**) R = CO_2Et; R' = H
(**303**) R = 3,4-$(MeO)_2C_6H_4$; R' = H
(**304**) R = 4-$MeO_2CC_6H_4$; R' = ^{t}Bu

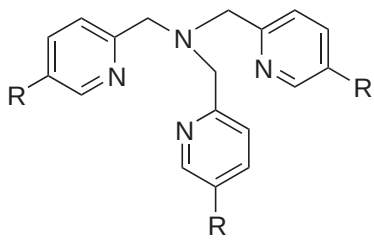


(**305**) R = CO_2Me; R' = H
(**306**) R = R' = H
(**307**) R = H; R' = Me

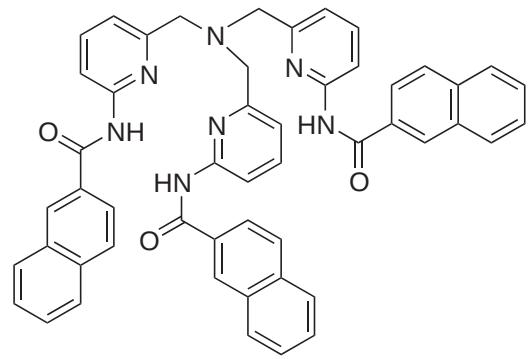


(**308**) R = R' = Me
(**309**) R = ^{i}Pr; R' = H

The substituted amine (**310**) acts as a tetradentate tripodal ligand, e.g., in *cis*-$[Ru(\mathbf{310})Cl(dmso)]^+$. The derivative $[Ru(\mathbf{311})Cl(dmso)]^+$ has been structurally characterized as the perchlorate salt. The dinuclear complexes $[\{Ru(\mathbf{310})\}_2(\mu\text{-}Cl)_2]^{2+}$ and $[\{Ru(\mathbf{311})\}_2(\mu\text{-}Cl)_2]^{2+}$ have also been prepared and characterized. The electron-donating effects of the Me groups in (**311**) lowers the Ru^{II}/Ru^{III} redox potential in each (**311**)-containing complex compared to the analogous complex with ligand (**310**).[1208] Related Ru^{III} complexes have also been reported.[1208,1209] The reaction between **310**·$3HClO_4$ and $Ru_3(CO)_{12}$ in the presence of $MeCO_2H$ leads to the formation of *cis*-$[Ru(\mathbf{310})(CO)(MeCO_2\text{-}O)][ClO_4]$.[1210] In the complex $[Ru(\mathbf{312})Cl]^+$, ligand (**312**) is an *N,N′,N″,N‴,O*-donor, with one amide O atom residing *cis*- to the chloro ligand; $[Ru(\mathbf{312})Cl]^+$ is fluxional in solution.[1211]



(**310**) R = H
(**311**) R = Me



(**312**)

5.5.3.1.18 Complexes containing porphyrin ligands

In this first part of this section, complexes are grouped according to the axial ligands. We then move to pocket and picket-fence porphyrins and finally focus on multinuclear species.

Methyl to CO transformation has been observed in the reaction of [Ru(OEP)Me] with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). There is clear evidence that the CO ligand in the

product [Ru(OEP)(CO)] is derived from the axially bound CH_3 group.[47] The complexes [Ru(TPTBP)(CO)] and [RuL(CO)(ax)], where H_2TPTBP is *meso*-tetraphenyltetrabenzoporphyrin and the axial ligand, ax, is NEt_3, piperidine, 1-Meim, py, or PBu_3, have been synthesized and characterized. The wave number of the absorption assigned to ν(CO) in the IR spectra of the complexes is sensitive to the π-bonding abilities of the axial ligand, indicating that there is $Ru^{II} \rightarrow CO$ backbonding. A comparison of values of ν(CO) along the series [Ru(TPTBP)(CO)], [Ru(OEP)(CO)], and [Ru(TPP)(CO)] indicates that $TPTBP^{2-}$ is a better σ-donor and π-acceptor than TPP^{2-} or OEP^{2-} and, probably, than other commonly used prophyrinato ligands. Oxidation processes in [Ru(TPTBP)(CO)] are discussed in relation to those in other [Ru(porph)(CO)] systems.[1212] Resonance Raman spectroscopic studies of [Ru(OETPP)L] (H_2OETPP = 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetraphenylporphyrin, L = CO or py) provide evidence for $Ru^{II} \rightarrow$ porph backbonding; the effects of the substituents on the orbital energy levels is discussed.[1213] $Ru^{II} \rightarrow$ porph backbonding is also apparent in Ru^{II} derivatives involving octachloro- and octabromotetra(pentafluorophenyl)porphyrin and CO and py axial ligands; it is also noted that the reduction potentials of these complexes are significantly more positive than those for the corresponding non-halogenated species.[1214] An important property of the 5,10,15,20-tetra(pentafluorophenyl)porphyrinato complex [Ru(TPFPP)(CO)] is its ability to act as an efficient catalyst in hydrocarbon oxygenations; there is evidence that the reaction proceeds through an Ru^{III} intermediate.[1215] Static and time-resolved emission spectroscopy and ultra-fast transient absorption measurements have been used to probe the lowest-energy excited states (shown to be Os-to-ring 3(d,π*) CT) of [Os(OEP)(CO)L], [Os(OEP)L_2], [Os(TTP)(CO)L], and [Os(TTP)L_2] (L = σ-donor, e.g., py). These results have been compared with those reported for analogous Ru^{II} complexes, and the part played by the axial ligands in determining the character of the lowest excited states has been assessed.[1216] The electrochemical behavior of [Ru(OEP)(CO)L] and [Ru(OEP)(CO)] (L = various axial ligands) in a range of different solvents has been investigated. Depending on the solvent, the complexes undergo two porphyrin-centered oxidations and either one or two reduction processes which may be either porphyrin or Ru-centered, depending on solvent and the nature of the ligand L.[1217] Ruthenium(II) porphyrinato complexes incorporating an axial thiocarbonyl ligand include [Ru(TPP)(CS)(EtOH)] which has been structurally characterized.[1218] The reaction of the analogous carbonyl complex with an excess of diethyl diazomalonate results in the formation of a carbene species; reactions of [Ru(TPP)(CO)(EtOH)] with CO, py, and PPh_3 have also been studied.[1219] The one-electron oxidation of [Ru(TPP)(CS)(EtOH)] yields the corresponding radical cation which has been characterized spectroscopically. It has been noted that the Ru—CS bond is strong and resists attack by nucelophiles.[1220] The coordination of PF_3 as an axial ligand in Ru^{II} porphyrinato complexes has also been reported.[1221]

The solid-state structures of ruthenium porpyrinato complexes containing axial NO ligands have been included in a structure-based review.[1222] The reaction of [Ru(OEP)(CO)] with NO^+ and exposure to air leads to the formation of $[Ru(OEP)(NO)(H_2O)]^+$, the structure of which has been determined. $[Ru(OEP)(NO)(H_2O)]^+$ is a convenient precursor to a number of complexes including some with novel ligands, e.g., [Ru(OEP)(NO)(SR)], $[Ru(OEP)(NO)(Et_2NNO\text{-}O)]^+$, and $[Ru(OEP)(NO)(NHEt_2)]^+$.[1223,1224] The Os^{II} complex $[Os(OEP)(NO)(Et_2NNO\text{-}O)]^+$ may be prepared by the reaction of NO^+ with [Os(OEP)(CO)(Et_2NNO-*O*)], itself made by reaction of the nitrosamine with [Os(OEP)(CO)].[1224] As well as the OEP^{2-} derivative described above, $[Ru(TPP)(NO)(H_2O)]^+$ has also been prepared, and treatment with pyridine yields $[Ru(TPP)(NO)(py)]^+$. Both $[Ru(TPP)(NO)(H_2O)]^+$ and [Ru(TPP)(NO)(NO_2-*O*)] (the structure of which has been determined)[1225,1226] undergo irreversible Ru-centered reduction with concomitant dissociation of the ligand *trans* to NO.[1225] Starting from the appropriate carbonyl complex, [Ru(OEP)(NO)(NO_2-*O*)], [Ru(OEP)(NO)(OH)], and [Ru(TPP)(NO)(OH)] have been prepared and structurally characterized.[1226] The kinetics of the reactions between nitric oxide and [Ru(OEP)(CO)] or [Ru(TMTP)(CO)] to give [Ru(OEP)(NO)(NO_2-*O*)] or [Ru(TMTP)-(NO)(NO_2-*O*)] (H_2TMTP = 5,10,15,20-tetra(3-tolyl)porphyrin) and N_2O have been investigated. The data are consistent with an initial rate-limiting step in which CO dissociates from a reactive intermediate which is formed in low concentrations by the reversible addition of NO to [Ru(porph)(CO)].[1227] Grignard reagents react with [Ru(TPP)(NO)Cl] to give alkyl or aryl derivatives [Ru(TPP)(NO)R] and the crystal structure of [Ru(TPP)(NO)(4-FC_6H_4)] has been elucidated. Insertion by SO into the Ru—C bond in [Ru(TPP)(NO)Me] has been observed.[1228] The preparation of Os^{II} alkyl and aryl derivatives [Os(OEP)(NO)R] has been carried out by reaction of [Os(OEP)(CO)] with NO^+ followed by treatment with an appropriate Grignard reagent RMgX. Depending on the reaction conditions, the products may include [Os(OEP)R_2], [Os(OEP)(NO)X], and [{Os(OEP)(NO)}$_2$(μ-O)].[1229] The synthesis and crystal structure of

[Ru(TTP)(NO)(OMe)] have been described; this complex undergoes substitution of the MeO^- ligand and is a useful starting material for a range of compounds, including [Ru(TTP)-(NO)(SC_6H_4-4-Me)], (considered to be an analog of an NO adduct of P-450 monooxygenases), [Ru(TTP)(NO)Cl], [Ru(TTP)(NO)(NO_2-*O*)], and [Ru(TTP)(NO)(NO_3-*O*)].[1230] The reactions of [Os(OEP)(CO)] and [Os(TTP)(CO)] with RSNO or RONO lead to the formation of [Os(OEP)(NO)(SR)] and [Os(OEP)(NO)(OR)] or [Os(TTP)(NO)(SR)] and [Os(TTP)(NO)(OR)] respectively. Representative structures have been determined.[1231] The complex [Os(OEP)(CO)] reacts with *n*-butyl nitrite, iso-pentyl nitrite, or iso-pentyl thionitrite to give [Os(OEP)(NO)(OBu)], [Os(OEP)(NO)($O^iC_5H_{11}$)], or [Os(OEP) (NO)($S^iC_5H_{11}$)] respectively. The reaction of $[Os_2(OEP)_2][PF_6]_2$ with iso-pentyl thionitrite results in the formation of [Os(OEP)(NO)][PF_6], hydrolysis of which affords [Os(OEP)(NO)(O_2PF_2)], the structure of which has been been confirmed by an X-ray diffraction study.[1232] Starting from the appropriate thionitrite, reaction with [Ru(OEP)(CO)] gives a route to [Ru(OEP) (NO)($SCMe_2CH_2NHCOMe$)], protonation of which yields [Ru(OEP)(NO)($HSCMe_2CH_2NHCOMe$)]$^+$ almost quantitatively. Both the thiolate and thiol complexes have been structurally characterized.[1233] When [Ru(OEP)(NO)L] (HL = $^iC_5H_{11}OH$, CF_3CH_2SH) are irradiated at low temperature, metastable η^1-O and η^2-NO linkage isomers are formed.[1234] The reactions of [Ru(OEP)(NO)(OTf)] and [Ru(TTP)(NO)(OTf)] with [Bu_4N][OsO_3N] yield [(OEP)(NO)Ru^{II}(μ-N)$Os^{VIII}O_3$] and [(TTP)(NO)Ru^{II}(μ-N)$Os^{VIII}O_3$], respectively. Formation of the nitrido bridge has been confirmed by the structural determination of [(OEP)(NO)Ru^{II}(μ-N)$Os^{VIII}O_3$]; pertinent bond angles are Ru—N—O = 153(1)° and Ru—N—Os = 138.4(8)°. Several related nitrido-bridged species have also been reported.[1235] On treatment of [Ru(TTP)(NS)Cl] with $AgNO_2$, an unexpected thionitrosyl/nitrite to nitrosyl/thiazate transformation is observed.[1236] The direct transfer of an O atom from N_2O to [Ru(TMP)($thf)_2$] (H_2TMP = 5,10,15,20-tetramesitylporphyrin) has been observed with the formation of [Ru^{VI}(TMP)$(O)_2$].[1237] [Ru(TMP)($PhCH_2NH_2)_2$] has been isolated and structurally characterized; this complex and analogous species are intermediates in the aerobic dehydrogenation of amines catalyzed by [Ru(TMP)$(O)_2$].[1238] The reactions of [Ru(porph)$(O)_2$] (H_2porph = H_2TTP or $H_2$4-ClTPP) with Et_3N result in the formation of [Ru(porph)($EtN{=}CHMe)_2$] complexes which have been characterized spectroscopically and by the crystal structure determination of [Ru(TTP)-($EtN{=}Me)_2$].[1239]

The addition of CF_3CH_2NC or CH_2FCH_2NC to [Ru(TPP)(CO)] yields [Ru(TPP)($CF_3CH_2NC)_2$] or [Ru(TPP)($CFCH_2CH_2NC)_2$] respectively. ^{1}H and ^{19}F NMR spectroscopic data for these and the corresponding alkyl isocyanide derivatives suggest similarities in the bonding properties of members of this family of compounds.[1240]

The photophysical properties of [Ru(TBP)(CO)(EtOH)], [Ru(TBP)$(pyz)_2$], [Ru(TBP)$(pyz)]_n$ (H_2TBP = 5,10,15,20-tetra(3,5-*tert*-butyl-4-hydroxyphenyl)porphyrin) have been investigated by steady-state and time-resolved absorption and emission spectroscopies. The complexes are weakly luminescent, and the origins of this behavior is discussed.[1241] Transient Raman spectroscopic data have been reported for [Ru(TPP)$(py)_2$], [Ru(TPP)(CO)(py), and [Ru(TPP)$(pip)_2$] (pip = piperidine),[1242] and nanosecond time-resolved resonance Raman spectroscopy has been used to examine the CT excited states of [Ru(OEP)$(py)_2$] and [Ru(TPP)$(py)_2$].[1243]

The reaction of $[Ru_2(OEP)_2]$ with RR′S or RR′SO (R = Me, Et, $C_{10}H_{20}$; R′ = Me, Et) produces [Ru(OEP)(RR′S)$_2$] or [Ru(OEP)(RR′SO-*S*)$_2$], respectively. Electrochemical oxidation of the sulfoxide complex is accompanied by *S*- to *O*-bound linkage isomerization.[1244] When solutions of the [Ru(OEP)(RR′S)$_2$] complexes containing $PhCO_2H$ are exposed to O_2 or air, the thioether ligands are oxidized to sulfoxides. A possible mechanism for this process is discussed.[1245] Heating [Ru(OEP)($SCH_2CH_2)_2$] (SCH_2CH_2 = ethylene sulfide) under vacuum leads to the formation of [(OEP)Ru(μ-S)Ru(OEP)], confirmed by a crystal structure determination.[1246]

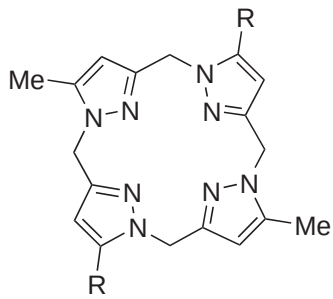
The reaction of *cis*-carbonaldehydic methyl ester and pyrrole leads to the formation of the D_2-symmetric atropisomer of tetramethylchiroporphyrin, H_2TMCP. The complex [Ru(TMCP)-(CO)(EtOH)] has been prepared and its structure determined; the cyclopropyl substituents are alternatively above and below the N_4-containing ring. The complex enantioselectively binds chiral aliphatic alcohols and the intermolecular interactions that lead to this recognition are discussed.[1247] The chiral recognition of amino esters[1248,1249] and racemic benzylmethylphenylphosphine[1250] by Ru^{II} picket-fence porphyrin complexes bearing α-methoxy-α-(trifluoromethyl)phenylacetyl groups has also been reported. The preparations and structural characterization of [Ru(TPP)(CO)(1-Meim)] and the pocket-porphyrinato complex [Ru(α-PocPivP)(CO)(1-Meim)] have been described; the structural parameters have been compared with those of a range of related complexes.[1251] The protected pocket of [Ru(β-PocPivP)(CO)(H_2O)] hosts the H_2O axial ligand, and hydrogen bonding between the guest molecule and amide O atom is observed in the solid-state

structure of the complex.[1252] In a related structural study, an axially bound H_2O ligand in a capped-porphyrinato Ru^{II} complex also resides in the sterically protected site, but in this case, the important intermolecular interactions are between H_2O and the aromatic π-system of the capping unit.[1252]

A number of polynuclear porphyrin-containing Ru^{II} and Os^{II} complexes have been reported. These fall into three general types, although there is overlap between the categories: (i) systems assembled by bridging [Ru(porph)] units via the axial ligand sites, (ii) [Ru(porph)] complexes carrying peripheral metal-binding domains, or (iii) porphyrin ligands carrying peripheral Ru^{II}-binding domains. Photochemical decarbonylation of [Ru(TBP)(CO)] ($H_2TBP = 5,10,15,20$-tetra(3,5-*tert*-butyl-4-hydroxyphenyl)porphyrin) in the presence of pyrazine or 4,4′-azopyridine results in oligomers consisting of Ru(TBP) units bridged by pyz or 4,4′-azopyridine ligands (the so-called "shish kebab" oligomers). Diiodine oxidizes the Ru^{II} centers, and intervalence transitions between Ru^{II} and Ru^{III} are observed in the near-IR region.[1253] The electrochemical, two-electron oxidation of [Ru(TPP)L_2] (e.g., L = 4,4′-bpy, (*E*)-1,2-bis(4-pyridyl)ethene, 4,4′-azopyridine) gives rise to "shish kebab" oligomers which differ from those formed by chemical oxidation.[1254] Discrete dinuclear and trinuclear complexes which also contain diaza bridges have been prepared: [(OEP)(CO)Ru(μ-L)Ru(CO(OEP)],[1255] [(OEP)(CO)Ru(μ-pyz){Ru(CO(OEP)}(μ-pyz)Ru-(CO(OEP)],[1256] and [(TPP)(CO)Ru(μ-4,4′-bpy){Ru(CO(TPP)}(μ-4,4′-bpy)Ru(CO(TPP)].[1256] The monomers [Ru(OPTAP)L_2] (H_2OPTAP = octaphenyl tetraazaporphyrin; L = py, pyz, 1,2,4,5-tetrazine, ^{t}BuNC, 1,4-$(NC)_2$-2,3,5,6-Me_4C_6) have been prepared and characterized. For L = pyz and 1,2,4,5-tetrazine, heating solutions of [Ru(OPTAP) L_2] at reflux results in the formation of [L(OPTAP)Ru(μ-L)Ru(OPTAP)L] and some oligomeric products. For L = 1,4-$(NC)_2$-2,3,5,6-Me_4C_6, insoluble polymers are formed on heating the monomer.[1257] The reaction between H_2Py_4P (5,10,15,20-tetra(4-pyridyl)porphyrin) and [Ru(TPP)(CO)(EtOH)] leads to substitution of the EtOH ligands and the formation of [{(CO)(TPP) Ru}$_4$(H_2Py_4P)] with each pyridyl group of the H_2Py_4P acting as an axial ligand to a Ru(TPP)(CO) unit. The Zn^{II} complex [{(CO)(TPP)-Ru}$_4$($ZnPy_4P$)] has also been prepared. The two complexes have box-like structures and the zinc complex captures $Ru^{II}(Me_2SO)$ species into the cavity via S → Zn bond formation.[1258] In related chemistry, the direct reactions of a series of pyridyl porphyrins $H_2Py_nPh_{4-n}P$ ($n = 1$–4) with $Ru^{II}(Me_2SO)$ species have been studied.[1259] Members of this series of porphyrins have been used as building blocks to create assemblies with porphyrin units that are mutually perpendicular, e.g., *cis*-[{Os(OEP)(CO)}$_2$($H_2Py_2Ph_2P$)], *trans*-[{Os(OEP)(CO)}$_2$($H_2Py_2Ph_2P$)], [{Os(OEP)(CO)}$_3$-(H_2Py_3PhP)], [{Os(OEP)(CO)}$_4$(H_2Py_4P)],[1260] and Ru^{II} analogs.[1261] The crystal structure of [Ru(OEP)(CO)(H_2PyPh_3P)] has been elucidated.[1261] A similar methodology, but with Ru^{II} coordinated within the pyridyl porphyrin, is used to construct cyclic tetramers such as [{Ru($PyPh_3P$)(CO)}$_4$],[1262] as well as cofacially arranged chain-like tetramers.[1263] The cyclic tetramer [{Ru($PyPh_3P$)(CO)}$_4$] undergoes a photochemical substitution reaction in which each CO is replaced by an H_2PyT_3P ligand (H_2PyT_3P = 5-(4-pyridyl)-10,15,20-tetra(4′-methylphenyl) porphyrin) thereby generating a Ru_4(porph) core surrounded by four porphyrin ligands capable of acting as metal-binding domains.[1264] Ruthenium(II) porphyrin-centered complexes bearing peripheral Ni^{II} or Zn^{II} porphyrin groups have been prepared and used as building blocks for the assembly of much larger arrays consisting of, for example, 21 porphyrin units.[1265]

Collman *et al*. have reported the syntheses, characterization, and properties (including magnetic behavior, representative structural details, and resonance Raman spectroscopic data) of a range of homo- and heterometallic porphyrin dimers and tetramers supported by metal–metal multiple bonds: [Ru_2(OETAP)$_2$],[1266,1267], [Ru_2(OEP)$_2$],[1267] [Os_2(OEP)$_2$],[1267] [Os(OETAP)$_2$],[1266] [(OEP)RuRu-(OETAP)],[1266] [(OEP)RuRu(OETAP)]$^+$,[1266] [(OEP)OsRu(OETAP)],[1266] [(OEP)MoOs-(OEP)],[1268,1269] [(OEP)MoRu (TOEP)],[1268] [(OEP)MoRu(OEP)],[1270] [(OEP)WRu(OEP)],[1269] [(OEP) WOs(OEP)],[1270] [(OEP)MoRu(TPP)]$^+$,[1270,1271] [(OEP)MoOs(TPP)]$^+$,[1269] [(OEP)WRu-(TPP)]$^+$,[1269] [Ru_2(TPP)$_2$]$^+$,[1272] and [(OETAP)Ru_2(μ-DPA)Ru_2(OETAP)][1273] (H_2OETAP = octaethyltetraazaporphyrin; H_2TOEP = 5-(4-methylphenyl)-2,3,7,8,12,13,17, 18-octaethylporphyrin; H_4DPA = 1,8-bis{5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrinyl}anthracene).

Ruthenium(II) complexes [Ru(**313**)XY] containing the tetraazaporphyrinogens (**313**) have been prepared and characterized (X = Y = py, pz, MeCN, PhCN, 4-MeOpy, 3-Mepyz, 3,5-Me_2pyz; X = dmso, Y = H_2O, py; X = MeCN, Y = py). The dynamic behavior of these complexes in solution has been investigated using variable-temperature ^{1}H NMR spectroscopy.[1274] Ligands (**314**) are closely related to (**313**), and the properties and solution behavior of the complexes [Ru(**314**)XY][PF_6]$_2$ (X, Y = dmso, MeCN, py, pz, or 3,5-Me_2pz) have been compared to their tetrapyrazole analogs.[1275] Development of this work has led to the introduction of ferrocenyl substituents into ligand (**313**).[1276]



(**313**) R = Me, Ph
(**314**) R = OMe, OH

5.5.3.1.19 Complexes containing phthalocyanine ligands

Much of the work described in this section comes from the independent groups of Hanack and Homborg. The bis(isocyanide) complexes $[Ru(Pc)(CNR)_2]$ (H_2Pc = phthalocyanine; R = ^{t}Bu, Cy, Bz, Ph, 2,6-$Me_2C_6H_3$) and their Fe^{II} analogs have been prepared and characterized, and the effects of changing the metal ion on metal–ligand bonding have been assessed.[1277] Azanaphthalene has also been introduced as an axial ligand in $[Ru(Pc)L_2]$ complexes.[1278] The reactions of phthalonitrile with $[Ru_2Cl_3(PEt_2Ph)_6]Cl$ in the presence of DBU, and of [RuPc] with PEt_2Ph or PPh_3 lead to the complexes $[Ru(Pc)L_2]$ where L = PEt_2Ph or PPh_3.[1279] Molten $[Bu_4N]X$ (X = Cl, Br) reacts with $[Ru(Pc)(py)_2]$ to produce the $[Bu_4N]^+$ salts of $[Ru(Pc)X_2]^{2-}$ for which spectroscopic and electrochemical data have been reported.[1280] Halogen oxidation of $[Ru(Pc)X_2]^{2-}$ (X = Cl, Br, OH) yields the corresponding Ru^{III} complexes. The values of $\mu_{eff} = 2.48$ and 2.56 μ_B for $[Ru(Pc)Cl_2]^-$ and $[Ru(Pc)Br_2]^{2-}$ respectively are consistent with systems consisting of two independent spins, i.e., low-spin Ru^{III} and Pc^-.[1281] Oxidation of $[Ru^{II}(Pc^{2-})(CO)X]^-$ (X = Cl, Br) is ligand-centered and produces $[Ru^{II}(Pc^-)(CO)X]$.[1282] Carbon monoxide reduces $[Ru(Pc)(OH)_2]^-$ to the Ru^{II} complex $[Ru(Pc)(CO)(H_2O)]$, and treatment of this with excess $[Bu_4N]X$ (X = Cl, Br, I, NCO, NCS, N_3) yields diamagnetic salts of $[Ru(Pc)(CO)X]^-$.[1283] The compounds $[Bu_4N][Ru(Pc)(py)X]$ (X = CN, N_3, NCO, NCS, NO_2) can be prepared from $[Bu_4N]_2[Ru(Pc)X_2]$ in boiling pyridine; the crystal structure of $[Bu_4N][Ru(Pc)(py)(CN)]$ has been determined.[1284] The complexes [Ru(Pc)(NO)X] (X = F, Cl, Br, I, CN, NCO, NCS, NCSe, N_3, NO_2) have been prepared starting from the bis(nitro) derivative.[1285] Electrochemical studies of $[Os(Pc)(CN)_2]^{2-}$ and $[Os(Pc)(py)_2]$ in MeCN, dmf, and aqueous solutions have been carried out.[1286]

Initial attempts to prepare the tetrakis(*tert*-butyl) derivative $[Ru(^tBu_4Pc)]$ led to an impure product from which, after treatment of pyridine, $[Ru(^tBu_4Pc)(py)_2]$ can be isolated. The adducts $[Ru(^tBu_4Pc)(2\text{-pic})_2]$, $[Ru(^tBu_4Pc)(3\text{-pic})_2]$, $[Ru(^tBu_4Pc)(4\text{-pic})_2]$ (pic = picoline), $[Ru(^tBu_4Pc)(2,5\text{-lut})_2]$, and $[Ru(^tBu_4Pc)(2,6\text{-lut})_2]$ (lut = lutidine) have also been prepared and characterized.[1287] The photophysical properties of $[Ru(^tBu_4Pc)(py)_2]$ have been investigated; the complex phosphoresces at room temperature.[1288] The thermal decomposition of $[Ru(^tBu_4Pc)L_2]$ (L = NH_3, 3-Clpy) proves to be a successful route to $[Ru(^tBu_4Pc)]$.[1289] Thermal loss of axial 3-Clpy ligands is also observed from the complex $[Ru\{(Me_3Si)_4Pc\}(3\text{-Clpy})_2]$ and allows the synthesis of $[Ru\{(Me_3Si)_4Pc\}]$, which has been spectroscopically characterized.[1290]

The synthesis of [RuL] where H_2L = 2,3-naphthalocyanine has been reported. Reactions with suitable bridging ligands lead to oligomers, electrical conductivity data for which have been compared with those of related compounds.[1291] The tetrakis(*tert*-butyl) derivative $[Ru(^tBu_4L)]$ has been prepared by the thermal decomposition of the $[Ru(^tBu_4L)(L_{ax})_2]$ (L_{ax} = NH_3, 3-Clpy).[1289]

The results of an EXAFS study of [Ru(Pc)] have been compared with those of $[Ru(Pc)(BuNH_2)_2]$. Data for [Ru(Pc)] confirm a dimeric structure.[1292] This has been independently confirmed from large-angle X-ray scattering studies.[1293] The wide-angle X-ray scattering technique has been used to investigate the structure of [Os(Pc)], obtained from the bis(pyridine) adduct. A dimeric structure is consistent with the data.[1294] Vacuum pyrolysis of $[Ru(R_8Pc)(3\text{-Clpy})_2]$ (H_2R_8Pc = octa-substituted H_2Pc derivatives with R = $C_5H_{11}O$, 2-ethylhexyloxy) leads to $[Ru(R_8Pc)]$. This reacts with 1,4-diisocyanobenzene or 1,4-diisocyano-2,3,5,6-tetramethylbenzene (L) to produce oligomers in which the ligands L bridge between the Ru^{II} centers.[1295] 1,2,4-Triazines (L) have also been used as bridging ligands in oligomeric complexes; the oligomeric species $[Ru(Pc)L]_n$ show good semiconducting properties.[1296]

5.5.3.1.20 Complexes containing aza-macrocyclic ligands

The azamacrocycle 1,4,7-triazacyclononane (tacn) and its tris(*N*-methyl) analog (Me_3tacn) are popular ligands in macrocyclic chemistry. Complexes of both M^{II} and M^{III} (M = Ru, Os) containing the tacn ligand are dealt with together in this section along with several dinuclear, M—M bonded species.

The reaction of tacn with $[Os_2Br_4(CO)_2(PPh_3)_4]$ in the presence of a small amount of $ZnCl_2$ leads to the formation of $[Os(tacn)(CO)Cl(PPh_3)]^+$ as a minor product. The product was isolated as the $[ZnCl_4]^{2-}$ salt and has been structurally characterized.[1297] The crystal structures of the ruthenium-blue complexes $[Ru_2(\mu\text{-}X)_3(tacn)_2][PF_6]_2 \cdot nH_2O$ (X = Cl, $n = 4$; X = Br, $n = 2$; X = I, $n = 0$) have been determined; structural parameters have been compared with those of the analogous ammine complexes.[1298] In $[Ru(Me_3tacn)Cl_3]$, the Cl^- ligands are readily substituted by NCO^-, NCS^-, and N_3^- in aqueous solution. The azido complex $[Ru(Me_3tacn)(N_3)_3]$ readily converts to $[Ru(Me_3tacn)(N_3)_2(N_2)]$.[1299] The preparation and crystal structure of $[Ru(Me_3tacn)(bpy)(H_2O)]^{2+}$ have been reported; the complex exhibits two reversible proton-coupled one-electron redox processes assigned to the stepwise oxidation of Ru^{II} to Ru^{III} to Ru^{IV}.[1300] The complexes $[Os(Me_3tacn)Cl_3]$ and $[Os(tacn)Cl_3]$ have been prepared starting from $[Os_2Cl_8]^{2-}$. Reaction of the tacn derivatives with triflic acid generates $[LOs(\mu\text{-}Cl)_3OsL]^{3+}$ (L = tacn, Me_3tacn). These Os^{III}–Os^{III} species are reduced to mixed valence complexes on treatment with zinc amalgam in solution, and the latter can also be accessed electrochemically. Further electrochemical reduction leads to the formation of the corresponding Os^{II}–Os^{II} species.[1301] The reaction of $[Ru^{III}(Me_3tacn)Cl_3]$ with 1,2-phenylenediamine, L, in aqueous solution in air yields $[Ru^{II}(Me_3tacn)(L')(H_2O)]^{2+}$ where L′ is the diimine ligand derived from L. At pH 12, this is converted into $[(Me_3tacn)(L')Ru^{II}(\mu\text{-}H_3O_2)Ru^{II}(Me_3tacn)(L')]^{3+}$. Reactions of $[Ru(Me_3tacn)(L')(H_2O)]^{2+}$ with MeCN and N_3^- result in replacement of the aqua ligand; $[Ru(Me_3tacn)(L')(I)]^+$ can be obtained directly from $[Ru^{III}(Me_3tacn)Cl_3]$ by treatment with L and I^- in aqueous solution. Structural and electrochemical data are presented for the new products.[1302] The protonation of [Ru(tacn)H(LL′)] and $[Ru(Me_3tacn)H(LL')]$ where LL′ = $(PPh_3)_2$, dppe or $(CO)(PPh_3)$, leads to $[Ru(tacn)(H_2)(LL')]^{2+}$ and $[Ru(Me_3tacn)(H_2)(LL')]^{2+}$ respectively. The acidities of these species have been investigated and compared with those of corresponding complexes in which the azamacrocycle is replaced by $[HBpz_3]^-$ or Cp^-.[1303]

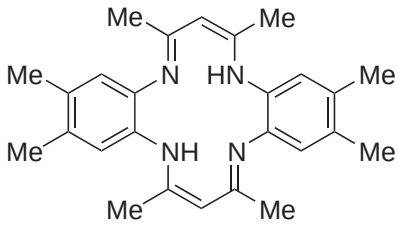
1,4,8,11-Tetraazacyclotetradecane (cyclam) forms the complexes *trans*-$[Ru(cyclam)Cl(L)]^+$ in which L = 4-pic, py, isonicotinamide or 4-acetylpyridine; the precursor is *trans*-$[RuCl_2(cyclam)]^+$. The Cl^- ligand in $[Ru(cyclam)Cl(L)]^+$ is inert to substitution.[1304] When an aqueous solution of *trans*-$[RuCl_2(16\text{-}TMC)]^+$ (16-TMC = 1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane) under N_2 is reduced with Zn, the product is *trans*-$[RuCl(N_2)(16\text{-}TMC)]^+$, confirmed by a structure determination.[1305]

The reaction of Li_2(**315**) with $[RuCl_2(PPh_3)_3]$ results, after workup, in the formation of *trans*-[Ru(**315**)$(PPh_3)_2$]. The crystal structure of the complex reveals a geometry for the macrocyclic ligand that illustrates a distortion from the saddle-shaped structure found for the free H_2(**315**) ligand. At low temperature, the solution ^{31}P NMR spectrum of [Ru(**315**)$(PPh_3)_2$] exhibits two signals, consistent with the presence of major and minor isomers. The ability of [Ru(**315**)$(PPh_3)_2$] to act as a catalyst for the hydrogenation and isomerization of hex-1-ene has been studied.[1306] In work that is related to that described at the end of Section 5.5.3.1.19,[1275,1276] the syntheses and complex formation of a series of unsymmetrical macrocyclic ligands have been described. Representative members of the group of ligand groups are (**316**) and (**317**), and each reacts with $[RuCl_2(dmso)_4]$ to give an $[RuLCl_2]$ complex.[1307]

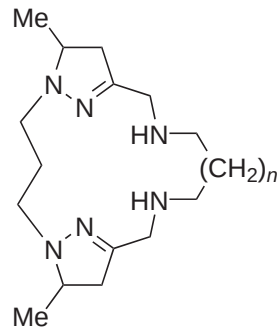
5.5.3.1.21 Complexes with miscellaneous N-donor heterocyclic ligands

This section covers Ru^{II} and Os^{II} complexes of a number of *N*-heterocyclic ligands that were not readily included in previous sections. There is some overlap with coverage in Section 5.5.3.1.1.

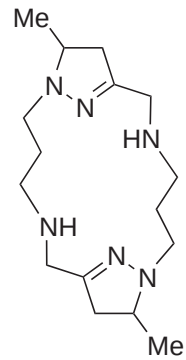
The ligand pyrazin-2-yl 2-pyridyl sulfide (L) has been prepared and its reactions with $[Ru(bpy)_2(NO)(NO_2)]^{2+}$, $[Ru(dps)_2(NO)(NO_2)]^{2+}$, and *cis*-$[Ru(dps)_2Cl_2]$ (dps = di(2-pyridyl) sulfide) studied. In each of the products $[Ru(bpy)_2(L)(NO_2)]^{2+}$, $[Ru(dps)_2(L)(NO_2)]^{2+}$, and $[Ru(dps)_2(L)Cl]^+$, L is monodentate and has the potential to act as a bridging ligand as is observed in $[(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2(NO_2)]^{3+}$, for example.[1308] The carbazole ligand (**318**) has been incorporated into the complexes [Ru(**318**)$(NH_3)_5]^{2+}$ and [Ru(**318**)(bpy)(tpy)]$^{2+}$ in which (**318**) binds through the pyridine *N*-donor. The ground-state electronic properties of the



H_2 (315)

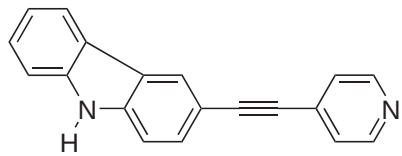


(316) $n = 0, 1$



(317)

complexes have been investigated using electrochemical and UV–vis spectroscopic methods. The fluorescence of the carbazole unit is reduced on complex formation.[1309] The 2,3-dpp ligand (**88**) forms the complex $[Ru(2,3\text{-dpp})(CN)_4]^{2-}$, the spectroscopic properties of which indicate that, in these types of complexes, 2,3-dpp possesses π-acceptor properties partway between those of bpy and bpz. The mixed-valence complex $[(CN)_4Ru(\mu\text{-}2,3\text{-dpp})Ru(CN)_4]^{3-}$ has also been prepared and exhibits a weak interaction between the Ru centers.[1310]



(318)

The basicity of the non-coordinated pyrazine N atom in the complexes $[Ru(pyz)(NH_3)_5]^{2+}$ and $[Ru(pyz)(CN)_5]^{3-}$ has been probed by DFT methods. For a representation of behavior in solution, solvent effects were modeled using a self-consistent reaction field Onsager model.[1311] The reaction of 2,6-Me_2pyz with $[RuCl_2(dmso)_4]$ leads to the formation of a mixture of geometrical isomers of $[RuCl_2(dmso)_2(2,6\text{-}Me_2pyz)_2]$. The more stable isomer of the two formed possesses *cis*-Cl, *cis*-dmso and *trans*-2,6-Me_2pyz ligands.[1312]

Pyrazole complexes of type $[RuCl_2(pz)(dmso\text{-}S)_3]$ and $[RuCl_2(pz)_2(dmso\text{-}S)_2]$ have been synthesized and characterized spectroscopically and crystallographically. The complexes react with a range of species including CO, NO^+, and H^-.[1313]

Benzotriazole (Hbta) reacts with $[MH(Cl)(CO)(PPh_3)_3]$ (M = Ru, Os) to yield isomers of $[MH(Cl)(Hbta)(CO)(PPh_3)_2]$. Starting from $[M(H)_2(CO)(PPh_3)_3]$, the reaction with Hbta produces $[MH(bta)(Hbta)(CO)(PPh_3)_2]$ for which a crystal structure has been determined for M = Os. The bta^- Hbta ligands are mutually *cis* and are associated by hydrogen bonding.[1314,1315] The reactions of $[Ru(dmf)_6]^{3+}$ with imidazole, *N*-methylimidazole, and 5-methylimidazole (L) lead to the formation of $[RuL_6]^{2+}$; with 2-methylimidizaole, it was possible to isolate *trans*-[Ru(CO)(dmf)-(2-Meim)$_4$] (from which CO is readily lost) in which the CO ligand originates from dmf. Structural data are presented for $[Ru(im)_6][CF_3SO_3]_2$, $[Ru(1\text{-}Meim)_6][CF_3SO_3]_2$, and $[Ru(5\text{-}Meim)_6][CF_3SO_3]_2$.[1316] A series of Ru^{II} complexes involving 1,3-thiazole (thz) and anti-leukaemia drug thiopurines has been reported; these include $[RuCl_2(PPh_3)_2(thz)_2]$, $[RuCl_2(PPh_3)(thz)_3]$ (for which the crystal structure was determined), $[Ru(H_2L)_2(PPh_3)(thz)]^{2+}$ (HL = purine-6-thione), and $[Ru(H_2L')_2(PPh_3)_2]^{2+}$ (H_2L' = purine-6-thione, purine-2-amino-6-thione, purine-6-thione 2′,3′,5′-tri-O-acetylriboside).[1317]

5.5.3.1.22 Interactions of ruthenium(II) complexes with DNA and related work

Interest in the interactions between DNA and Ru^{II} complexes such as $[Ru(phen)_3]^{2+}$ has led to a large number of publications between the mid-1980s and 2002. Severe page constraints on this

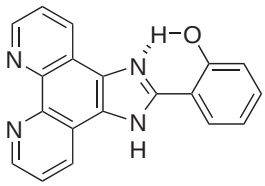
review mean that is not possible to provide a fully comprehensive survey of this area. However, it is hoped that the discussion that follows will give the reader an appropriate entry into the literature. Chiral polypyridyl complexes of, for example, Ru^{II} find wide use as probes of DNA structure. The exact mode of binding between ligand/complex and DNA is, however, open to much discussion concerning nonintercalative vs. intercalative interactions. This is well illustrated by the results reported in this section. A highly pertinent review looks at the applications of phen and its derivatives in, for example, the chiral recognition of DNA and the development of DNA assays.[1318]

Before looking at individual complexes and models, we focus on some work of general significance. One particularly interesting step forward into probing ligand–DNA binding is the use of scanning force microscopy (SFM). Using $[Ru(phen)_3]^{2+}$ as the test complex, it is concluded that $[Ru(phen)_3]^{2+}$ binds to duplex nucleic acids through nonintercalative modes.[1319] One recent method for the site-specific incorporation of polypyridyl complexes into oligonucleotides applies automated phosphoramidite chemistry. $[M(3\text{-ethynyl-phen})(bpy)_2]^{2+}$ (M = Ru, Os) units are covalently linked via the terminus of the ethynyl substituent to 2′-deoxyuridine residues (see also refs. 1359, 1360). This provides a route to metal-containing phosphoramidites with predetermined absolute configuration at the M^{II} center which can be used in the preparation of diastereomerically pure M^{II}-containing DNA oligonucleotides.[1320,1321] Molecular modeling calculations that allow for solvent effects have been applied to the interactions between Δ- and Λ-$[Ru(phen)_3]^{2+}$ and DNA. For both optical isomers, the lowest-energy binding geometry places one phen ligand in the major groove, but is not intercalated. Significantly, the results show that positioning Δ-$[Ru(phen)_3]^{2+}$ with two phen ligands in the major groove gives a state that is energetically similar to that with one phen ligand in the groove. This is, however, not the case for Λ-$[Ru(phen)_3]^{2+}$. Complex binding in the minor groove results in no energetic preference over external electrostatic binding.[1322] When Λ-$[Ru(phen)_3]^{2+}$ binds in the major groove of DNA, molecular mechanics calculations indicate that there is a preference for interactions involving purine-3′,5′-pyrimidine rather than pyrimidine-3′,5′-purine sites.[1323] Using a new parameter set at the semi-empirical INDO level, geometry optimizations have been carried out on a large number of Ru^{II} complexes including phen-containing species. DNA-binding of $[Ru(phen)_2(\mathbf{98})]^{2+}$ (**98** = dipyrido[3,2-a:2′,3′-c]phenazine) has been modeled using a complex of $[Ru(phen)_2(\mathbf{98})]^{2+}$ with poly(dA-dT).[1324]

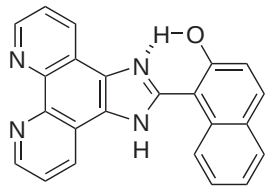
The remaining part of this section is organized by metal-bound ligand, e.g., phen, bpy, phenazine derivatives. The crystal structure of $[Ru(4,7\text{-}Ph_2phen)_3]Cl_2$ was determined and the structural details used to propose a model for the binding of Δ-$[Ru(4,7\text{-}Ph_2phen)_3]$ to right-handed DNA.[1325] The results of equilibrium binding studies have shown that both Δ- and Λ-$[Ru(phen)_3]^{2+}$ bind only weakly to DNA ($K = (4.9 \pm 0.3) \times 10^4$ for Δ and $(2.8 \pm 0.2) \times 10^4$ for Λ-isomer, 293 K). The conclusion of this work is that electrostatic interactions are dominant, and viscosity data support the lack of intercalation.[1326] In a related study, competition dialysis was used to probe the preferences for the Λ- and Δ-isomers of $[Ru(phen)_3]^{2+}$ for binding to right-handed (B-form) and left-handed (Z-form) DNA. The results do not suggest that there is any significant selectivity.[1327] Little enantioselectivity is also observed in the interactions of Δ- and Λ-$[Ru(4,7\text{-}Ph_2phen)_3]^{2+}$ with the B-form of DNA.[1328] NMR spectroscopic techniques have advanced dramatically over the past 20 years, and a 2D NMR investigation of the binding of $[Ru(phen)_3]^{2+}$ to the decanucleotide duplex $[d(CGCGATCGCG)]_2$ was reported in 1992. The data indicate that both Δ- and Λ-$[Ru(phen)_3]^{2+}$ interact with the AT region of the minor groove in a nonintercalative mode.[1329] Extension of this work using NOESY spectroscopy supports these conclusions.[1330] Absorption, linear dichroism (LD), and circular dichroism (CD) spectroscopies and molecular modeling have been used to probe the interactions of Λ- and Δ-$[Ru(phen)_3]^{2+}$, $[Ru(4,7\text{-}Me_2phen)_3]^{2+}$, $[Ru(5,6\text{-}Me_2phen)_3]^{2+}$, and $[Ru(3,4,7,8\text{-}Me_4phen)_3]^{2+}$ with DNA, poly(dA-dT)$_2$, and poly(dG-dC)$_2$. The conclusions reached are that the binding mode depends on the enantiomer, the DNA base sequence, and the phen substituents; concentration effects are also discussed.[1331] The results of studies into the binding of Λ- and Δ-$[Ru(phen)_2(phi)]^{2+}$ and $[Ru(bpy)_2(phi)]^{2+}$ with a number of duplex polynucleotides including calf thymus DNA have led to the conclusions that the phi ligands are intercalated between the base pairs of the polynucleotides and that DNA exhibits chiral discrimination.[1332]

The phen derivatives (**319**) and (**320**) contain intramolecular hydrogen bonds, and have been incorporated into the complexes $[Ru(\mathbf{319})(bpy)_2]^{2+}$ and $[Ru(\mathbf{320})(bpy)_2]^{2+}$. Spectroscopic methods and viscosity data have been used to investigate the interactions between these species and calf thymus DNA. It is proposed that binding of $[Ru(\mathbf{319})(bpy)_2]^{2+}$ involves the intercalation of ligand (**319**) between the base pairs of DNA; partial intercalation is proposed for $[Ru(\mathbf{320})(bpy)_2]^{2+}$.[1333,1334] The length of the spacer in the bridging ligand (**321**) in $[(phen)_2Ru(\mu\text{-}\mathbf{321})$

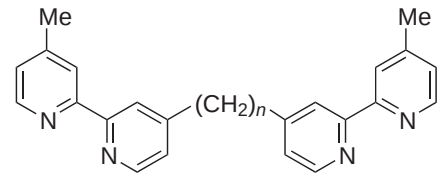
$Ru(phen)_2]^{4+}$ influences the binding of the complex to double-stranded DNA,[1335] and it is found that the related complex $[(bpy)_2Ru(\mu\text{-}\mathbf{321})Ru(bpy)_2]^{4+}$ ($n = 5$ or 7 in (**321**)) binds more strongly to DNA and shows enhanced photocleavage properties than $[Ru(bpy)_3]^{2+}$ or $[Ru(bpy)_2(4,4'\text{-}Me_2bpy)]^{2+}$.[1336,1337] 1,4-Aryl diazopentane-2,4-diones, H_2L, have been prepared along with the Ru^{II} complex $[(phen)_2Ru(\mu\text{-}L)Ru(phen)_2]^{2+}$. Luminescence and UV–vis spectroscopic properties of this complex and the results of studies of its interactions with DNA have been reported.[1338]



(**319**)

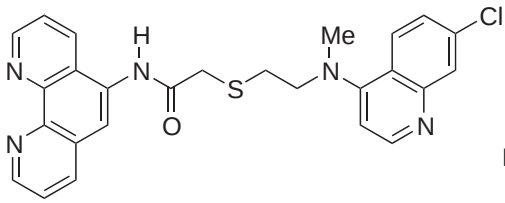


(**320**)

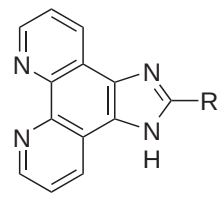


(**321**) n = 5, 7, 10

The complexes $[Ru(bpy)_2(\mathbf{322})]^{2+}$ and $[Ru(tap)_2(\mathbf{322})]^{2+}$ (tap = 102) containing the phen derivative, (**322**), have been prepared and characterized; protonation and deprotonation of the quinoline unit causes unfolding and folding of the complexes. This phenomenon is discussed in terms of the interactions with DNA,[1339] and the interaction of $[Ru(bpy)_2(\mathbf{322})]^{2+}$ with DNA has been studied using luminescence and absorption spectroscopies.[1340] $[Ru(tap)_2(\mathbf{322})]^{2+}$ and $[Ru(tap)_2(phen)]^{2+}$ have been tested as photoprobes of DNA; when $[Ru(tap)_2(\mathbf{322})]^{2+}$ binds to DNA, an emission enhancement of 16–17 times is observed, and the emission depends on the guanine content of the polynucleotide to which the complex binds.[1341] A series of complexes $[Ru(bpy)_2(\mathbf{323})]^{2+}$ has been synthesized and characterized. Their interactions with DNA lead to increased emission lifetimes. It is proposed that the complexes bind to DNA through intercalation.[1342–1344] DNA-binding studies have also been carried out with $[Ru(bpy)_2L]^{2+}$ where L = (**323**) with R = 2-ClC_6H_4 or 2-$O_2NC_6H_4$. Here, data indicate that the complexes bind through a partial intercalative mode which differs from that suggested for the binding of $[Ru(bpy)_2(\mathbf{323}, R = H)]^{2+}$.[1345] Ligand (**324**) has been prepared and characterized, along with the complexes $[Ru(bpy)_2(\mathbf{324})]^{2+}$ and $[(bpy)_2Ru(\mu\text{-}\mathbf{324})Ru(bpy)_2]^{4+}$. Spectrophotometric and viscosity measurements have been used to show that $[Ru(bpy)_2(\mathbf{324})]^{2+}$ binds to DNA through intercalation, whereas electrostatic interactions are involved in binding $[(bpy)_2Ru(\mu\text{-}\mathbf{324})Ru(bpy)_2]^{4+}$ to DNA.[1346]

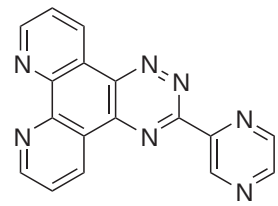


(**322**)



R = H, Ph, 4-ClC_6H_4, 4-HOC_6H_4, 4-$O_2NC_6H_4$, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$

(**323**)



(**324**)

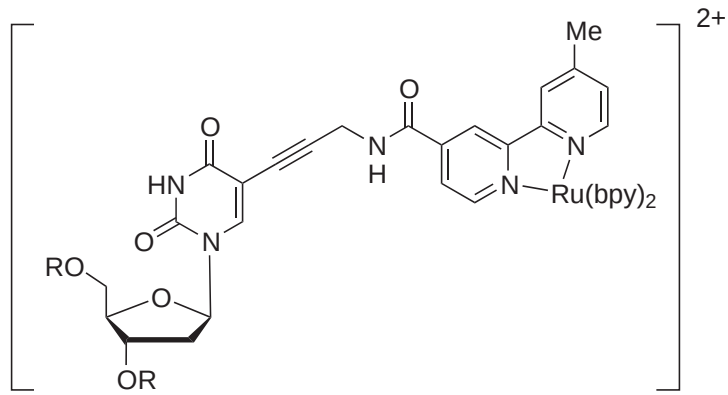
The interactions of the complexes Λ- and Δ-*cis*-*β*-$[Ru(phen)(picchxn)]^{2+}$, where picchxn = *N,N′*-dimethyl-*N,N′*-di(2-picolyl)-1*R*,2*R*-diaminocyclohexane, with [d(CGCGAT CGCG)]$_2$ have been investigated by NMR spectroscopy. It is shown that binding occurs in the minor groove, but that the interactions differ for the different forms of the complex.[1347] Studies of closely related systems have been independently reported. Results for the interaction of Δ-*cis*-*α*-$[Ru(dpq)(picchxn)]^{2+}$ (dpq = dipyrido[3,2-f:2′,3′-h]quinoxaline) with [d(CGCGATCGCG)]$_2$ suggests minor-groove intercalation at the GA base site. For the binding of Δ-*cis*-*α*- and Δ-*cis*-*β*-$[Ru(phi)(picchxn)]^{2+}$, binding in the major groove is proposed.[1348]

Stereoselective covalent binding to DNA was observed in a study that involved the complexes $[Ru(phen)_2(H_2O)_2]^{2+}$, $[Ru(phen)(tpy)(H_2O)]^{2+}$, $[Ru(bpy)(tpy)(H_2O)]^{2+}$, $[Ru(bpy)_2(H_2O)_2]^{2+}$, $[Ru(phen)_2(H_2O)_2]^{2+}$, $[Ru(phen)_2(py)(H_2O)]^{2+}$, and $[Ru(tmen)(tpy)H_2O)]^{2+}$ (tmen = *N,N,N′*,

N′-tetramethylethylenediamine).[1349] Differences in the ability of $[Ru(bpy)_3]^{2+}$, $[Ru(bpz)_3]^{2+}$ and *cis*-$[Ru(bpy)_2Cl_2]$ to photosensitize DNA damage have been assessed.[1350] The complexes $[Ru(bpy)_2L]^{2+}$ and $[Ru(phen)_2L]^{2+}$ (L = Schiff bases or phenylhydrazones derived form 4,5-diazafluoren-9-one) have been prepared; it is proposed that their modes of binding to DNA involve electrostatic interactions, and nonintercalative and intercalative modes depending on the overall shape of each complex.[1351] Changes to the ^{1}H NMR spectra of Δ,Δ- and Λ,Λ-$[(4,4'\text{-}Me_2bpy)_2Ru(\mu\text{-}bpm)Ru(4,4'\text{-}Me_2bpy)_2]^{4+}$ upon addition to $[d(CAATCCGGATTG)]_2$ have been investigated, along with NOESY and nOe studies. The results indicate that the complex binds into the minor groove of DNA, but that steric effects limit the possible sites of binding.[1352] Intramolecular quenching of the excited state of $[Ru(bpy)_2L]^{2+}$ (L = 2,2′-bipyridine-5-carboxamide linked to a 1,4,5,8-naphthalene diimide acceptor) has been studied in the absence or presence of DNA. The diimide group intercalates into DNA. Significantly, the interaction with DNA does little to alter the electron transfer within the complex.[1353]

A number of bpy-containing systems have involved nucleobases and are included in this section. For example, derivatives of $[M(4,4'\text{-}^tBu_2bpy)_2(bpy)]^{2+}$ (M = Ru or Os) carrying cytosine or guanine nucleobases on the bpy ligand have been prepared and their ability to interact through complementary base-pairing has been studied. Photoinduced energy transfer from Ru to Os is observed for the Ru(cytosine)–(guanine)Os base-pair.[1354] The work has been extended to include adenine–thymine base pairs, but there is significantly less association between the Ru(adenine) and Os(thymine) complexes than between Ru(cytosine) and Os(guanine) species.[1355] Structural data for adenine and thymine-containing $[M(bpy)_2L]^{2+}$ and $[M(4,4'\text{-}^tBu_2bpy)_2L]^{2+}$ (L is a bpt ligand with pendant nucleobase) have provided insight into adenine-protonated adenine (Watson–Crick type) and thymine–thymine (Hoogsteen type) hydrogen-bonded interactions.[1356] Hydrogen-bonded interactions between 2′,3′-isopropylidine adenosine and $[Ru(tpy)_2]^{2+}$ derivatives bearing a thymine group have also been investigated.[1357] 9-Methyladenine (9-MeAde) acts as an *N,N*′-chelate in the complexes $[Ru(bpy)_2(9\text{-MeAde})]^{2+}$ and $[Ru(\mathbf{218})_2(9\text{-MeAde})]^{2+}$ (**218** = 2-phenylazopyridine), and ^{1}H NMR spectroscopic data reveal that the 9-MeAde ligand is present as the imino tautomer.[1358]

Earlier, we described the development of automated phosphoramidite chemistry with respect to DNA-binding studies.[1310,1321] By using an automated synthesizer, three Ru^{II}-containing oligonucleotide conjugates with complementary arms have been prepared. Molecular modeling studies show that these oligonucleotides may form low-energy hairpin conformations. Studies of emission lifetimes and quantum yields illustrate that the presence of the nucleobases adjacent to the $Ru(bpy)_3^{2+}$ unit has little effect on the photophysical properties of the complexes.[1359] Large-scale syntheses of $[Ru(bpy)_2L]^{2+}$ (L = 2′-iminomethylpyridyl-2′-deoxyuridine) containing oligonucleotides has been achieved; as in the previous example, the presence of the nucleobases do not significantly alter the emission properties of the $Ru(bpy)_3^{2+}$ unit.[1360] The synthesis of the 2′-deoxyuridine derivative (**325**) has been reported, and the complex exhibits an ^{3}MLCT excited state lifetime of 1300 ns.[1361]



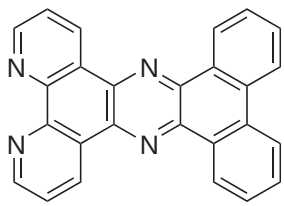
(**325**)

DNA-binding studies involving Ru^{II} tpy complexes included a study of the interactions between $[Ru(phen)(tpy)(H_2O)]^{2+}$, $[Ru(bpy)(tpy)(H_2O)]^{2+}$, and $[Ru(tmen)(tpy)H_2O)]^{2+}$ (tmen = *N,N,N′,N*′-tetramethylethylenediamine) and DNA.[1349] The addition of DNA to solutions

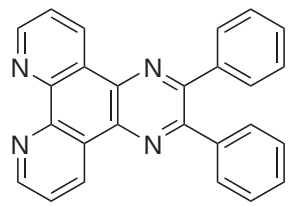
of these complexes results in a significant decrease in current for the Ru^{IV}/Ru^{III} and Ru^{III}/Ru^{II} couples, consistent with complex-DNA binding; the results of an investigation of the electrocatalytic cleavage of DNA are presented.[1362] Binding to DNA by $[Ru(tpy)(bpy)(H_2O)]^{2+}$ and $[Ru(tpy)(phen)(H_2O)]^{2+}$ results in enhancement of their emission in fluid solution; solutions of $[Ru(tpy)(dppz)(H_2O)]^{2+}$ (dppz = dipyridophenazine, (**98**)) are not emissive but become so when the complex binds to DNA. Each complex is able to bind to DNA by the replacement of the aqua ligand by a donor in DNA.[1363]

The complex $[Ru(tpy)Cl_3]$ binds to DNA, and is active as a cytostatic in L1210 leukemia cells. Its activity lies between those of cisplatin and carboplatin. Model complexes $[Ru(tpy)L(H_2O)]^{2+}$ in which L = 9-ethylguanine or 9-methylhypoxanthine, have been prepared and characterized using ^1H NMR spectroscopy.[1364] Proton NMR spectroscopy has been applied to a study of hydrogen bonding between 2′,3′-isopropylidine adenosine and $[Ru(tpy)_2]^{2+}$ derivatives bearing a thymine group.[1346]

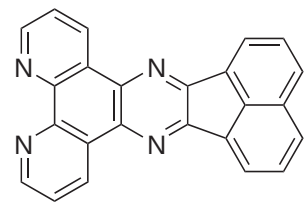
A number of binding studies involve Ru^{II} or Os^{II} complexes containing the hat (**101**) and tap (**102**) ligands. The efficiency of electron transfer between photoexcited $[Ru(tap)_2(hat)]^{2+}$ or $[Ru(phen)_3]^{2+}$ and a range of cationic quenchers increases in the presence of sodium poly(dA-dT)·poly(dA-dT) or DNA. Reasons for this enhancement are discussed.[1365] Luminescence quenching of $[Ru(tap)_3]^{2+}$ by nucleotides is found to approach the diffusion rate when the nucleotide is guanosine-5′-monophosphate (GMP),[1366] and the rate of quenching[1367] by GMP of the excited states of hat and tap-containing Ru^{II} complexes depends on the reduction potential of the excited-state complex. The excited state of, for example, $[Ru(tap)_3]^{2+}$, is oxidizing enough to remove an electron from guanine in DNA. Photoinduced electron transfer from guanine to the Ru^{II} complex is crucial to photoadduct formation between $[Ru(tap)_3]^{2+}$ and DNA in which covalent bond formation occurs between atom N(2) of guanine and one tap ligand in the complex. The proposed mechanism involves (i) initial oxidation of guanine by the excited state of the Ru^{II} complex, (ii) H^+ transfer, (iii) coupling of the radicals formed, and (iv) loss of two H atoms to give $[Ru(tap)_2(2\text{-tap-GMP})]$.[1368] A related adduct is formed between $[Ru(tap)_2(bpy)]^{2+}$ and a guanine residue in DNA.[1369] The dinuclear complex $[(tap)_2Ru\{\mu\text{-bistap}\}Ru(tap)_2]^{4+}$ (bistap = 2,2′-bis(1,4,5,8-tetraazaphenanthrene)) has been isolated from the photoreaction of $[Ru(tap)_3]^{2+}$ in the presence of GMP.[1370] Comparisons have been made between the absorption spectroscopic, and luminescence and electrochemical properties of $[Os(tap)_3]^{2+}$ (which is photostable), $[Ru(tap)_3]^{2+}$, and $[Os(phen)_3]^{2+}$. The emission from the excited state of $[Os(tap)_3]^{2+}$ is quenched in the presence of GMP; photoinduced electron transfer occurs leading to adduct formation.[1371] Phenanthrolino[5,6-b]-1,4,5,8,9,12-hexaazatriphenylene (**167**) is related to the ligand hat. The excited state of $[Ru(phen)_2(\mathbf{167})]^{2+}$ does not luminescence in aqueous solution, but does so upon binding to DNA; intercalation into DNA involves ligand (**167**). The excited state of $[Ru(phen)_2(\mathbf{167})]^{2+}$ can remove an electron from GMP, but no photoadduct is formed.[1372] Ligands (**326**) and (**327**) are structurally similar to (**167**). $[Ru(bpy)_2(\mathbf{326})]^{2+}$ and $[Ru(bpy)_2(\mathbf{327})]^{2+}$ have been prepared and characterized, and DNA binding studies indicate that both complexes bind enantioselectively through intercalation, the latter being more effective for the planar ligand (**326**) than for the diphenyl derivative (**327**).[1373] Acetonitrile solutions of $[Ru(bpy)_2(\mathbf{328})]^{2+}$ and $[Ru(phen)_2(\mathbf{328})]^{2+}$ exhibit strong luminescence, although aqueous solutions are only weakly luminescent, and solutions (MeCN or aqueous) of $[Ru(2,9\text{-}Me_2phen)_2(\mathbf{328})]^{2+}$ are nonluminescent. Each complex binds to DNA, $[Ru(bpy)_2(\mathbf{328})]^{2+}$ and $[Ru(phen)_2(\mathbf{328})]^{2+}$ through an intercalative mode and $[Ru(2,9\text{-}Me_2phen)_2(\mathbf{328})]^{2+}$ via nonintercalation.[1374]



(**326**)



(**327**)

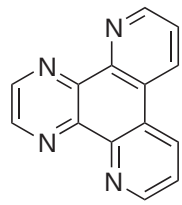


(**328**)

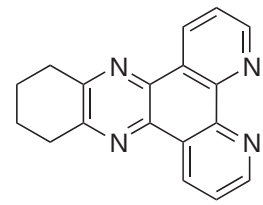
The interactions between each of the stereoisomers of $[(phen)_2Ru(\mu\text{-hat})Ru(phen)_2]^{4+}$ and GMP and adenosine-5′-monophosphate (AMP) have been investigated,[1375] and the effects on the photophysical properties of this complex of the presence of mono- and polynucleotides have been examined. Strong ion pairs are formed between $[(phen)_2Ru(\mu\text{-hat})Ru(phen)_2]^{4+}$ and GMP or

AMP. Luminescence studies indicate that this diruthenium complex is a good photoprobe for denatured DNA, there being significant emission enhancement not observed with normal calf-thymus DNA.[1376] Ruthenium(II)-labeled oligonucleotides have been assembled using $[Ru(tap)_2(4,7\text{-}Ph_2phen)]^{2+}$ connected to a nucleotide base, and bind to complementary single-stranded DNA. Observed luminescence quenching is attributed to photoinduced electron transfer[1377,1378] from guanine to tap, from which photoproducts result with concomitant cross-linking of oligonucleotide strands.[1378]

The pyrazine derivative (**329**) is related to 2,3-dpp (**88**), but whereas (**329**) is constrained to being rigidly planar, 2,3-dpp is not. In a study that looks at the effects of ligand planarity on the binding of $[Ru(bpy)_2L]^{2+}$ to DNA, there is evidence for intercalative binding when L = (**329**) but not when L = 2,3-dpp. An intercalative mode is also proposed for the complex $[(bpy)_2Ru(\mu\text{-}\mathbf{329})PtX_2]^{2+}$, although significant perturbation of the DNA backbone is caused by the steric demands of the bridging (vs. mono-chelating) ligand (**329**).[1379] Both enantiomers of $[Ru(bpy)_2(\mathbf{329})]^{2+}$ bind to DNA, and the results of absorption, fluorescence, and resonance enhanced Raman spectroscopic studies are consistent with binding within the major groove.[1380] More generally, studies with Ru^{II} dipyridophenazine complexes have led to the conclusion that resonance Raman spectroscopy is an effective probe for the interactions between such complexes and DNA,[1381] and examples have involved $[Ru(phen)_2(dppz)]^{2+}$,[1382,1383] and $[Ru(tap)_2(dppz)]^{2+}$ (dppz = dipyridophenazine, **98**).[1384] Ruthenium(II) complexes containing the dppz ligand (**98**) have been investigated in detail with respect to DNA binding and development of molecular "light switches", i.e., emission enhancement associated with binding. In the last part of this section, we focus on this group of complexes.



(**329**)



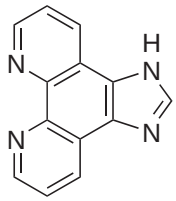
(**330**)

The complex $[Ru(bpy)_2(dppz)]^{2+}$ does not exhibit detectable photoluminescence in aqueous solution, but luminesces strongly when it binds to DNA, the enhancement of luminescence being $\geq 10^4$.[1385] $[Ru(phen)_2(dppz)]^{2+}$ behaves likewise, and a series of other dppz complexes has been investigated to assess the extent of these effects.[1386] The complex $[Os(phen)_2(dppz)]^{2+}$ acts as a red-emitting DNA probe,[1387] and a number of complexes of type $[Os(dppz)(L)(L')]^{2+}$, where L and L′ are bpy, phen, or derivatives thereof, emit at $\lambda \approx 740$ nm on binding to DNA with excited-state lifetimes around 10 ns.[1388] The range of techniques used to investigate the binding of $[Ru(phen)_2(dppz)]^{2+}$ to DNA has included fluorescence and absorption spectroscopies, isothermal titration calorimetry, viscosity measurements,[1389] and NMR spectroscopy[1390–1393] (see below). The interactions of Δ- and Λ-$[Ru(phen)_2(dppz)]^{2+}$ with DNA have been examined using LD spectroscopy, and the results are consistent with both enantiomers binding by intercalative modes.[1394,1395] Deuteration of selected ligands in $[Ru(phen)_2(dppz)]^{2+}$ has been used to simplify ^1H NMR spectra and aid in the analysis of variable-temperature spectra obtained for the Δ-$[Ru(phen)_2(dppz)]^{2+}$/$[d(GTCGAC)]_2$ system. The data have been used to argue in favor of major-groove binding.[1390] In contrast, ^1H NMR spectroscopic data including NOESY and nOe results for the Δ-$[Ru(2,9\text{-}Me_2phen)_2(dppz)]^{2+}$/$[d(GTCGAC)]_2$ system are consistent with intercalation into the minor groove of this duplex.[1391] A ^1H NMR spectroscopic investigation of the interactions between $[Ru(phen)_3]^{2+}$, $[Ru(phen)_2(dpq)]^{2+}$ (dpq = 2,3-bis(2-pyridyl)quinoxaline), and $[Ru(phen)_2(\mathbf{330})]^{2+}$ and oligonucleotides also support binding in the minor groove. Details of the interactions are addressed using molecular modeling.[1392] Photophysical data have been presented that are consistent with the intercalation of $[Ru(phen)_2(dppz)]^{2+}$ into the minor groove of DNA. The results also show that biexponential decay accompanies the binding of Δ- or Λ-forms of $[Ru(phen)_2(dppz)]^{2+}$ to any sequence of nucleic acids, and it is concluded that the interaction of $[Ru(phen)_2(dppz)]^{2+}$ with nucleic acids is more complex than binding of a simple intercalator.[1396]

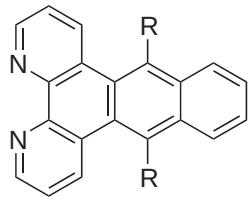
The "light switch" effects of $[Ru(phen)_2(dppz)]^{2+}$, $[Ru(phen)_2(dppz)]^{2+}$, and related complexes depend on the lack of a detectable luminescence in aqueous solutions. The emission of $[Ru(phen)_2(dppz)]^{2+}$ in water and in mixtures of water and acetonitrile has been studied in detail.

In water, there is an initial emission arising from a typical MLCT excited state; the very low quantum yield is due to the efficient formation of another MLCT state followed by its radiationless decay.[1397] An investigation of the photoluminescence of $[Ru(phen)_2(dppz)]^{2+}$ in a variety of nonaqueous solvents (with and without DNA present) shows that solvent polarity is a crucial factor in determining luminescence lifetimes.[1398] Binding constants have been measured for the interaction of $[Ru(phen)_2(dppz)]^{2+}$ with a range of oligonucleotides, and an intercalated mode is proposed for all examples studied; relationships between oligonucleotide structure ("straight", "kinked", and "bent") and mode of interaction are discussed.[1399] DNA-binding studies by the same researchers have been extended to $[Ru(NH_3)_4(dppz)]^{2+}$.[1400]

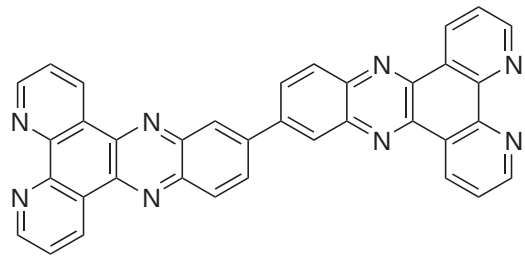
Binding studies for a number of complexes related to $[Ru(phen)_2(dppz)]^{2+}$ have also been reported. Evidence for an intercalative binding mode for $[Ru(phen)_2(7,8\text{-}Me_2dppz)]^{2+}$ in DNA comes from fluorescence and UV–vis spectroscopic data in which it is observed that $[Fe(CN)_6]^{4-}$ and NaCl do not quench the fluorescence of the bound complex.[1401] The complex $[Ru(\mathbf{331})_2(dppz)]^{2+}$ has been prepared and characterized, and a binding constant of 2.1×10^7 has been determined for its interaction with DNA.[1402] The ligand dppz possesses an extended π-system, and, therefore, complexes related to $[Ru(bpy)_2(dppz)]^{2+}$ and $[Ru(phen)_2(dppz)]^{2+}$ in which the non-bpy ligand also has an extended π-system are of interest in terms of their luminescent and DNA light-switch effects. Ligands (**332**) and (**333**) have been chosen as two examples of such ligands. The photophysical properties of $[Ru(bpy)_2(\mathbf{332})]^{2+}$ and $[Ru(bpy)_2(\mathbf{333})]^{2+}$ are significantly different. While $[Ru(bpy)_2(\mathbf{332})]^{2+}$ is reminiscent of $[Ru(bpy)_3]^{2+}$, it does, nonetheless, show an enhanced luminescence quantum yield in the presence of DNA. Spectroscopic data are consistent with ligand (**333**) in $[Ru(bpy)_2(\mathbf{333})]^{2+}$ binding to DNA.[1403] The dinuclear complex $[(phen)_2Ru(\mu\text{-}\mathbf{334})Ru(phen)_2]^{4+}$ binds strongly to DNA, and different binding geometries have been proposed for the Δ,Δ- and Λ,Λ-isomers. The Δ,Δ- and Λ,Λ-$[(bpy)_2Ru(\mu\text{-}\mathbf{334})Ru(bpy)_2]^{4+}$ complexes also bind strongly, but in a similar manner to each other.[1404] The interactions of $[(bpy)_2M(\mu\text{-dpb})PtCl_2]^{2+}$ (M = Ru or Os) with DNA have been investigated and results are consistent with binding of the complexes inducing a significant perturbation to the conformation of DNA.[1405,1406] The synthesis and characterization of the complexes $[Ru(phen)_{3-n}L_n]^{2+}$ (L = 6,7-dicyanodipyrido[2,2-d:2′,3′-f]quinoxaline, $n = 1$–3) have been described. The complexes bind quite strongly to DNA, and $[Ru(phen)_2L]^{2+}$ and $[Ru(phen)L_2]^{2+}$ (but not $[RuL_3]^{2+}$) act as "light-switches" for DNA.[1407]



(**331**)



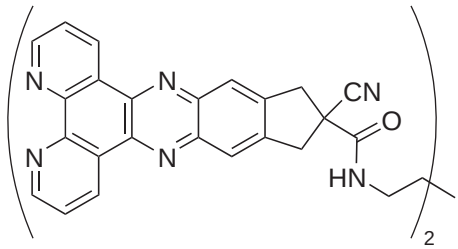
(**332**) R = H
(**333**) R = CN



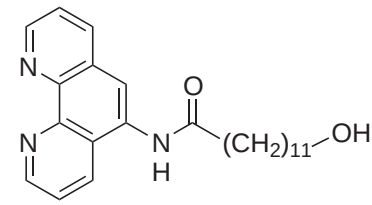
(**334**)

Dynamic quenching of the MLCT excited state of $[Ru(phen)_2(dppz)]^{2+}$ by H^+ transfer in MeCN solution occurs for proton donors with pK_a values in the range 4.7–15.7. Comparisons of the quenching have been made in the presence and absence of DNA.[1408] The addition of Cu^{2+} to DNA-bound $[Ru(bpy)_2L]^{2+}$ (L is the phenazine derivative (**167**)) leads to luminescence quenching. This is explained in terms of complexation of Cu^{2+} with the vacant coordination site of L in $[Ru(bpy)_2L]^{2+}$. Formation of the $[Ru(bpy)_2L]^{2+}/Cu^{2+}$ complex in the presence of DNA is proposed to place one metal center in the major groove and one in the minor groove.[1409]

LD spectra of Δ- and Λ-$[Ru(phen)_2(dppz)]^{2+}$ intercalated in DNA are very different and this is rationalized in terms of deviations from the idealized intercalation geometry. LD spectroscopic data for intercalated *meso*-, Δ,Δ-, and Λ,Λ-$[(phen)_2Ru(\mu\text{-}\mathbf{335})Ru(phen)_2]^{4+}$ indicate that the $Ru(phen)_2(dppz)$-like units bind in similar orientations to the mononuclear complexes. Formation of the intercalated species must involve threading of the $[(phen)_2Ru(\mu\text{-}\mathbf{335})Ru(phen)_2]^{4+}$ complex through the DNA strands.[1410]



(**335**)



(**336**) R = H
(**337**) R = P(O)H(OH)

Studies involving $[Ru(phen)_2(dppz)]^{2+}$ tethered to oligonucleotides include work from Barton *et al*. in which the phen ligands are replaced by 5-(glutaric acid monoamide)-1,10-phenanthroline (phen′). A 15-mer functionalized with a hexylamine at its 5′-terminus is then coupled to $[Ru(phen')_2(dppz)]^{2+}$. When the complementary oligonucleotide strand is added, the system luminesces, consistent with intercalation of the $[Ru(phen')_2(dppz)]^{2+}$ complex into the helical oligonucleotide assembly.[1411] Studies have also been made of $[Ru(phen)_2(dppz)]^{2+}$ tethered to the 3′ or 5′-terminii or a middle site of oligodeoxyribonucleotide.[1412,1413] The preparation and characterization of [Ru(phen)(**336**)(dppz)]$^{2+}$ have been described. Conversion of [Ru(phen)(**336**)(dppz)]$^{2+}$ to the corresponding phosphonate [Ru(phen)(**337**)(dppz)]$^{2+}$ provides a complex that can be readily coupled to the 5′-terminus of an oligonucleotide, and the isolation of enantiomerically pure Δ- and Λ-Ru^{II}-labeled oligonucleotides, and the results of studies with these systems, have been reported.[1414]

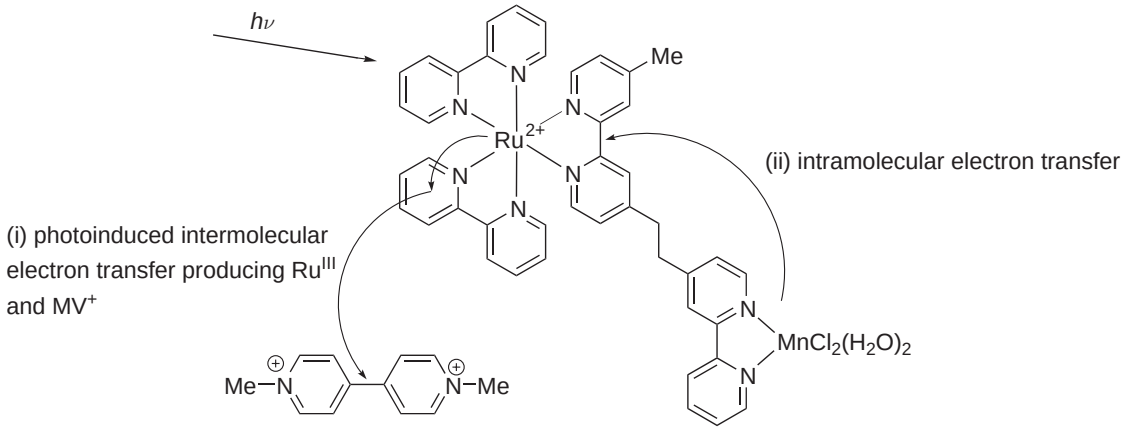
The emission spectrum of $[Os(phen)_2(dppz)]^{2+}$ is red-shifted with respect to the Ru^{II} analog. The photoinduced electron transfer between DNA-bound Δ-$[Os(phen)_2(dppz)]^{2+}$ and Δ-$[Rh(phi)_2(bpy)]^{3+}$ has been investigated, and comparisons are made between the behaviors of the complexes $[M(phen)_2(dppz)]^{2+}$ for M = Os and Ru.[1415] Electron transfer between DNA-bound $[M(phen)_2(dppz)]^{2+}$ and $[Rh(phi)_2(bpy)]^{3+}$ (an intercalated acceptor) or $[Rh(NH_3)_6]^{3+}$ (an externally bound acceptor) has been investigated using different oligonucleotide sequences. The two Rh^{III} acceptors exhibit different quenching behaviors. The most efficient quenching by $[Rh(phi)_2(bpy)]^{3+}$ is observed for AT-only oligonucleotides, whereas high efficiencies for $[Rh(NH_3)_6]^{3+}$ are observed when the DNA polymers consist of GC-only sequences.[1416]

Designing potential DNA intercalators has led to an investigation of a series of $[Ru([9]aneS_3)LCl]^+$ complexes where L is a didentate polypyridyl ligand. Structural data for the complexes are discussed in terms of hydrogen-bonded interactions and π-stacking between extended aromatic systems, e.g., dppz and 4,7-Ph_2phen.[1417]

5.5.3.1.23 Complexes as models for Photosystem II

Two pertinent reviews cover the applications of ruthenium polypyridine complexes as photosensitizers in biomimetic models for Photosystem II (PSII).[1418,1419] Scheme 2 summarizes a proposed pathway for photoinduced electron transfer in a model $Ru(bpy)_3^{2+}$–Mn^{II} system in the presence of MV^{2+}. The $Ru^{II}Mn^{II}$ complex was prepared by treating $[Ru(bpy)_2(4\text{-}MebpyCH_2CH_2bpy\text{-}4\text{-}Me)]^{2+}$ with $MnCl_2$. Compared to that in $[Ru(bpy)_2$ $(4\text{-}MebpyCH_2CH_2bpy\text{-}4\text{-}Me)]^{2+}$ ($\tau = 980$ ns), the emission in the $Ru(bpy)_3^{2+}$–Mn^{II} complex was significantly quenched ($\tau = 260$ ns).[1420] This system (reported to be the first in which an Mn^{II} complex has been utilized as an electron donor to a photo-oxidized photosensitizer) has been developed by changing the coordination environment around the Mn^{II} center,[1421] and by linking both Mn^{II} and tyrosine to the $Ru(bpy)_3^{2+}$ group. In the latter, stepwise electron transfer from Mn to tyrosine to Ru has been shown to occur.[1422]

Flash photolysis has been used to investigate the kinetics of electron transfer from tyrosine to Ru in $[Ru(bpy)_2(4\text{-Me-}4'\text{-CONH-L-tyrosine ethyl ester-}2,2'\text{-bpy})]^{2+}$ as a function of pH and temperature.[1423] Model systems for PSII have moved to di- and trimanganese systems containing up to six $Ru(bpy)_2^{2+}$ units[1424] and are continuing to be developed.



Scheme 2

5.5.3.2 Phosphorus-, Arsenic-, and Antimony-donor Ligands

5.5.3.2.1 Mononuclear complexes containing monodentate ligands

The molecular structure of *cis*-$[Ru(PMe_3)_4H_2]$ has been reported and compared with that of $[Ru\{P(CH_2CH_2CH_2PMe_2)_3\}H_2]$. Deviations from an idealized octahedral coordination environment are discussed for the two complexes.[1425] The reaction of *cis*-$[Ru(PMe_3)_4H_2]$ with NH_4PF_6 in Et_2O leads to the formation of *cis*-$[Ru(PMe_3)_4H(NH_3)]^+$ or, when NH_4PF_6 is used in excess, *cis*-$[Ru(PMe_3)_4(NH_3)_2]^{2+}$. Substitution reactions of $[Ru(PMe_3)_4H(NH_3)]^+$ have been studied, with NH_3 being displaced by a range of ligands.[1426] The complexes *cis*-$[RuX_2(PMe_2Ph)_4]$ (X = Cl, Br) and *trans*-$[RuX_2L_4]$ (X = Cl, Br, I; L = PMe_3, AsM_2Ph, $SbMe_2Ph$) have been prepared and characterized. Oxidation of *trans*-$[RuX_2L_4]$ to the corresponding Ru^{III} complexes occurs with $AgBF_4$ or concentrated HNO_3 in aqueous HBF_4. The crystal structures of *trans*-$[RuX_2L_4]$ (X = I, L = $AsMe_2Ph$; X = Br, L = $SbMe_2Ph$), $[Ru_2Br_5(SbMe_2Ph)_4]$, and $[Ru_2I_3$ $(PMe_2Ph)_6][CF_3SO_3]$ have been determined.[1427] The preparation and characterization of *trans*-$[OsI_2L_4]$ (L = PMe_3, $AsMe_3$, and $SbMe_3$) have been reported along with related Os^{III} chemistry which includes the crystal structure of *trans*-$[Os(AsMe_3)_4I_2][I_3]$.[67] The photochemically induced *trans-cis* isomerization of $[OsCl_2(PMe_2Ph)_4]$ has been investigated by IR and NMR spectroscopies.[1428] A study of *mer*-$[RuX_3L_3]$ (X = Cl, Br; L = PMe_2Ph, $AsMe_2Ph$) has included assignments of UV–vis spectra and structural determinations of the arsine complexes. Attempts to prepare analogous stibine complexes were not successful. Decomposition of the complexes in solution yielded $[Ru_2X_5L_4]$ species, and the structures of $[Ru_2Br_5(PMe_2Ph)_4]$, $[Ru_2Br_5(AsMe_2Ph)_4]$, and $[Ru_2I_5(AsMe_2Ph)_4]$ have been determined.[1429]

The complex *trans,mer*-$[OsCl_2(MeCN)(PMe_2Ph)_3]$ has been prepared by an electrosynthetic method. The structure of the complex was confirmed by X-ray crystallography.[1430] The reaction of $[OsHCl(CO)(PPh_3)_3]$ with MeCN results in the formation of $[OsH(CO)(MeCN)_2(PPh_3)_2]^+$ (isolated as the BF_4^-) salt. The cationic complex is a precatalyst for the hydrogenation of, for example, cyclohexanone, cyclohexene, and quinoline.[1430] The *cis*,*cis*,*trans*-isomers of $[RuCl_2(CO)_2(PPh_3)_2]$ and $[RuCl_2(CO)_2(AsPh_3)_2]$ have been synthesized and characterized, the structures being confirmed crystallographically.[1431] The structures of the all-*trans* isomer of $[OsBr_2(CO)_2(PPh_3)_2]$[1432] and the all-*cis* and all-*trans* isomers of $[OsBr_2(CO)(MeCN)(PPh_3)_2]$[1433] have also been determined. A series of $[OsCl_2$ $(CO)_2L_2]$ complexes (L = various phosphines) has been prepared starting from $[Os_2Cl_2(CO)_6$ $(\mu\text{-}Cl)_2]$. The crystal structure of $[OsCl_2(CO)_2(PEt_3)_2]$ confirms *cis*-Cl, *cis*-CO, and *trans*-PEt_3 ligands.[1434] The reactions of $AgBF_4$ with *cis*- or *trans*-$[RuCl_2(CO)_2(PPh_3)_2]$ yield $[Ru(CO)_2(PPh_3)_2]^{2+}$ (stabilized by coordination of BF_4^- ions), $[RuCl(CO)_2(PPh_3)_2]^+$, or $[Ru(CO)_3(PPh_3)_2]^{2+}$. The reactivity of these cationic species has been investigated, and products include $[Ru(CO_2Me)_2(CO)_2(PPh_3)_2]$ and $[Ru(CO_2Me)Cl(CO)_2(PPh_3)_2]$.[1435] NMR ($^1H$ and ^{31}P) spectroscopic data are consistent with there being two conformers of each of $[Ru(COMe)I(CO)(P^tBu_2Me)_2]$ and $[Ru(H)Cl(CO)(P^tBu_2Me)_2]$. These differ in their rotational conformation about the Ru—P bonds. Two conformers also exist for

$[Ru(Me)I(CO)(P^tBu_2Me)_2]$, but the barrier for interconversion between them is lower than for $[Ru(COMe)I(CO)(P^tBu_2Me)_2]$.[1436]

The reactions of $[RuCl_2(PPh_3)_3]$ with the pyridine derivatives 4-^{t}Bupy, 4-CNpy, 4-Mepy, 3-Mepy, 4-Me_2Npy, 4-Phpy, 4-$CONH_2$py, or 4-vinylpy (L) or with bpy, phen, 4,4′-Me_2bpy, 4,4′-$(MeO)_2$bpy, 4,4′$(MeS)_2$bpy, or 4,4′-Cl_2bpy (L_2), result in phosphine substitution and an increase in coordination number to give $[RuCl_2(PPh_3)_2L_2]$. The crystal structure of $[RuCl_2(PPh_3)_2(phen)]$ has been determined, and the electrochemical behavior of the complexes has been discussed. $[RuCl_2(PPh_3)_2(4\text{-}^tBupy)_2]$ is an efficient precatalyst for the hydrogenation of cyclohexane and benzaldehyde.[801,1437] Addition reactions occur between $[RuCl_2(CO)(P^iPr_2Me)_2]$ and two-electron donors such as CO, pz, and 3,5-Me_2pz, and metathesis reactions take place with $Na[S_2CNEt_2]$, $K[S_2COR]$ (R = Me, Et, ^{i}Pr), and K[acac].[1438] Tris(*N*-pyrrolyl)phosphine ($Ppyr_3$) is a strong π acceptor and reacts with $[OsHCl(CO)(PPh_3)_3]$, displacing the PPh_3 *trans* to the H^- ligand. The complex $[OsH(4\text{-}MeC_6H_4)(CO)(Ppyr_3)(PPh_3)_2]$ has also been prepared.[1439]

Several complexes possess novel phosphine ligands and intra- or intermolecular interactions. The complex $[RuCl_2\{PPh_2(2,6\text{-}Me_2C_6H_3)_2\}]$ was the first example of a neutral Ru complex exhibiting two agostic interactions. These involve one Me group from each 2,6-$Me_2C_6H_3$ substituent and complete the octahedral coordination environment of the Ru^{II} center.[1440] Treatment of $RuCl_3{\cdot}xH_2O$ or $[RuCl_2(PPh_3)_3]$ with excess $P(CH_2OH)_3$ yields $[Ru\{P(CH_2OH)_3\}_2\{PH(CH_2OH)_2\}_2Cl_2]$, which is water soluble. The solid-state structure of the complex exhibits a network of hydrogen-bonded interactions.[1441] The ligand 6-$Ph_2PCH_2CH_2$bpy (L) has been prepared and reacted with $[Ru(CO)_2Cl_2]_n$ to yield $[RuCl_2(CO)_2(6\text{-}Ph_2PCH_2CH_2bpy\text{-}P)_2]$ in which the phosphine ligands are mutually *trans*. The complex has available two *N,N*-donor sets and combines with Cu^{II} to form a macrocyclic Ru_2Cu_2 complex.[1442]

Several arsine and stibine complexes were described earlier in the section.[1427,1429,1431] The crystal structure of *trans*-$[RuCl_2(SbPh_3)_4]$ has been determined as part of an investigation of Ru^{II} and Ru^{III} complexes of $SbPh_3$.[1443] 1,9-Dimethylpurine-6-thione (L) reacts with *trans*-$[RuCl_2(SbPh_3)_4]$ to give $[RuCl_2(SbPh_3)_2(L\text{-}N,S)]$; no further substitution of stibine ligand is observed and this is also true with other *N*-donor ligands such as 3,5-dimethylpyridine and 1,4-pyrazine.[1444] The syntheses of $[Ru(H)_2(CO)(AsPh_3)_3]$ and $[Ru(H)_2(CO)(AsPh_3)L]$ (L = dppe, $Ph_2AsCH_2CH_2AsPh_2$, $Ph_2AsCH_2CH_2PPh_2$) have been reported; the catalytic activities of the complexes have been investigated and compared to those of the PPh_3-containing analogs.[1445] The series of complexes $[RuX_2(EPh_3)L_2]$ (X = Cl, Br; E = P, As; L = 2-HOC_6H_4CHO, 4-$MeOC_6H_4CHO$) has been synthesized and characterized, and the compounds tested as catalysts for the aerobic oxidation of PPh_3.[1446] The study follows earlier studies of similar complexes containing aromatic aldehyde ligands.[1447]

The structure of $[Ru(H)(CO)(H_2Bpz_2)(AsPh_3)_2]{\cdot}H_2O$ (with *trans* $AsPh_3$) has been determined and shows significant hydrogen-bonded interactions in the crystal lattice.[1448]

5.5.3.2.2 Mononuclear complexes containing didentate ligands

This section begins with a look at complexes containing dppm, dppe, dppp, dppb, and related ligands. The reactions of $[RuCl_2(dppm)_2]$ with isocyanides (RNC, R = ^{t}Bu, Ph) lead to various products depending on conditions. Complexes that have been isolated and characterized are *trans*-$[RuCl(CNR)(dppm\text{-}P,P')_2]Cl$, *trans*-$[RuCl(CNR)(dppm\text{-}P,P')_2][PF_6]$, $[RuCl(CNR)_2(dppm\text{-}P,P')(dppm\text{-}P)][PF_6]$, and $[Ru(CNR)_2(dppm\text{-}P,P')_2][PF_6]_2$. Treatment of $[RuCl(CN^tBu)_2(dppm\text{-}P,P')(dppm\text{-}P)]^+$ with H_2O_2 results in the formation of $[RuCl(CN^tBu)_2(dppm\text{-}P,P')(dppmO\text{-}P)]^+$ from which $[Ru(CN^tBu)_2(dppm\text{-}P,P')(dppmO\text{-}P,P')]^{2+}$ can be made.[1449] The complexes *fac*-$[RuCl_3(NO)(dppm)]$, *cis*-$[RuCl_2(dppm)_2]$, and *mer*-$[RuCl_3(NO)(dppb)]$ have been isolated and their solid-state structures determined.[1450] The reaction of $RuCl_3{\cdot}xH_2O$ and Hquin in the presence of dppm in basic solution gives rise to the 2-quinaldinate complex *trans*-$[Ru(dppm\text{-}P)_2(quin\text{-}N,O)_2]$; when the phosphine is PPh_3, the products are *cis*- and *trans*-$[Ru(PPh_3)_2(quin\text{-}N,O)_2]$. The monodentate nature of the dppm ligands is confirmed by a structure determination of *trans*-$[Ru(dppm\text{-}P)_2(quin\text{-}N,O)_2]{\cdot}2MeOH$.[1451] The reaction between $[Ru(CO)_2(PPh_3)_2(thf)_2]^{2+}$ and LiTCNQ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) produces $[Ru(CO)_2(PPh_3)_2(TCNQ)]^+$. The preparation and characterization of $[Ru(dppm\text{-}P,P')_2(dppm\text{-}P)(TCNQ)]^+$ and $[\{Ru(dppe\text{-}P,P')(dppe\text{-}P)\}_2(\mu\text{-}TCNQ)_2]^{2+}$ have also been described.[1452]

The syntheses and characterization of *trans*-$[RuCl_2(dppe)_2]$ and $[RuCl(dppe)_2]^+$ have been reported; the crystal structures of both complexes have been determined.[1453] A comparison of

structural data for the tetrafluoroborate salts of *trans*-$[RuCl(CO)(dppe)_2]^+$ and *trans*-$[RuCl(CO)(dppm)_2]^+$ illustrates the increased steric effects on going from the bis(dppm) to bis(dppe) complex. This is further implied by the differences in redox properties of the two complexes.[1454] The complexes $[RuHCl(CO)(PPh_3)L]$ (L = dppe, $Ph_2AsCH_2CH_2PPh_2$ and $Ph_2AsCH_2CH_2AsPh_2$) have been made starting from $[RuHCl(CO)(PPh_3)_3]$, and the products have been tested as catalysts for the hydrogenation of propanal.[1455] The complex *trans*-$[RuCl_2(dppe)_2]$ reacts in neat Me_3Al to yield *trans*-$[RuCl(Me)(dppe)_2]$ and $[RuCl(dppe\text{-}P,P')\{Ph_2PCH_2CH_2PPh(C_6H_4)\text{-}P,C\}]$, the latter being structurally confirmed.[1456]

The complex *cis*-$[RuH_2(dmpe)_2]$ has been the subject of a photochemical investigation, and $[Ru(dmpe)_2]$ has been isolated in an argon matrix. Reactions of this unsaturated species that have been described include those with CO, PMe_3, and ethene.[1457] Reactions of $[RuH_2(dmpe)_2]$ with $(CF_3)_2C{=}CFCF_2CF_3$ and with $CF_3CF{=}CF_2$ result in Ru—F bond formation in the novel complex *cis*-$[Ru(dmpe)_2F_2]HF$ in which there is association between the fluoro ligand and HF.[1458]

The crystal structures of *trans*-$[RuCl_2(dppp)_2]$[1459] and $[RuCl(dppp)_2][PF_6]$[1460] have been determined. The latter complex cation was formed electrochemically. The reaction of $[RuF(dppp)_2]^+$ with diphenylallyl bromide results in the formation of $[RuBr(dppp)_2]^+$.[1461] The unsaturated center in $[RuH(dppp)_2]^+$ is brought up to six-coordination by an agostic interaction involving a C–H group of one ligand. A structure determination confirms that the C–H—Ru interaction is *cis* to the Ru—H bond.[1462]

Several routes to $[RuCl_2(dppb)(NH_2CH_2Ph)_2]$ starting from dinuclear precursors have been described. However, when $(PhCH_2)_2NH$ is used in place of $PhCH_2NH_2$ in the reactions, no mononuclear species is obtained and the reactions are accompanied by dealkyation of the amine.[1463] The preparations of $[RuBr_2(dppb)(PPh_3)]$ and $[Br(dppb)Ru(\mu\text{-}dppb)RuBr(dppb)]$ and the reactions of $[RuBr_2(dppb)(PPh_3)]$ with dmso, Me_2S, and related ligands have been reported. Structural data for $[RuCl_2(dppb)(PPh_3)]$, $[RuBr_2(PPh_3)_3]$, and $[RuCl_2(PPh_3)_3]$ are compared with data obtained from ^{31}P CP/MAS NMR spectroscopy in order to illustrate the application of the latter technique to the characterization of Ru^{II} phosphine complexes.[1464] A series of Ru^{II} complexes containing dppb and *N*-donor ligands have been prepared. These include $[RuCl_2(dppb)(py)_2]$ (with *cis*-py and *trans*-Cl), *cis*-$[RuCl_2(dppb)(bpy)]$ and *cis*-$[RuCl_2(dppb)(phen)]$ for which crystal structures have been determined.[1465] (see also Section 5.5.3.2.4.)

1,2-Bis(diisopropylphosphino)ethane (dippe) contains sterically demanding substituents. It reacts with $[RuCl_2(PPh_3)_3]$ to give $[RuCl_2(dippe)_2]$. Treatment of this with $NaBH_4$ yields *cis*-$[RuH_2(dippe)_2]$. The reaction between $[RuHCl(PPh_3)_3]$ and dippe produces $[RuHCl(dippe)_2]$, dissociation of which leads to $[RuH(dippe)_2]^+$. The reactivity of this cationic complex has been investigated. An interesting reaction of *cis*-$[RuH_2(dippe)_2]$ is that with O_2 to give $[RuH(\eta^2\text{-}O_2)(dippe)_2]^+$, the crystal structure of which confirms the unusual nature of the product.[1466] The related complexes $[OsX(\eta^2\text{-}O_2)(dcpe)_2]^+$ (dcep = 1,2-bis(cyclohexylphosphino)ethane, X = Cl, Br) have also been reported; treatment of these with gaseous HCl results in Os^{IV} oxo species.[1467] When $[RuCl_2(dippe)_2]$ reacts with $NaBPh_4$ in MeOH, chloride abstraction leads to the formation of $[RuCl(dippe)_2]^+$. The analogous Os^{II} complex has also been isolated, via $[OsCl_2(dippe)_2]$, itself prepared from $[OsCl_6]^{2-}$ and dippe. The two cationic complexes react with PhSH to yield $[M(SPh)(dippe)_2]^+$ (M = Ru, Os).[1468]

The diphos ligands dppe, dppp, dppb, and dppf react with $[RuH(CO)(MeCN)_2(PPh_3)_2]^+$ to give $[RuH(CO)(MeCN)(PPh_3)_2(diphos\text{-}P)]^+$ and $[RuH(CO)(MeCN)(PPh_3)(diphos\text{-}P,P')]^+$. The catalytic properties of the complexes with respect to homogeneous propanal hydrogenation have been studied.[1469] The reactions of $[RuHCl(CO)(PPh_3)_3]$ with the diphos ligands dppm, dppe, dppp, dppf, and (*Z*)-1,2-bis(diphenylphosphino)ethene result in the formation of $[RuHCl(CO)(PPh_3)(diphos)]$. These species catalyze the hydrogenation of cyclohexene.[1470] The bisphosphines dppe, dppp, dppb, and dppf react with $[RuH_2(CO)(PPh_3)_3]$ yielding $[RuH_2(CO)(PPh_3)(diphos)]$. The crystal structure of the dppp complex has been established.[1471]

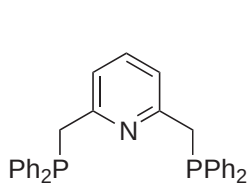
The complex $[RuCl_2(dmso)_4]$ reacts with dcpe in the presence of BPh_4^- or PF_6^- to form, not the chloro, but the hydrido species, $[RuH(dcpe)_2]^+$. The preference for this cation is anion-dependent. When the dcpe ligand is replaced in the reaction by bis(dicyclohexylphosphino)-methane (dcpm), the isolated products are *trans*-$[RuHCl(dcpm)_2]$ or *trans*-$[RuCl_2(dcpm)_2]$. A structural determination of the BPh_4^- salt of $[RuH(dcpe)_2]^+$ reveals an almost planar RuP_4 unit. This is consistent with the hydrido ligand completing a square-based pyramidal coordination environment for the Ru^{II} center rather than the more usual trigonal bipyramidal arrangement.[1472]

Nitrosyl complexes of formula $[Ru(NO)Cl_3(diphos)]$ in which diphos = dppm, dppe, dppp, or (*Z*)-1,2-bis(diphenylphosphino)ethene have been synthesized. Although ^{31}P NMR spectroscopic data are consistent with a *fac* isomer in each case, the solid-state structure of $[Ru(NO)Cl_3(dppp)]$

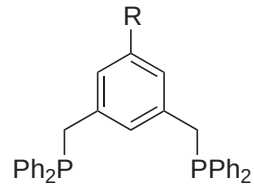
reveals a *mer* arrangement of chloro ligands.[1473] Related to (*Z*)-1,2-bis(diphenylphosphino)ethene is the 2,3-bis(diphenylphosphino)propene (dpppn) ligand, the coordination chemistry of which has been relatively poorly explored. It reacts with $[RuCl_2(PPh_3)_3]$ to produce *trans*-$[RuCl_2(dpppn)_2]$.[1474] The reaction of $(Ph_2P)_2C{=}CH_2$ (L) with $[RuCl_2(PPh_3)_3]$ yields *trans*-$[RuCl_2L_2]$, treatment of which with $[NO][BF_4]$ generates $[RuCl_2L_2][BF_4]$. Isomerization of *trans*-$[RuCl_2L_2]$ to *cis*-$[RuCl_2L_2]$ occurs when the *trans* isomer is refluxed in chlorobenzene. The unsaturated ligand L in *trans*-$[RuCl_2L_2]$ reacts with primary amines to give complexes of the type *trans*-$[RuCl_2\{(Ph_2P)_2CHCH_2NHR\}_2]$.[1475] A series of luminescent complexes of Ru^{II} and Os^{II} containing $(Ph_2P)_2C{=}CH_2$ and $(Ph_2P)_2C{=}C{=}C(PPh_2)_2$ ligands has been prepared and characterized.[1476]

The bisphosphine $Ph_2PNMeNMePPh_2$ (L) reacts with $[RuCl_2(cod)]_x$ in the presence of NaOMe to produce $[RuL_2H_2]$. Products from the reactions of this complex with CO, O_2, S_8, CH_2Cl_2, $PhC{\equiv}CH$, $EtO_2C{\equiv}CH$, and C_6H_6 have been characterized, including the crystal structures of $[RuL_2(\eta^2\text{-}O_2)]$ (O–O = 1.452(10) Å), $[RuL_2(\eta^2\text{-}S_2)]$ (S–S = 2.0518(13) Å) and $[RuL_2H(Cl)]$.[1477] Ligands related to L, the coordination chemistry of which have also been studied, are $Ph_2PNPhCH_2CH_2NPhPPh_2$, $Ph_2PN(CH_2Ph)CH_2CH_2N(CH_2Ph)PPh_2$, and $C_6H_4O_2PN(CH_2Ph)CH_2CH_2N(CH_2Ph)PO_2C_6H_4$.[1478] The reactions of $[RuCl_2(CO)_3(thf)]$ with $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (L, $n = 4$ or 5) lead to the formation of complexes in the family $[RuCl_2(CO)_2L]_x$ where $x = 1, 2, 3\ldots$. The major product has $x = 1$; ligand L is didentate with the two P atoms mutually *trans*. In the oligomers that form as minor products, each bisphosphine ligand bridges between two Ru^{II} centers.[1479] A calix[4]arene bearing two ester and two PPh_2 groups has been synthesized; it adopts a cone conformation with the PPh_2 groups oriented to the outside of the upper rim. Several metal complexation reactions of the ligand have been studied, including the reaction of $RuCl_3{\cdot}xH_2O$ with CO and then the bisphosphine ligand in 2-ethoxy ethanol. The calix[4]arene acts as a *P,P′*-donor with the P atoms *trans* to each other in the complex $[Ru(CO)_2Cl_2L]$.[1480]

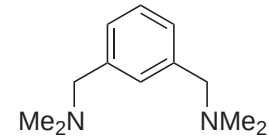
Ligand (**338**) reacts with $[RuCl_2(PPh_3)_3]$ to give $[RuCl_2(PPh_3)$(**338**)$]$ in which (**338**) acts as a *P,N,P*-donor. $[RuCl_2(PPh_3)$(**338**)$]$ reacts with $NaBH_4$ to yield the hydrido species $[RuCl(H)(PPh_3)$(**338**)$]$ which protonates with HBF_4 to give $[RuCl(H_2)(PPh_3)$(**338**)$]^+$. Analogous Os^{II} chemistry can be carried out.[1481] When H(**339**) reacts with $[RuCl_2(PPh_3)_3]$, the orthometallated product $[RuCl(PPh_3)$(**339**)$]$ is produced in which the Ru^{II} center is five-coordinate. Addition of 4-Phpy to $[RuCl(PPh_3)$(**339**)$]$ occurs to complete the octahedral coordination sphere, while treatment of $[RuCl(PPh_3)$(**339**)$]$ with CO or PMe_3 yields $[RuCl(PMe_3)_2$(**339**)$]$ or $[RuCl(CO)_2$(**339**)$]$. The hydrido complexes $[RuH(PPh_3)$(**339**)$]$, $[RuH(CO)$(**339**)$]$, and $[RuH(PMe_3)_2$(**339**)$]$ have also been prepared and characterized.[1482] Surprisingly, the reaction of $[RuCl_2(PPh_3)_3]$ with H(**340**) yields the same product as the reaction of that with H(**340**) (i.e., $[RuCl(PPh_3)$(**340**)$]$), and $[RuCl(PPh_3)$(**340**)$]$ could only be produced by treating the orthometallated $[RuCl(PPh_3)$(**341**)$]$ with H(**340**).[1483]



(**338**)



H(**339**) R = H
H(**340**) R = $SiMe_3$

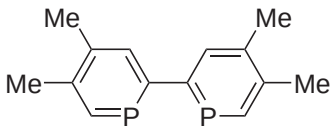


H(**341**)

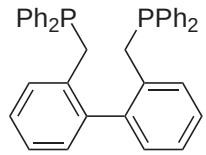
The complex *trans*-$[RuCl_2\{1,2\text{-}(MePhP)_2C_6H_4\}_2]$ has been structurally characterized for the *R,R* form of the ligand; it is a useful starting material for optically active σ-acetylide complexes.[1484] Selective use of *cis* or *trans*-$[OsCl_2(dmso)_4]$ as precursor allows the controlled preparation of either *cis* or *trans*-$[RuCl_2\{(R,R)\text{-}1,2\text{-}(MePhP)_2C_6H_4\}_2]$. The crystal structure of the *trans* isomer has been determined.[1485] The ligands $1,2\text{-}(Ph_2P)_2C_6H_4$, $1,2\text{-}(Me_2As)_2C_6H_4$, $Ph_2AsCH_2CH_2AsPh_2$, and dppe (all represented by L) have been incorporated into the complexes *trans*-$[OsI_2L_2]$; the corresponding Os^{III} species $[OsI_2L_2]^+$ have also been described.[70] Related *trans*-$[RuI_2L_2]$ complexes (L = dppe, (*Z*)-$Ph_2PCH{=}CHPPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, and $1,2\text{-}(Me_2As)_2C_6H_4$) have been prepared by treating $[Ru(H_2O)_6]^{2+}$ with L and NaI in aqueous EtOH.[1486] The tris chelate complexes $[RuL_3]^{2+}$ where L = dmpm, dmpe, and $1,2\text{-}(Me_2As)_2C_6H_4$ have been isolated as

the TfO^- salts; the solid-state structure of $[Ru\{1,2\text{-}(Me_2As)_2C_6H_4\}_3]Cl_2$ has been determined.[1487] The reactions of *trans*-$[RuCl(NO)\{1,2\text{-}(Me_2As)_2C_6H_4\}_2]^{2+}$ with NaN_3 followed by treatment with ligands L (L = MeCN, PhCN, py, 4-Etpy, 1-Meim, dmso, pyz, PPh_3, 4,4′-bpy, di-4-pyridyl disulfide, (*E*)-1,2-bis(4-pyridyl)ethene) produce the complexes *trans*-$[RuCl(L)\{1,2\text{-}(Me_2As)_2C_6H_4\}_2]^+$. Under room-temperature conditions, the reaction of *trans*-$[RuCl(NO)\{1,2\text{-}(Me_2As)_2C_6H_4\}_2]^{2+}$ in 1-Meim leads to the formation of *trans*-$[RuCl(NO_2)\{1,2\text{-}(Me_2As)_2C_6H_4\}_2]$. A number of other complexes in this series have been reported including dinuclear species where L is a potential bridging ligand.[1488–1490] The complex *fac*-$[RuCl_3(NO)\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ reacts with AgX ($X^- = CF_3CO_2^-$, NO_3^-, 4-$MeC_6H_4SO_3^-$) in MeCN to yield *cis*$[RuClX_2(NO)\{1,2\text{-}(Me_2As)_2C_6H_4\}]$. Under appropriate conditions, *fac*-$[RuCl_3(NO)\{1,2\text{-}(Me_2As)_2C_6H_4\}]$ has also been converted to *cis*-$[Ru(py)_2(MeO)(NO)\{1,2\text{-}(Me_2As)_2C_6H_4\}]^{2+}$, *cis*-$[Ru(py)_2Cl(NO)\{1,2\text{-}(Me_2As)_2C_6H_4\}]^{2+}$, and *trans*-$[RuCl(NO)(L)\{1,2\text{-}(Me_2As)_2C_6H_4\}]^{2+}$ where L = bpy, phen, 4,4′-Me_2bpy, or dppe.[1491] The complex *trans*-$[RuCl(NO)(bpy)\{1,2\text{-}(Me_2As)_2C_6H_4\}]^{2+}$ reacts with NaN_3 followed by a ligand, L, such as dmso, MeCN, 1-Meim, py, or pyz to produce *trans*-$[RuCl(bpy)(L)\{1,2\text{-}(Me_2As)_2C_6H_4\}]^+$. Analogous chemistry with phen replacing bpy has also been described. The electronic spectroscopic properties of the complexes have been investigated; all the products are slightly photosensitive in solution. Structural data for representative complexes are presented.[1492]

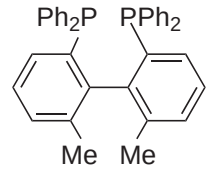
Ligand (**342**) is a good acceptor, and reacts with $[RuCl_2(dmso)_4]$ to give $[RuCl_2(\mathbf{342})_2]$ and $[RuCl_2(dmso)_2(\mathbf{342})]$, the crystal structure of which has been determined.[1493]



(**342**)



(**343**)

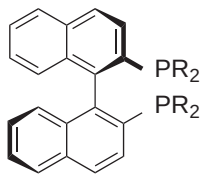


(**344**)

Bisphosphine (**343**) is flexible enough to coordinate with the P atoms mutually *trans* as is exemplified by the structure of $[RuH_2(CO)(PPh_3)(\mathbf{343})]$. The H atoms were not located but the P—Ru—P bond angle of 144.6° suggests that the P atoms should be described as being *trans* (although the ligand is clearly strained) leaving the hydrido ligands mutually *cis*. Two related complexes have been prepared and characterized, and all three species exhibit higher catalytic activity with respect to selected hydrogenations than the corresponding PPh_3 derivatives.[1494]

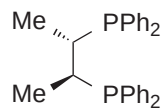
An aspect of the development of chiral catalysts involves studies of chiral bisphosphine ligands, and structures (**24**), (**25**), (**344**)–(**348**) show chiral ligands included in the discussion below. In the presence of NEt_3, $[RuCl_2(PPh_3)(S\text{-}\mathbf{344})]$ reacts with Hacac to generate $[RuCl(acac)(PPh_3)(S\text{-}\mathbf{344})]$; $[RuH(acac)(PPh_3)(S\text{-}\mathbf{344})]$ and $[Ru(acac)_2(S\text{-}(\mathbf{344})]$ have also been prepared. These complexes have been discussed in terms of their relevance to the hydrogenation of 2,4-diketones to diols for which $[RuCl_2(PPh_3)(\mathbf{344})]$ is an enantioselective catalyst.[1495,1496] Treatment of $[RuCl_2(cod)]_n$ with chiral bisphosphines including (*R,R*)-diop, (*R*)-binap, and (*S,S*)-chiraphos in the presence of NEt_3 in toluene leads to the formation of complexes that include $[RuCl_2\{(S,S)\text{-chiraphos}\}_2]$, $[Ru_2Cl_4\{(R,R)\text{-diop}\}_3]$, and $[Ru_2Cl_4\{(R)\text{-binap}\}_2(NEt_3)]$. Changing solvent to ethanol gives a route to *trans*-$[RuHCl\{(R)\text{-binap}\}_2]$. The structures of the complexes have been investigated in solution using NMR spectroscopy, and the crystal structure of *trans*-$[RuHCl\{(R)\text{-binap}\}_2]$ has been determined.[1497] A series of Ru^{II} complexes containing the ligands chiraphos, diop, binap, and, for comparison, achiral ligands dppe and dppb, has been studied for their ability to catalyze imine hydrogenation.[1498] The complexes $[RuCl_2(PR_3)_2(en)]$ (R = Ph or 4-MeC_6H_4) and $[RuCl_2L(dpen)]$ where dpen = (*R,R*)- or (*S,S*)-$Ph(NH_2)CHCH(NH_2)Ph$ and L = (*R*)- or (*S*)-binap, (*R*)- or (*S*)-tolbinap, (*S,S*)-diop, or (*S,S*)-chiraphos are among a group of Ru^{II} complexes that have been prepared, characterized, and shown to be efficient hydrogenation precatalysts.[1499] The syntheses and structural characterizations of *trans*-$[RuCl_2\{(S,S)\text{-}\mathbf{346}\}_2]$ and *trans*-$[RuCl_2\{(S,S)\text{-}\mathbf{347}\}_2]$ have been reported. The complexes react with $TlPF_6$ with the abstraction of Cl^- and formation of $[RuClL_2]^+$. For L = (*S,S*)-**347**, a five-coordinate species is confirmed by a structure determination and this persists in solution, but for L = (*S,S*)-**346**, $[RuClL_2]^+$ dimerizes. These cationic species catalyze the decomposition of ethyl diazoacetate and, in the presence of styrene, cyclopropanation products are formed with enantioselectivity up to 35%. They also act as catalysts for the epoxidation of alkenes with iodosyl benzene as oxidant.[1500] The crystal

structure of *trans*-[Ru(H)Cl{(*R*)-binap}$_2$] has been determined,[1501] and the preparation and reactivity of [RuH{(*R*)-binap}$_2$]$^+$ (which exists as a mixture of two isomers in solution) have been investigated.[1502] Starting from [RuX{(*S*)-binap}(C_6H_6)]Y or [RuX{(*S*)-binap}(4-MeC_6H_4^{i}Pr)]Y (X^-, Y^- = halide or BF_4^-), it has been possible to isolate [Ru_3X_5{(*S*)-binap}$_3$]Y (X = Y = Cl or Br; X = Cl, Y = BF_4) although the success of the reaction depends on conditions. The [$Ru_3(\mu_3$-X)$_2$-(μ-X)$_3${(*S*)-binap}$_3$]$^+$ cation contains a triangular arrangement of Ru^{II} centers with a chelating bisphosphine associated with each Ru atom.[1503] Phosphine exchange is used to prepare [$RuCl_2(PPh_3)$(binap)] from [$RuCl_2(PPh_3)_3$]. In solution, [$RuCl_2(PPh_3)$(binap)] loses PPh_3 and forms [Ru_2Cl_2(binap)$_2(\mu$-Cl)$_2$]. Related dinuclear Ru^{II} complexes containing $Ph_2P(CH_2)_nPPh_2$ (n = 3–6) or chiral bisphosphines such as diop and chiraphos, have also been prepared and their reactivities studied.[1504]



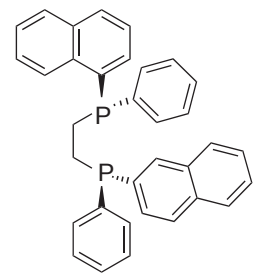
(*R*)-binap R = Ph
(*R*)-tolbinap R = 4-MeC_6H_4

(**345**)

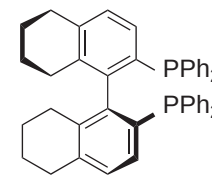


(*S*,*S*)-chiraphos

(**346**)



(*S*,*S*)-(**347**)



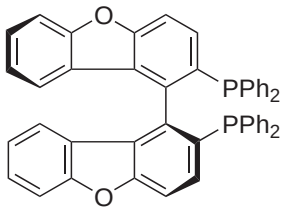
(*S*)-binap-H_8

(**348**)

High-yield syntheses of [Ru(binap)$(OAc)_2$] have been developed starting from [Ru(cod)Cl]$_n$[1505] and utilizing the reduction of [$Ru(acac)_3$] by activated Zn in the presence of binap. The crystal structure of [Ru{(*S*)-binap}$(OAc)_2$] has been determined. The molecules exhibit a mixture of Λ- and Δ-configurations, with the binap-chelate rings each having a δ-conformation. [Ru{(*S*)-binap}$(OAc)_2$] catalyzes the asymmetric hydrogenation of 2-(6′-methoxy-2′-naphthyl) acrylic acid to produce the anti-inflammatory drug (*S*)-naproxen in high optical purity.[1506] A better catalyst for this transformation was found to be [Ru{(*S*)-binap}(OAc)(MeOH)L] where HL = 2-(6′-methoxy-2′-naphthyl)acrylic acid; the structure of this complex has been confirmed by X-ray crystallography.[1507] The asymmetric hydrogenation of α,β- and β,γ-unsaturated carboxylic acids is catalyzed by [Ru{(*S*)-binap-H_8}$(OAc)_2$] where (*S*)-binap-H_8 = (**348**). This catalyst gives higher ee's than (*R*)-binap, and reaction rates are also increased. Other comparative catalytic studies have been carried out with these two complexes.[1508] A general method of preparing [Ru$(ArCO_2)_2$(binap)] catalysts starting from $RuCl_3 \cdot xH_2O$ has been described. The strategy involves the formation of [Ru(cod)(2-methylallyl)$_2$], substitution of allyl by carboxylate ligands, and, finally, substitution of cod by binap. The [Ru$(ArCO_2)_2${(*R*)-binap}] complexes catalyze the enantioselective hydrogenation of 2′-chloroacetophenone to 2′-chlorophenylethanol.[1509] The preparation and catalytic activity of [Ru{(*R*)-binap}(H)(MeCN)$(thf)_2$]$^+$ have been reported; the complex is an active catalyst for the hydrosilylation of ketones and the isomerization, intramolecular hydrosilylation, and hydrogenation of alkenes.[1510] [Ru{(*R*)-binap}(H)(MeCN)L_2]$^+$ (L = e.g., acetone, thf, MeOH) catalyzes the hydrogenation of (*Z*)-methyl-α-acetamidocinnamate (mac) to give H_2mac in 86% ee (*R*). The 1:1 reaction of [Ru{(*R*)-binap}(H)(MeCN)L_2]$^+$ with mac results in the formation of [Ru{(*R*)-binap} (MeCN)(Hmac-*C*,*O*,*O*′)]$^+$, the structure of which has been determined. Experimental data are consistent with this complex being the main species in solution during the catalytic process.[1511] A series of *cis*-[RuX_2{(*R*)-binap}L] complexes in which L = phen, bpy, 4,4′-Me_2bpy, 4,7-Ph_2phen, or bis(2-pyridyl)amine and X = Cl, Br, or I, has been investigated. The crystal structure of *cis*-[$RuBr_2${(*R*)-binap}(bpy)] confirms a λ-conformation for the *R*)-binap chelate ring, and a Λ-configuration at the Ru^{II} center. These and ^{31}P NMR spectroscopic data for all the complexes indicate that the complexes are formed stereoselectively. Furthermore, the spectroscopic data reveal a temperature-dependent, accidental degeneracy of the ^{31}P NMR chemical shifts.[1512] The complex [Ru_2Cl_4{(*S*)-tolbinap}$_2$(NEt_3)] is an active catalyst for the enantioselective hydrosilylation of nitrones with Ph_2SiH_2 up to 91% ee.[1513]

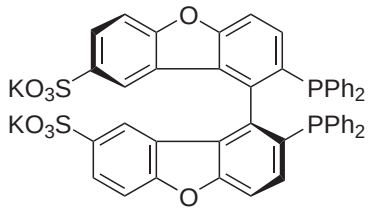
Ligand (**349**), water-soluble (**350**), and their (*R*)-enantiomers have been synthesized, and their Ru^{II} complexes used as catalysts (see also Section 5.5.3.2.5) for the asymmetric hydrogenation of methyl acetoacetate and (*Z*)-acetamidocinnamic acid.[1514] The complex [Ru{(*S*)-**351**}$(OAc)_2$]$^-$ and

the analog containing the (*R*)-bisphosphine are efficient catalysts for the enantioselective hydrogenation (86–98% ee) of 2-pyrones, and details of the reaction mechanism have been discussed.[1515,1516]



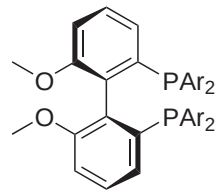
(*S*)-bifap

(**349**)



(*S*)-bifaps

(**350**)



Ar = 3,5-^{t}Bu$_2$C$_6$H$_3$

(*S*)-(**351**)

(See also ref. 1560 in Section 5.5.3.2.5.)

5.5.3.2.3 Mononuclear complexes containing tridentate and tetradentate ligands

Trisphosphine ligands include both linear (e.g., $PhP(CH_2CH_2PPh_2)_2$) and tripodal (e.g., $Me(CH_2PPh_2)_3$) ligands. The complex formulated as $[RuCl_2\{PhP(CH_2CH_2PPh_2)_2\}]$ has been shown to exist as $[Ru_2(\mu\text{-}Cl)_3\{PhP(CH_2CH_2PPh_2)_2\}_2]^+Cl^-$. Both staggered and eclipsed forms of the cation are present in $CDCl_3$ solution, but in the solid state only the eclipsed form is observed. In contrast, the related complex $[RuCl_2\{PhP(CH_2CH_2CH_2PPh_2)_2\}]$ is mononuclear. In the solid state, it is a five-coordinate species, while in coordinating solvents (solv) such as MeCN, six-coordinate $[RuCl(solv)_2\{PhP(CH_2CH_2CH_2PPh_2)_2\}]^+$ is present.[1517] The oxidative addition of I_2 and MeI to $[Ru(CO)_2L]$ where the ligands L are $L^1 = PhP(CH_2CH_2PPh_2)_2$, $L^2 = PhP(CH_2CH_2CH_2PPh_2)_2$, and $L^3 = PhP(CH_2CH_2CH_2PCy_2)_2$, leads to the formation of *fac*-$[RuX(CO)_2L^1]I$ (X = I, Me), *cis,mer*-$[RuI(CO)_2L^2]I$, and *cis,mer*-$[RuI(CO)_2L^3]I$. Under appropriate conditions, the complexes $[RuI_2(CO)L^2]$ and $[RuI_2(CO)L^3]$ could be isolated.[1518] The reaction of $[RuCl_2L^3]$ with AgO_2CMe yields *mer*-$[RuCl(MeCO_2)L^3]$; when AgO_2CMe is replaced by an excess of NaO_2CMe, the product is *fac*-$[RuCl(MeCO_2)L^3]$. When the phosphine ligand is L^2, *fac*-$[RuCl(MeCO_2)L^2]$ can be made starting from $[RuCl_2L^2]_x$. The crystal structure of *fac*-$[RuCl(MeCO_2)L^3]$ has been determined.[1519] The reaction between $[RuCl_2L^3]$ and excess $NaBH_4$ leads to the formation of $[RuH(BH_4)L^3]$, while treatment with excess LiH gives $[RuCl(H)L^3]$. This complex adds CO, $P(OMe)_3$, or MeCN. Under an atmosphere of H_2, $[RuCl_2L^3]$ reacts with NaH to yield $[Ru(H)_2H_2L^3]$ and this is the precursor to a series of compounds $[Ru(H)_2(L)L^3]$ where L = CO, N_2, $P(OMe)_3$, $PhCH_2CN$, and $P(OPh)_3$.[1520] The reactions of $[Ru(H)_2H_2L^3]$ and $[RuCl(H)L^3]$ with acetylenes have also been studied.[1521] The solution isomerization of $[RuCl_2L^3]$ has been investigated. In nonpolar solvents, the *fac* and *mer* isomers are present in equal amounts, while in chlorinated solvents such as CH_2Cl_2 or $CHCl_3$, the major isomer is *fac*-$[RuCl_2L^3]$ with minor amounts of $[Ru_2(\mu\text{-}Cl)_2(L^3)_2]Cl$ and *mer*-$[RuCl_2L^3]$. In polar solvents such as acetic acid or nitromethane, $[Ru_2(\mu\text{-}Cl)_2(L^3)_2]Cl$ is the dominant species.[1522] Displacement of the PPh_3 ligands in $[RuCl_2(PPh_3)_3]$ by (*S,S*)-$PhP(CH_2CHMeCH_2PPh_2)_2$ gives the expected 16-electron product which has been characterized spectroscopically.[1523]

Amino acid complexes $[RuCl\{PhP(CH_2CH_2PPh_2)_2\}A]$ where HA = L-Hala or L-Hval, have been prepared starting from $[Ru_2(\mu\text{-}Cl)_3\{PhP(CH_2CH_2PPh_2)_2\}_2]^+$ and HA. The crystal structure of $[RuCl\{PhP(CH_2CH_2PPh_2)_2\}(L\text{-val})]$ confirms that $PhP(CH_2CH_2PPh_2)_2$ adopts a *fac* arrangement. Reactions of dipeptides with $[Ru_2(\mu\text{-}Cl)_3\{PhP(CH_2CH_2PPh_2)_2\}_2]^+$ have also been investigated, and the complexes $[Ru\{PhP(CH_2CH_2PPh_2)_2\}(glygly)]$ and $[Ru\{PhP(CH_2CH_2PPh_2)_2\}(metgly)]$ have been isolated and characterized.[1524]

Reactions between $PhP\{CH_2CH_2P(C_6H_4\text{-}4\text{-}X)_2\}_2$ (ligand L with X = F, Me, OMe) and *cis*-$[RuCl_2(dmso)_4]$ yield $[Ru_2(\mu\text{-}Cl)_3L_2]Cl$ which exist in solution as equilibrium mixtures of the eclipsed and staggered forms. When the central Ph group in L is changed to a mesityl group, the products of the analogous reactions are mononuclear complexes $[RuCl_2L']$. Reactions of $[Ru_2(\mu\text{-}Cl)_3L_2]Cl$ and $[RuCl_2L']$ with CO have been investigated.[1525] The linear and tripodal ligands $PhP(CH_2CH_2PPh_2)_2(L^1)$, $MeC(CH_2PPh_2)_3(L^2)$, and $P(CH_2CH_2PPh_2)_3(L^3)$ react with $[RuH(Cl)(CO)(AsPh_3)_3]$ to give $[RuH(Cl)(CO)(L^1)]$, $[RuH(Cl)(CO)(L^2)]$, and $[RuH(Cl)(L^3)]$.

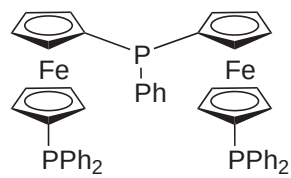
The complexes catalyze the hydrogenation of cyclohexene, cyclohexanone, propanal, and 2-cyclohexen-1-one and their activity exceeds that of analogous complexes containing monodentate PR_3 or AsR_3 ligands.[1526] The crystal structure of $[RuCl_2\{PhP(CH_2CH_2PPh_2)_2\}(dmso\text{-}S)]\cdot C_6H_5Me$ has been determined, confirming a mononuclear species.[1527]

Studies of Ru^{II} complexes containing the tripodal ligand $MeC(CH_2PPh_2)_3(L)$ have included the reactivity of $[RuL(H)(BH_4)]$.[1528,1529] It reacts with benzo[b]thiophene in thf to give a mixture of $[RuL(H)\{BH_3(2\text{-}S(C_6H_4)CH_2CH_3\}]$, $[RuL\{\eta^4\text{-}S(C_6H_4)CH(CH_3)\}]$, $[L(H)Ru\{\mu\text{-}S(C_6H_4)\text{-}CH_2CH_3\}_2Ru(H)L]$, and $[L(H)Ru(\mu\text{-}BH_4)Ru(H)L]^+$. This product distribution is formed at 40 °C and in 3 h. If the reaction is continued for a further 2 h, $[RuL\{\eta^4\text{-}S(C_6H_4)CH(CH_3)\}]$ is absent from the mixture, being converted to $[L(H)Ru\{\mu\text{-}S(C_6H_4)CH_2\ CH_3\}_2Ru(H)L]$. Mechanistic studies have been performed, and the crystal structure of $[RuL(H)\{BH_3(2\text{-}S(C_6H_4)CH_2CH_3\}]$ has been determined.[1528] With KO^tBu, $[RuL(H)(BH_4)]$ reacts to give $K[RuLH_3]$ and BH_2O^tBu, and $K[RuLH_3]$ is also formed in the reaction of $[RuL(MeCN)_3]^{2+}$ with BH_2O^tBu. The complexes $[RuL(H)(BH_4)]$ and $[RuL(MeCN)_3]^{2+}$ are catalyst precursors for the hydrogenolysis of benzo[b]thiophene to 2-ethylthiophenol and this catalytic process has been studied in detail.[1529] The salt $K[RuLH_3]$ reacts with a CO-saturated EtOH solution to yield $[RuLH_2(CO)]$ which has been structurally characterized. Adduct formation via hydrogen bonding between $[RuLH_2(CO)]$ and $(CF_3)_2CHOH$ has been investigated by NMR and IR spectroscopies, and the experimental data reveal that an equilibrium is established involving proton transfer and the formation of $[RuLH(\eta^2\text{-}H_2)(CO)]^+$.[1530] The solution dynamic behavior of $[RuL(MeCN)L']^+$ (L = MeC $(CH_2PPh_2)_3$; L′ = diorganyldithicarbamate or *N,S*-thioamide) has been studied using ^1H and ^{31}P NMR spectroscopies. While these species are fluxional in solution, the complexes $[Ru(Et_2NCS_2)L(X)]^{n+}$ (X = CO, $n = 1$; X = CN, $n = 0$; X = H, $n = 0$) are static. Treatment of $[Ru(MeCN)_3L]^{2+}$ with two or three equivalents of $Na[Et_2NCS_2]$ ultimately results in a change in the coordination mode of the tripodal ligand L (to didentate) and oxidation of the non-coordinated arm of the ligand.[1531] The coordination of $MeC\{CH_2P(3\text{-}CF_3C_6H_4)_2\}_3$ (L′) to Ru and Ir has been investigated. Among the complexes prepared and characterized are $[RuL'(CF_3CO_2)_2]$, $[Ru_2(\mu\text{-}Cl)_3(L')_2]^+$, $[RuH(MeCN)_2(L')]^+$, and $[Ru(MeCN)_3(L')]^{2+}$.[1532]

The ligand $P(CH_2CH_2PCy_2)_3$ has been used in the formation of Ru^{II} hydrido complexes,[1533] and structural features of $[RuH_2\{P(CH_2CH_2PMe_2)_3\}]$ have been described.[1425]

Changing the central atom in $MeC(CH_2PPh_2)_3$ to Si or Sn can have significant affects on the coordination chemistry of the ligand. The complexes $[Ru(CF_3CO_2)_2\{MeSi(CH_2PPh_2)_3\}]$ and $[Ru(CF_3CO_2)_2\{BuSn(CH_2PPh_2)_3\}]$ have been prepared and characterized. A study of the coordination of $BuSn(CH_2PPh_2)_3$ indicates that this ligand cannot stabilize mononuclear five-coordinate dichloro derivatives of Ru^{II}.[1534] The related ligand $MeSi(CH_2PMe_2)_3$ has also been prepared and incorporated into the complex $[RuCl_2\{MeSi(CH_2PMe_2)_3\}(PMe_3)]$. Reduction of this complex by Na/Hg in the presence of aromatic hydrocarbons leads to C—H bond activation and the formation of $[Ru\{MeSi(CH_2PMe_2)_3\}(PMe_3)H(Ar)]$ where Ar = Ph, 3-MeC_6H_4, 4-MeC_6H_4, 3,4-$Me_2C_6H_3$, 3,5-MeC_6H_3, 3-$CF_3C_6H_4$, and 4-$CF_3C_6H_4$. Reactions of $[Ru\{MeSi(CH_2PMe_2)_3\}\text{-}(PMe_3)H(Ph)]$ have been explored.[1535]

Ligand (**352**) reacts with $[RuCl_2(PPh_3)_3]$ with phosphine substitution to yield $[RuCl_2(\mathbf{352})]$ in which the three *P*-donors of (**352**) span one equatorial and two axial sites of the trigonal bipyramidal coordination sphere. Treatment of $[RuCl_2(\mathbf{352})]$ with CO leads to the formation of $[RuCl_2(CO)(\mathbf{352})]$, while reaction with PMe_2Ph results in loss of ligand (**352**).[1536]



(**352**)

Ligands containing four *P*-donor atoms include those of type $P\{(CH_2)_nPR_2\}_3$. Photolysis of $[RuH_2\{P(CH_2CH_2PPh_2)_3\}]$ in thf under an inert atmosphere results in the formation of $[RuH\{P(CH_2CH_2PPh_2)_2(CH_2CH_2PPhC_6H_4\}]$ in which one arm of the ligand has undergone cyclometallation. When reacted with H_2, $[RuH\{P(CH_2CH_2PPh_2)_2(CH_2CH_2PPhC_6H_4\}]$ is converted back to $[RuH_2\{P(CH_2CH_2PPh_2)_3\}]$. The cyclometallated complex also reacts with N_2 to give an end-on N_2 complex of Ru^0. Reactions of $[RuH_2\{P(CH_2CH_2PPh_2)_3\}]$ with CO, ethene,

$HSiEt_3$, and C_6H_6, and the reactivity of $[OsH_2\{P(CH_2CH_2PPh_2)_3\}]$ have also been investigated.[1537] The preparation of $[M^ICl\{P(CH_2CH_2PPh_2)_3\}]$ (M = Fe, Ru, Os) has been achieved by the one-electron reduction of $[MCl\{P(CH_2CH_2PPh_2)_3\}]^+$.[1527,1528] The crystal structure of $[RuCl\{P(CH_2CH_2PPh_2)_3\}][BPh_4]$ has been determined, confirming a square-pyramidal coordination environment.[1538] The electrochemical properties of $[MCl(H)\{P(CH_2CH_2PPh_2)_3\}]$ (M = Fe, Ru, Os) have been investigated. Anodically induced loss of H^- leads to the formation of $[RuCl\{P(CH_2CH_2PPh_2)_3\}]^+$.[1539] The complexes $[MH(H_2)L]^+$ (M = Fe, Ru, or Os) containing the ligand (*S,R*)-$Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$ (L) have been reported. The Os^{II} complex is made by the reaction of *cis*-$[OsCl_2L]$ with H_2 and $NaBPh_4$ in thf, or from *trans*-[OsCl(H)L], H_2 and $NaBPh_4$. The complex $[RuH(H_2)L]^+$ is formed either from *trans*-[RuCl(H)L] or *trans*-$[RuH_2L]$. Proton NMR spectroscopic properties of $[MH(H_2)L]^+$ have been described, and the H—H bond lengths have been calculated to be 0.88 Å (M = Fe), 0.89 Å (M = Ru) and 0.99 Å (M = Os).[1540]

The ligand 1,2,4,5-$(CH_2PPh_2)_4C_6H_2$ has been synthesized by treatment of the corresponding phosphine oxide (prepared from 1,2,4,5-$(CH_2Br)_4C_6H_2$) with $HSiCl_3$. The reaction of 1,2,4,5-$(CH_2PPh_2)_4C_6H_2$ with $[RuCl_2(PPh_3)_4]$ yields $[Cl_2(PPh_3)_2Ru\{\mu$-1,2,4,5-$(CH_2PPh_2)_4C_6H_2\}$-$RuCl_2(PPh_3)_2]$ which has been structurally characterized.[1541]

A number of phosphine-bridged systems containing terminal $M(bpy)_2$ units were described in Sections 5.5.3.1.4 and 5.5.3.1.11. These included $[(bpy)_2XRu(\mu$-*trans*-$Ph_2PCH{=}CHPPh_2)RuX(bpy)_2]^{2+}$ (X = Cl, NO_2),[625] $[(\mathbf{136})M(\mu$-**137**$)Os(bpy)_2]^{4+}$ (M = Ni, Pd, Pt),[626] $[(bpy)_2Ru(\mu$-**138**$)Ru(bpy)_2]^{4+}$,[627] $[(bpy)(MeCN)_2Ru(\mu$-**138**$)Ru(bpy)(MeCN)_2]^{4+}$,[627] and $[(bpy)_2M\{\mu$-$(Ph_2P)_2C{=}C{=}C{=}C(PPh_2)_2\}M(bpy)_2]^{4+}$ (M–M = Ru–Ru, Ru–Os, Os–Os).[955] The allene derivative $(Ph_2P)_2C{=}C{=}C(PPh_2)_2$ acts as a bis(phosphine) ligand to each metal center in $[(bpy)_2Ru\{\mu$-$(Ph_2P)_2C{=}C{=}C(PPh_2)_2\}Os(bpy)_2]^{4+}$. Luminescence from the $Ru(bpy)_2^{2+}$ group is quenched by energy transfer to the Os^{II} center.[1542]

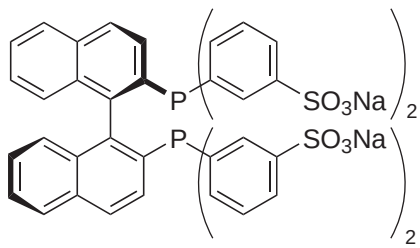
5.5.3.2.4 Dinuclear complexes

A number of Ru^{II} dinuclear complexes containing phosphine ligands have already been mentioned: those listed at the end of the last section,[625,627,955] $[Ru_2Cl_2(binap)_2(\mu$-$Cl)_2]$,[1493] $[Ru_2(\mu$-$Cl)_3\{PhP(CH_2CH_2PPh_2)_2\}_2]^+$,[1517,1524] $[Ru_2(\mu$-$Cl)_2\{PhP(CH_2CH_2CH_2PCy_2)_2\}_2]^+$,[1522] $[Ru_2(\mu$-$Cl)_3\{PhP\{CH_2CH_2P(C_6H_4$-4-$X)_2\}_2\}_2]^+$ (X = F, Me, OMe),[1525] and $[Ru_2(\mu$-$Cl)_3\{MeC\{CH_2P(3$-$CF_3C_6H_4)_2\}_3\}_2]^+$.[1531] The reaction of $[Cl_2(dppb)Ru(\mu$-$dppb)RuCl_2(dppb)]$ with Cl_2 in MeOH results in the formation of *mer*-$[RuCl_3(dppb)(H_2O)]$ when the reaction time is 30 min, and the mixed-valence $[Cl(dppb)Ru(\mu$-$Cl)_3RuCl(dppb)]$ when the reaction is carried out for only 10 min. In the solid state of *mer*-$[RuCl_3(dppb)(H_2O)]$, hydrogen bonding occurs between the aqua and chloro ligands of adjacent molecules.[1543] Complexes of the type $[L_3Ru(\mu$-$X)_3RuL_3]^+$ where L = $AsMe_3$, $AsMe_2Ph$, $AsMePh_2$, and X = Cl or Br have been prepared and characterized along with analogous monodentate phosphine complexes and the complex $[(Ph_3P)(Me_3As)_2Ru(\mu$-$Cl)_3Ru(Ph_3P)(Me_3As)_2]^+$. Mixed-valent species have been generated electrochemically; the properties of the $Ru^{II}Ru^{III}$ arsine-containing systems are reminiscent of ruthenium-blues.[1544]

5.5.3.2.5 Development of water-soluble catalysts

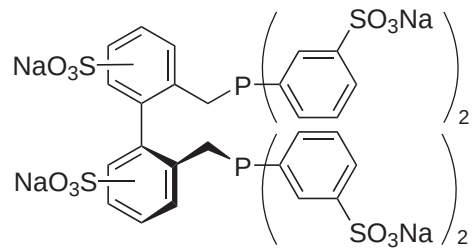
The development of water-soluble compounds for use as homogeneous catalysts has been an important area of research since the early 1990s.[1545–1547] A major advantage of using biphasic mixtures is the recovery of the catalyst from the aqueous phase. One strategy has been to attach sodium sulfonate groups onto phenyl substituents of phosphine ligands, and we have already mentioned the water-soluble ligand (**350**) and the use of its Ru^{II} complex as an asymmetric hydrogenation catalyst.[1514] For $L = P\{(3$-$SO_3Na)C_6H_4\}_3 \cdot 3H_2O$, the complexes $[Ru_2Cl_4L_4]$, $[RuHClL_3]$, $[RuH(OAc)L_3]$, $[RuH_2L_4]$, $[RuHIL_3]$, $[RuCl_2(CO)_2L_2]$, and $[Ru_2(OAc)_2(CO)_4L_2]$ have been prepared, characterized, and studied as catalysts for the hydrogenation of propanal. A kinetic investigation has been undertaken which includes the effects of having salts present in aqueous solution.[1548,1549] The complex $[RuH(Cl)L'_3] \cdot 2H_2O$ ($L' = Ph_2P\{(3$-$SO_3Na)C_6H_4\} \cdot 3H_2O$) has been prepared by ligand exchange in biphasic water/toluene medium, and has been characterized by spectroscopic methods. The water stability of $[RuH(Cl)L'_3] \cdot 2H_2O$ has been confirmed, and it is an active catalyst for the hydrogenation of styrene and cyclohexene.[1550] The related

water-soluble complex $[RuCl_2L'_2]$ catalyzes C–X (X = Cl, Br) to C–H transformations in CCl_4, $CHCl_3$, and 1-halohexanes with an activity that exceeds that of the corresponding PPh_3 complex.[1551] For $L = P\{(3\text{-}SO_3Na)C_6H_4\}_3 \cdot 3H_2O$, the complexes $[Ru_2Cl_2(\mu\text{-}Cl)_2L_4]$ and $[Ru(H)XL_3]$ (X = Cl or OAc), have been synthesized from $[RuCl_2(PPh_3)_3]$ and $[Ru(H)X(PPh_3)_3] \cdot [Ru_2Cl_2(\mu\text{-}Cl)_2L_4]$ has then been used to prepare $[RuH_2L_4]$, $[RuH_2(CO)L_3]$, and $[Ru(H)(\eta^6\text{-}ArH)L_2]Cl$ (e.g., $ArH = C_6H_6$, MeC_6H_5, 1,4-$Me_2C_6H_4$, EtC_6H_5). The water-soluble compounds have been characterized by multinuclear NMR spectroscopy.[1552] Of a range of these complexes studied as catalysts for the hydrogenation of α,β-unsaturated carbonyl compounds, the most promising is $[RuH_2L_4]$.[1553] In solution, spectroscopic data indicate that $[RuCl(H)(CO)L_3]$ and $[RuCl(H)(CO)L'_3]$ (L and L′ as defined above) are structurally analogous to $[RuCl(H)(CO)(PPh_3)_3]$.[1554] Dimeric structures have been confirmed for $[L'_2ClRu(\mu\text{-}Cl)_2RuClL'_2]$ and $[L'_2HRu(\mu\text{-}Cl)_2RuHL'_2]$ where $L' = Ph_2P\{(3\text{-}SO_3Na)C_6H_4\}_3 \cdot 3H_2O$; in earlier studies, these complexes are formulated as unsaturated, mononuclear species. Water-soluble Os^{II} complexes containing $Ph_2P\{(3\text{-}SO_3Na)C_6H_4\}_3 \cdot 3H_2O$ (L′) have also been prepared and characterized: $[L'_2ClOs(\mu\text{-}Cl)_2OsClL'_2]$, $[OsH_4L'_2]$ and $[OsH(Cl)(CO)L'_2]$. Comparisons have been made between the catalytic activities of these Os^{II} and Ru^{II} complexes and related species containing PPh_3 ligands, and the advantages of the water-soluble catalysts are discussed.[1555] Although formulated as $[Ru_2Cl_4L'_4]$, the exact nature of this species depends on pH. The equilibrium distribution of $[Ru_2Cl_2H_2L'_4]$, $[RuH(Cl)L'_3]$, and $[RuH_2L'_4]$ in the presence of excess L′ and as a function of pH has been established using pH-potentiometric and NMR spectroscopic methods. At pH = 3.3, the main species is $[RuH(Cl)L'_3]$, and at pH = 7, $[RuH_2L'_4]$ is dominant. The change affects the catalytic properties of the system as is illustrated by a detailed study of the selectivity of hydrogenation of (*E*)-cinnamaldehyde.[1556] Application of the sulfonation strategy to chiral ligands is represented by the preparation of sulfonated binap and its incorporation into a water-soluble Ru^{II} complex, proposed to be $[Ru(\mathbf{353})(C_6H_6)]^{2+}$, which is an active asymmetric hydrogenation catalyst.[1557] The family of sulfonated ligands has been extended to (**354**) and related derivatives bearing up to six $SO_3^-Na^+$ groups[1558] and has potential for Ru^{II} catalyst development.



(*R*)-binap-4SO_3Na

(**353**)



(**354**)

Other strategies of effecting water solubility include the preparation of phosphines containing hydroxyl substituents. The complex $[RuCl_2\{PH(CH_2OH)_2\}_2\{P(CH_2OH)_3\}_2]$ is an efficient catalyst for the hydrogenation of supercritical (sc) CO_2 under sc-CO_2/H_2O multi-phasic conditions.[1559] The ligands $P(CH_2OH)_3$, $P(CH_2CH_2CH_2OH)_3$, and $P\{(3\text{-}SO_3Na)C_6H_4\}_3$ have been incorporated into water-soluble complexes of type $[(\eta^5\text{-}C_5Me_5)Ru(CO)Cl(PR_3)]$ and $[(\eta^5\text{-}C_5Me_5)Ru(CO)(PR_3)]^+$, the cationic species being formed *in situ*. The complexes have been evaluated as hydrogenation catalysts for conversion of hexa-2,4-dienoic acid to (*E*)- and (*Z*)-hex-3-enoic. Changing the PR_3 ligand provides some control over the stereochemistry of the reaction.[1560] The catalytic properties of water-soluble Ru^{II} complexes containing 1,3,5-triaza-7-phosphaadamantane (pta) have also been investigated. The reaction of $RuCl_3 \cdot xH_2O$ with pta in EtOH yields *cis*-$[RuCl_2(pta)_4]$ which has been structurally characterized.[1561] $[RuCl_2(pta)_4]$ catalyzes the regioselective transformation of unsaturated aldehydes to unsaturated alcohols,[1561] and the hydrogenation of CO_2 and HCO_3^-.[1562] The reaction of *cis*-$[RuCl_2(pta)_4]$ with H_2 (60 bar) in aqueous solution results in the formation of *cis*-$[Ru(H)_2(pta)_4]$ or *cis*-$[RuH(X)(pta)_4]$ (X = Cl or H_2O) depending on the pH. When excess pta is present, the product is $[RuH(pta)_5]^+$. The role of these hydrido complexes as active catalysts is discussed.[1562] The complex $[Ru(H_2O)_3(pta)_3]^{2+}$ catalyzes C–X (X = Cl, Br) to C–H transformations in CCl_4, $CHCl_3$, and 1-halohexanes, but is a less active catalyst than $[RuCl_2L'_2]$ where $L' = Ph_2P\{(3\text{-}SO_3Na)C_6H_4\}$.[1551]

Finally, it is worth noting that the water-soluble Ru^0 carbonyl cluster $[Ru_3(CO)_6L'_3]$ where $L' = Ph_2P\{(3\text{-}SO_3Na)C_6H_4\}$ has been prepared and shown to be an active hydrogenation and hydroformylation catalyst.[1563]

5.5.3.3 Oxygen-donor Ligands

This section is organized by ligand type, starting with aqua complexes, progressing through simple monodentate and didentate ligands, to catechol and quinone complexes, and finishing with tripodal ligands.

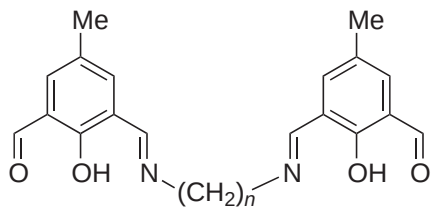
The kinetics of the substitution reactions between $[Ru(H_2O)_6]^{2+}$ and dmso, MeCN, 1,4-thioxane, tetrahydrothiophene, and the *N*-methylpyrazinium ion have been investigated using UV–vis spectrophotometry and ^1H NMR spectroscopy. The results are consistent with an interchange dissociation mechanism.[1564] The kinetics of the substitution reaction of $[Ru(H_2O)_6]^{2+}$ with $[C_2O_4]^{2-}$ have also been investigated.[1565] Ligand exchange reactions of $[Ru(cod)(H_2O)_4]^{2+}$ have formed part of a study that included the crystal structure of this complex.[1566] The complexes $[M(H_2O)(RSO_3)_2(CO)(PPh_3)_2]$ and $[M(RSO_3)_2(CO)_2(PPh_3)_2]$ (R = Me, CF_3, 4-MeC_6H_4) have been prepared starting from RSO_3H and $[MH_2(CO)(PPh_3)_3]$ (M = Ru, Os), $[Ru(CO)_3(PPh_3)_2]$ or $[OsH_2(CO)_2(PPh_3)_2]$. The solid-state structure of $[Ru(H_2O)(4\text{-}MeC_6H_4SO_3)_2(CO)(PPh_3)_2]$ has been confirmed, and strong hydrogen bonding is observed between H(aqua) and non-coordinated O(sulfonate).[1567] A further aqua carbonyl complex is *trans*-$[RuCl_2(PEt_3)_2(CO)(H_2O)]$, the synthesis, structure, and reactions of which have been reported.[1568]

A simple method for preparing $[Ru(dmso\text{-}O)_6]^{2+}$ starting from $RuCl_3{\cdot}xH_2O$ has been described; *O*-coordination is confirmed by a crystal structure determination of the $CF_3SO_3^-$ salt.[75] The complexes $[Ru(acac)_2(CO)L]$ (L = MeOH, EtOH, ^{i}PrOH) have been selectively prepared by the radiolysis of solutions of $[Ru(acac)_3]$ in the appropriate alcohol. The methanol derivative has been characterized by IR, NMR, and UV–vis spectroscopies as well as by a structure determination; there is a *trans* arrangement of CO and MeOH ligands.[1569] The complex *trans*-$[Ru^{III}(acac)_2Cl_2]^-$ is a precursor to *trans*-$[Ru^{II}(acac)_2L_2]$ where L = MeCN or pyrazine (pyz); the *cis* analogs result from direct reaction between $[Ru(acac)_3]$ and MeCN or pyz, or by thermal isomerism of the *trans* complexes.[84]

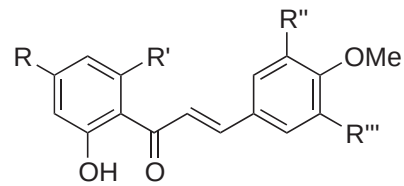
Simple carboxylate complexes of Os^{II} include $[Os(MeCO_2)Br(CO)(PPh_3)_2]$, the crystal structure of which has been determined; the acetate ligand is didentate and there are *cis*-arrangements of the two PPh_3 and of the Br^- and CO ligands.[1570] The reaction of $[Ru_2(CF_3CO_2)_4(H_2O)(cod)_2]$ with chiral bisphosphines (L) such as (*S,S*)-diop (see (**24**)) and (*S,S*)-$MeCH(PPh_2)$-$CH_2CH(PPh_2)Me$ in methanol or ethanol, lead to the formation of $[Ru(CF_3CO_2)_2(MeOH)_2L]$ and $[Ru(CF_3CO_2)_2(EtOH)_2L]$ which have been spectroscopically and structurally characterized. The trifluoroacetate groups are monodentate and *trans* to each other. Selected complexes were tested for their ability to act as asymmetric hydrogenation catalysts.[1571] In order to investigate species present in hydrogenation catalytic systems containing phosphine-substituted Ru carbonyl complexes, the reaction of H_2 with $[Ru(CO)_2(MeCO_2)_2(PR_3)_2]$ (R = Ph, Bu) in the presence of Na_2CO_3 (to facilitate removal of acetate ligand) has been studied under various conditions. The intermediate $[RuH(CO)_2(MeCO_2)(PR_3)_2]$ has been observed at low temperature. Starting with $[Ru_2(CO)_4(MeCO_2)_2(PR_3)_2]$, hydrogenolysis leads to cluster products. Mechanistic details of these reactions are discussed.[1572] The solid-state structure of *fac*-$[Ru(MeCO_2)_2(PPh_3)_3]{\cdot}2MeCO_2H$ reveals the presence of one monodentate and one didentate acetate ligand. A solution ^{31}P NMR spectroscopic study of the fluxional behavior of this complex reveals that two separate dynamic processes operate.[1573] A series of complexes of type $[Ru(CO)_2(MeCO_2)_2L]$ where L = bpy, phen, or related ligands has been studied. The acetate ligands are proposed to be monodentate and are mutually *cis*,[1574] and a crystallographic determination for $[Ru(CO)(HCO_2)(bpy)_2]$ confirms a monodentate mode for the formate ion.[1575] Related complexes have been prepared and characterized spectroscopically.[1575] The reactions between *N*-acyl-α-aminocarboxylates and $[RuHCl(CO)(PPh_3)_3]$ and $[RuH_2(PPh_3)_4]$ results in the formation of $[RuCl(\eta^2\text{-}RCONHCHR'CO_2)(CO)(PPh_3)_2]$ and $[RuH(\eta^2\text{-}RCONHCHR'CO_2)(PPh_3)_3]$. The crystal structure of $[RuCl(\eta^2\text{-}PhCONHCH_2CO_2)(CO)(PPh_3)_2]$ confirms the didentate mode for the carboxylate, and a *trans* disposition of the PPh_3 ligands.[1576]

The hydrolysis of $[OsH(CO)(Ph)(P^tBu_2Me)_2]$ produces the hydroxo complex $[OsH(CO)(OH)(P^tBu_2Me)_2]$, confirmed by an X-ray diffraction study. Dihydrogen reacts with $[OsH(CO)(OH)(P^tBu_2Me)_2]$ releasing H_2O and forming $[OsH_2(H)_2(CO)(P^tBu_2Me)_2]$.[1577] The hydroxo

complex $[RuH(OH)(PMe_3)_4]$ forms when *fac*-$[RuH(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ or $[Ru(\eta^2\text{-}C_2H_4)(PMe_3)_4]$ reacts with H_2O. Starting from *fac*-$[Ru(Me)(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ in place of *fac*-$[RuH(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ results in the formation of $[Ru(Me)(OH)(PMe_3)_4]$. Interestingly, the reaction of $[Ru(\eta^2\text{-}C_2H_4)(dmpe)_2]$ with an excess of water produces $[\{RuH(OH)(dmpe)_2\}_2(\mu\text{-}H_2O)_2]$ in which the hydroxo dimer is supported by hydrogen-bonded interactions involving two H_2O molecules.[1578] The complex *fac*-$[Os(H)(\eta^2\text{-}Me_2PCH_2)(PMe_3)_3]$ is a precursor to a series of phenoxide, thiophenoxide, and anilide complexes *cis*-$[Os(H)(PMe_3)_4(XC_6H_4\text{-}4\text{-}R)]$ (X = O and R = H, OMe, CF_3, NH_2, CN; X = S and R = H, OMe; X = NH and R = H, OMe, CF_3). The reactivities of these complexes with respect to substitutions have been compared.[1579] The reaction of 4-Me-2,6-$(CHO)_2C_6H_2OH$ with $[RuCl_2(PPh_3)_3]$ in the presence of 4-$MeC_6H_4NH_2$ in boiling ethanol yields a Ru^{II} Schiff base complex containing a four-membered RuCCO metallacycle involving the phenoxide O atom.[1580] Quite a different reaction pathway is reported for the condensation of 4-Me-2,6-$(CHO)_2C_6H_2OH$ with diamines in the presence of $[RuCl_2(dmso)_4]$. Dinuclear complexes $[Ru_2Cl_4(dmso)_4(\mu\text{-}\mathbf{355})]$ are formed in which ligand (**355**) acts as an *O,O′*-chelate to each Ru^{II} center.[1581] Treatment of the ligands H(**356**) with KO^{t}Bu followed by $[RuCl_2(dmso)_4]$ yields $[Ru(\mathbf{356})_2(dmso)_2]$. A related complex with the saturated analog of ligand H(**356**) (R = R′ = R″ = R‴ = OMe) has also been prepared. Detailed NMR spectroscopic characterization of the complexes indicates the presence of a number of isomers and in each, $(\mathbf{356})^-$ acts as an *O,O′*-donor.[1582] Starting from $[Ru(PPh_3)_3Cl_2]$, the Ru^{III} complexes $[Ru(PPh_3)_2Cl_2L]$ have been prepared where HL is salicylaldehyde, 2-hydroxyacetophenone, or 2-hydroxynaphthylaldehyde. However, when HL is used in a twofold excess in the presence of base, Ru^{II} complexes $[Ru(PPh_3)_2L_2]$ are formed. Two isomers of $[Ru(PPh_3)_2L_2]$ have been isolated, and characterized in solution by ^1H NMR spectroscopy. The crystal structure of one isomer of $[Ru(PPh_3)_2L_2]$ where HL = salicylaldehyde has been determined.[78]



n = 2, 3, 4
(**355**)



R = R′ = R″ = R‴ = H
R = R″ = R‴ = H; R′ = OMe
R = R′ = R″ = R‴ = OMe
H(356)

Assignment of oxidation states in metal quinone (Q)/semiquinone (SQ)/catechol (cat) complexes can be ambiguous and readers with an interest in this area should refer both to this section and to Section 5.5.2.3.2. Oxidation of the complexes $[Ru^{II}(cat)(py)_4]$ and $[Ru^{II}(cat)(bpy)_2]$ (H_2cat stands for catechol, 3,5-di-*tert*-butylcatechol or 3,4,5,6-tetrachlorocatechol) generates $[Ru^{II}(SQ)(py)_4]^+$ and $[Ru^{II}(SQ)(bpy)_2]^+$. ESR spectroscopic data are consistent with oxidation of the ligand rather than the Ru^{II} center, although low-temperature work in polar solvents indicates that the ground state contains partial Ru^{III} character.[1583] A crystallographic study of $[Ru(SQ)(bpy)_2][ClO_4]$ for SQ being the 3,5-di-*tert*-butylsemiquinonato ligand is also consistent with an Ru^{II} complex, but some distortion in the ligand towards a cat^{2-} form suggests some Ru^{III} character.[1584] Electrochemical and spectroscopic data indicate that further oxidation of $[Ru(SQ)(bpy)_2]^+$ is also ligand-centered and generates $[Ru^{II}(Q)(bpy)_2]^{2+}$.[1583] The study has been extended to complexes of type $[Ru(bpy)(dioxolene)_2]^{n+}$ and $[Ru(py)_2(dioxolene)_2]^{n+}$ where dioxolene is again derived from catechol, 3,5-di-*tert*-butylcatechol, or 3,4,5,6-tetrachlorocatechol.[1585,1586] Resonance Raman and electronic spectroscopies have been used to investigate the electronic structures of $[RuL(bpy)_2]^{n+}$ where L is quinone or a derivative in which the *O,O′*-donor is replaced, first by an *N,O*-, and then by an *N,N′*-donor (i.e., a diimine).[1587] Structural and electrochemical data have been used to gain an insight into the charge distribution in $[OsCl_2(Q)(PPh_3)_2]$ and $[Os(Q)_2(PPh_3)_2]$ (Q is derived from 3,5-di-*tert*-butylcatechol or 3,4,5,6-tetrachlorocatechol). It is concluded that $[Os(Q)_2(PPh_3)_2]$ is best described as an Os^{IV} species, contrasting with the analogous Ru species which is formulated as $[Ru^{II}(SQ)_2(PPh_3)_2]$.[1588] The reactions of $Ru_3(CO)_{12}$ with 3,6-di-*tert*-butyl-1,2-benzoquinone and 2,4,6,8-tetra-*tert*-butylphenoxazin-1-one lead to complexes of type *cis*-$[Ru(CO)_2L_2]$ in which the ligand radicals are

antiferromagnetically coupled; structural data are reported. Electrochemical studies reveal ligand-based redox processes.[1589] The synthesis of the paramagnetic complex $[Ru^{II}Cl(DBQ)(tpy)]$ (DBQ = 3,5-di-*tert*-butylquinone) has been described. The complex exhibits three reversible electrochemical processes: a metal-based oxidation, a DBSQ reduction, and a tpy reduction. $[Ru^{II}Cl(DBQ)(tpy)]$ can be reversibly converted to $[Ru^{II}(H_2O)(DBQ)(tpy)]^+$ which has been characterized as the perchlorate salt.[1590] The reactions of H_2L (H_2L = catechol, 4-^{t}Bu-catechol, 3,5-^{t}Bu$_2$-catechol, 3,4,5,6-Cl_4-catechol) with $[RuH(Hsal)(PPh_3)_3]$ (H_2sal = salicylic acid) result in the formation of $[Ru^{II}(SQ)_2(PPh_3)_2]$. There is evidence for significant $d\pi(Ru) \rightarrow p\pi^*(SQ)$ back-bonding. Electrochemical studies have been carried out and the initial one-electron reduction produces the $Ru^{III}(cat)_2^-$ species.[1591]

Tripodal *O,O′,O″*-donors are represented by the ligands $HC\{P(O)Ph_2\}_3$, $[RPO(C_6H_4O)_2]^{2-}$, and $[CpCo\{PO(OEt)_2\}_3]^-$. These ligands form complexes with Ru^{II} and the crystal structure of $[(\eta^6\text{-}4\text{-}^iPrC_6H_4Me)Ru\{\eta^3\text{-}PhPO(C_6H_4O)_2\}]$ has been determined.[1592] The $[P_3O_9]^{3-}$ anion is an effective tripodal ligand and reacts with $[(\eta^6\text{-}4\text{-}^iPrC_6H_4Me)_2Ru_2Cl_4]$ to give $[(\eta^6\text{-}4\text{-}^iPrC_6\ H_4Me)Ru(\eta^3\text{-}P_3O_9)]^-$ which has been characterized spectroscopically as the tetrabutylammonium salt. Prolonged photolysis of this complex in MeCN yields $[Ru(MeCN)_3(\eta^3\text{-}P_3O_9)]^-$.[1593] Polyoxometallates are also capable of acting as *O,O′,O″*-donors as exemplified in the Ru^{II} complex $[(\eta^6\text{-}4\text{-}^iPrC_6H_4Me)Ru(\eta^3\text{-}Nb_2W_4O_{19})]^{2-}$.[1593] The $[P_3O_9]^{3-}$ ligand also features within a series of dinuclear Ru^I carbonyl complexes: $[\{\eta^3\text{-}P_3O_9\}(CO)Ru(\mu\text{-}CO)_2Ru(CO)\{\eta^3\text{-}P_3O_9\}]^{4-}$ has been prepared and structurally characterized.[1594]

5.5.3.4 Sulfur-donor Ligands

5.5.3.4.1 Mononuclear complexes

The organization of this section is according to ligand type and begins with Ru^{II} and Os^{II} complexes where *S*-bound dmso is the primary ligand of interest. Both *cis*- and *trans*-$[RuCl_2(dmso)_4]$ exhibit anti-tumor activity and this property has resulted in increased interest in these and related compounds. Molecular mechanics force-field parameters have been developed for Ru^{II} sulfoxide complexes, and conformational analyses of complexes containing *S*- and *O*-bonded R_2SO have been carried out.[1595] The product of a published method of making $'[RuBr_2(dmso)_3]'$,[1596] has been reformulated as a mixture of $Li[fac\text{-}RuCl_nBr_{3-n}(dmso)_3]$ (n = 0–3). In addition to multinuclear NMR spectroscopic data, this result is confirmed by the crystal structure of solvated $[Et_4N][fac\text{-}RuBr_3(dmso\text{-}S)_3]$.[1597] This has implications on the report of the use of "$[RuBr_2(dmso)_3]$" as a starting material for the preparation of a range of Ru^{II} complexes including $[RuBr_2(dmso)_2L_2]$ (L_2 = $(py)_2$, $(AsPh_3)_2$, phen, bpy), $[RuBr_2(CS)(dmso)_2]$, and $[RuBr_2(AsPh_3)_2(dmso)]$.[1598] A crystallographic study of the series of salts $[RR'NHOH][fac\text{-}RuCl_3(dmso\text{-}S)_3]$ (R = R′ = H; R = Me, R′ = H; R = R′ = Et) has revealed the presence of hydrogen-bonded chain structures. The hydrogen bonds are between the cation OH groups and the Cl and dmso-O atoms of the complex anions. Application of molecular mechanics calculations[1595] indicate that the arrangement of the dmso ligands in $[fac\text{-}RuCl_3(dmso\text{-}S)_3]^-$ is a consequence of intramolecular interactions rather than intermolecular hydrogen bonding.[1599] A convenient route to *trans*-$[RuCl_2(dmso)_4]$,[102] the synthesis and solid-state structure[100,103] of *cis*-$[RuCl_2(tmso)_4]$ (tmso = tetramethylenesulfoxide), and the syntheses of *trans*-$[RuCl_2(tmso)_4]$, *cis*-$[RuBr_2(tmso)_4]$, and *trans*-$[RuBr_2(tmso)_4]$[104] have been described. It has been confirmed that the solid-state structures of the *cis* and *trans* isomers of $[OsCl_2(dmso)_4]$ involve all *S*-bound ligands. For the *trans* isomer, this agrees with spectroscopic data, but for the *cis* isomer, the results of the crystal structure determination contrast with the proposed solution structure of *cis*-$[OsCl_2(dmso\text{-}O)(dmso\text{-}S)_3]$.[1600] The reactions of *cis*-$[RuCl_2(dmso\text{-}O)(dmso\text{-}S)_3]$ with 5′-GMP and 5′-AMP have been investigated in aqueous solution and at physiological pH. NMR spectroscopic data indicate that 5′-GMP binds through guanine N(7) or the phosphate group to give two products, while 5′-AMP probably binds through the phosphate group.[1601] In a related study, electrospray mass spectrometry and ^{1}H NMR spectroscopy have been applied to analyze the products of the reactions between *trans*- and *cis*-$[RuCl_2(dmso\text{-}S)_4]$ and deoxynucleosides. The differences in interactions of the two isomers with 2′-deoxyguanosine, 2′-deoxyadenosine, 2′-deoxycytidine, and 2′-deoxythymidine are described; the results are of relevance to the anti-tumor activity of $[RuCl_2(dmso\text{-}S)_4]$.[1602] Linkage isomerism in dmso complexes may be induced electrochemically and this has been observed for $[Ru(NH_3)_5(dmso)]^{2+/3+}$ and $[Ru(NH_3)_4(dmso)_2]^{2+/3+}$. The rates of

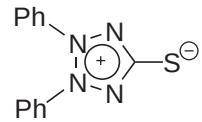
isomerization have been investigated.[1603] Isomerization is also observed in reactions of $[RuCl_2(dmso)_4]$ with CO where coordination of CO causes the dmso ligand *trans* to the CO to switch from *S*- to *O*-bound. Carbonyl derivatives that have been isolated and characterized (including representative structural determinations) are *trans,cis,cis*-$[Ru(CO)(dmso\text{-}O)(dmso\text{-}S)_2Cl_2]$, *cis,cis,cis*-$[Ru(CO)_2(dmso\text{-}O)(dmso\text{-}S)Cl_2]$, *cis,trans,cis*-$[Ru(CO)_2(dmso\text{-}S)_2Cl_2]$, *fac*-$[Ru(CO)_3Cl_2(dmso\text{-}O)]$, *trans,trans,trans*-$[Ru(CO)(dmso\text{-}O)(dmso\text{-}S)_2Cl_2]$, and *cis,cis,trans*-$[Ru(CO)_2(dmso\text{-}O)_2Cl_2]$.[1604] A third example of linkage isomerization for the Ru^{II}-bound dmso ligand is seen when a dmso solution of $[Ru(bpy)_2(dmso\text{-}S)_2]^{2+}$ is photolysed. The $S \rightarrow O$-bonded dmso rearrangement is reversible, and the solid-state structure of the thermodynamically favored $[Ru(bpy)_2(dmso\text{-}S)_2]^{2+}$ has been established for the $CF_3SO_3^-$ salt.[1605] A series of complexes derived from *cis*- and *trans*-$[RuCl_2(dmso)_4]$ and containing *N*-donor ligands has been reported. These include *cis,fac*-$[RuCl_2(dmso)_3L]$ ($L = NH_3$, im), *cis,cis,cis*-$[RuCl_2(dmso)_2(im)_2]$, *fac*-$[Ru(im)_3Cl(dmso)_2]^+$, *trans,cis,cis*-$[RuCl_2(dmso)_2L_2]$ ($L = NH_3$, im, bim), and *trans*-$[RuCl_2(dmso)_3(im)]$.[1595] The crystal structures of *cis,fac*-$[RuCl_2(dmso)_3(NH_3)]$,[1606] *trans,cis,cis*-$[RuCl_2(dmso)_2(NH_3)_2]\cdot H_2O$,[1595] and *trans,trans,trans*-$[RuCl_2(dmso)_2(im)_2]$[30] have been determined. The unusual complex $[Li_2Ru_2Br_6(tmso)_4(\mu\text{-}tmso)_2(\mu_3\text{-}tmso)_2]$ has been isolated from the reaction of $RuCl_3\cdot xH_2O$, tetramethylenesulfoxide (tmso) and LiBr in dry MeOH; *cis*-$[RuBr_2(tmso)_4]$ is formed as a minor product. When the solvent is changed to EtOH and dmso replaces tmso, the reaction yields *trans*-$[RuBr_2(dmso)_4]$. A structural determination of $[Li_2Ru_2Br_6(tmso)_4(\mu\text{-}tmso)_2(\mu_3\text{-}tmso)_2]$ shows that the dmso ligands coordinated to the Ru^{II} centers are *S*-bonded; the two $RuBr_3(dmso)_3$-units are connected via two Li centers, each bearing a terminal *O*-bonded dmso ligand and bridged to each Ru center via an Li(*O*-dmso-*S*)Ru interaction.[1607]

The results of a vibrational spectroscopic study of the SO_2 complexes $[RuX(SO_2)(NH_3)_4]^+$ (X = Cl, Br) and $[Ru(H_2O)(SO_2)NH_3)_4]^{2+}$ have been reported; the ν(sym) and ν(asym) modes of the *S*-bound SO_2 ligand come at lower frequencies than those of the free molecule.[1608] The ammonium salt of the sulfito complex *trans*-$[Ru(SO_3\text{-}S)_2(NH_3)_4]\cdot 4H_2O$ has been structurally characterized. Although the crystals are stable when retained in the mother liquor, the isolated compound is only stable at 298 K for several days. Relationships between the structural and vibrational spectroscopic data are discussed.[1609]

The complex $[Ru(NO)(NH_3)(S_4)_2]^-$ has been prepared and crystallographically characterized. It contains two S_4^{2-} chelating ligands, and the NO and NH_3 ligands are mutually *trans*. This complex was the first polysulfido nitrosyl complex of ruthenium.[1610]

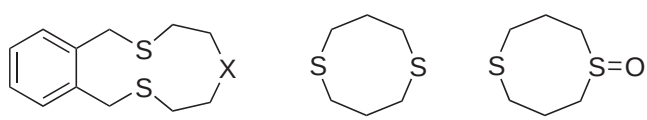
One method of preparing thiolate complexes of Ru^{II} has involved the use of $[Me_2SSMe][BF_4]$. For example, $[Ru(CO)_3(SMe)(PPh_3)_2]^+$ has been prepared by treating $[Ru(CO)_3(PPh_3)_2]$ with $[Me_2SSMe]^+$.[1611] As part of a study of Os^{II} and Os^{III} thiolate complexes, *trans,trans,trans*-$[Os(CO)_2(SC_6F_5)_2(PEt_2Ph_3)_2]$ has been prepared and structurally characterized.[109] The complex *cis,cis,trans*-$[Ru(CO)_2(SR)(H)(PPh_3)_2]$ has been made by the oxidative addition of RSH (R = H, alkyl, aryl) to $[Ru(CO)_2(PPh_3)_3]$. When RSSR (R = aryl) oxidatively adds to $[Ru(CO)_2(PPh_3)_3]$, the product is *cis,cis,trans*-$[Ru(CO)_2(SR)_2(PPh_3)_2]$.[1612] The reactions of $[Ru(CO)_2(PPh_3)_3]$ or *cis,cis,trans*-$[Ru(H)_2(CO)_2(PPh_3)_2]$ with H_2S in thf result in the formation of *cis,cis,trans*-$[Ru(CO)_2(SH)_2(PPh_3)_2]$. Hydrogen sulfide reacts with a mixture of *cis*- and *trans*-$[Ru(H)_2(dppm)_2]$ to produce only the *trans*-isomer of $[Ru(H)(SH)(dppm)_2]$, further reaction of which with H_2S leads to *cis*- and *trans*-$[Ru(SH)_2(dppm)_2]$. Details of H/D exchange reactions of *cis,cis,trans*-$[Ru(CO)_2(SH)_2(PPh_3)_2]$ and *cis,cis,trans*-$[Ru(CO)_2(SH)(H)(PPh_3)_2]$ with CD_3OD are also described.[1613] The reactions of NaSPh and *trans*-$[Ru(H)(H_2)(dppe)_2]^+$ or *trans*-$[Os(H)(Br)(dppe)_2]$ yield *trans*-$[Ru(H)(SPh)(dppe)_2]$ (structurally confirmed) and $[Os(H)(SPh)(dppe)_2]$. When these complexes are treated with $HBF_4\cdot Et_2O$, the coordinated PhS^- is protonated, and with excess HBF_4, $[Os(H_2)(HSPh)(dppe)_2]^{2+}$ is formed.[1614]

The reaction between ligand (**357**) and $[Ru(tpy)(H_2O)(bpy)]^{2+}$ yields $[Ru(tpy)(\mathbf{357})(bpy)]^{2+}$, isolated as the ClO_4^- salt. Coordination through the *S*-donor atom is confirmed by a single-crystal structure.[1615]



(**357**)

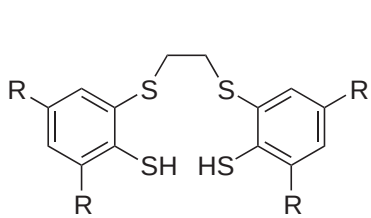
The thioether complex $[Ru(NH_3)_5(MeSEt)]^{2+}$ has been prepared by treating $[Ru(NH_3)_5Cl]Cl_2$ with Ag_2O in CF_3CO_2H, followed by reduction with Zn amalgam and reaction with MeSEt. $[Ru(NH_3)_5(MeSEt)]^{2+}$ was isolated as the PF_6^- salt and structurally characterized. The Ru—S (but not Ru—N) bond lengths are shorter than in the analogous Ru^{III} complex, indicating significant backbonding to the thioether ligand. The structural investigation is complemented by ab initio MO calculations.[1616] There is a range of examples of Ru^{II} and Os^{II} complexes containing cyclic thioethers. 1,4,7-Trithiacyclononane, [9]aneS$_3$, forms the complexes $[Ru([9]aneS_3)_2]^{2+}$,[1617] $[Os([9]aneS_3)_2]^{2+}$,[1618] $[Os(\{\eta^6\text{-}4\text{-}MeC_6H_4{}^iPr)([9]aneS_3)]^{2+}$,[1618] $[OsH(CO)(PPh_3)([9]aneS_3)]^{2+}$,[1618] $[RuCl_2(dmso)([9]aneS_3)]$,[1619] $[RuCl(L)([9]aneS_3)]^+$ (L = bpy, 4,4′-Ph$_2$bpy, phen, 4,7-Ph$_2$phen),[1619] $[Ru(MeCN)_3([9]aneS_3)]^{2+}$,[1620] $[Ru(MeCN)_2(PPh_3)([9]aneS_3)]^{2+}$,[1620] $[Ru(HBpz_3)([9]aneS_3)]^+$,[1620] $[Ru(HCpz_3)([9]aneS_3)]^{2+}$,[1620] and $[Ru(PPh_3)(S_2CNMe_2)([9]aneS_3)]^+$,[1620] structural data for most of which have been reported. The complex $[Ru(MeCN)_3([9]aneS_3)]^{2+}$ has been used to prepare the dinuclear species $[Ru_2([9]aneS_3)_2(\mu\text{-}S_2CNMe_2)_2]^{2+}$,[1620] and $[Ru_2([9]aneS_3)_2(\mu\text{-}L)_2]^{2+}$ (HL = 1,3-benzothiazol-2-thione or pyridine-2-thione).[1621] In the latter complexes, μ-L$^-$ is tridentate, utilizing *N*- and *S*-donors. Recrystallization of $[Ru_2([9]aneS_3)_2(\mu\text{-}L)_2]^{2+}$ (HL = 1,3-benzothiazol-2-thione) from MeCN solution results in the formation of $[Ru_2(MeCN)_2([9]aneS_3)_2(\mu\text{-}L)_2]^{2+}$ in which μ-L$^-$ coordinates only through sulfur. Further variation in L$^-$ bonding modes in related complexes has been described.[1621] The preparation, spectroscopic, and electrochemical properties and crystal structure of $[Ru([10]aneS_3)_2]^{2+}$ ([10]aneS$_3$ = 1,4,7-trithiacyclodecane) have been described.[1622] The ligands (**358**) react with $[RuCl_2(dmso)_4]$, $[RuCl_2(PPh_3)_3]$ and $[RuH(Cl)(PPh_3)_3]$ to give macrocyclic complexes that include $[RuCl_2(dmso)$(**358**, X = S)] and $[RuCl_2(PPh_3)$(**358**, X = O)], the solid-state structures of which have been established. In both, the Cl$^-$ ligands are mutually *cis*, and the dmso or PPh_3 ligand resides *trans* to the X atom of (**358**).[1623] 1,4,7,10-Tetrathiacyclododecane, [12]aneS$_4$, reacts with $[RuCl_2(dmso)_4]$ to yield $[Ru([12]aneS_4)Cl_2]$ which undergoes ligand substitution reactions to give $[Ru([12]aneS_4)L]Cl_2$ (L = bpy, phen, 4,7-Ph$_2$phen). In solution, variable temperature ^{1}H NMR spectroscopic data for these complexes are consistent with exchange processes, proposed to involve Ru—N cleavage.[1624] Treatment of $[RuLCl_2]$ where L = 6,6,13,13-tetramethyl-1,4,8,11-tetrathiacyclotetradecane (Me$_4$[14]aneS$_4$), 6,6,10,10,14,14-hexamethyl-1,4,8,12-tetrathiacyclopentadecane (Me$_6$[15]aneS$_4$), or 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane (Me$_8$[16]aneS$_4$), with $NaBH_4$ in MeOH or EtOH results in the formation of *trans*-[RuH(Cl)(*syn*-L)]. Structural details of these complexes have been investigated. An attempt to prepare *trans*-[RuH(Cl)(*syn*-Me$_4$[14]aneS$_4$)] directly from $[RuH(Cl)(PPh_3)_3]$ was unsuccessful.[1625] With an excess of $NaBH_4$ in EtOH, *cis*-$[RuCl_2L]$ (L = Me$_8$[16]aneS$_4$ or Me$_6$[15]aneS$_4$) react to yield the borohydride derivatives *trans*-[RuH(η^1-BH$_4$)L]. When treated with O_2 and then ROH (R = Me, Et), *trans*-[RuH(η^1-BH$_4$)(Me$_8$[16]aneS$_4$)] reacts to give the Ru^{III} complex *trans*-[Ru(OR)$_2$(*anti*-Me$_8$[16]aneS$_4$)]$^+$.[1626] 1,4,7,10,13-Pentathiacyclopentadecane, [15]aneS$_5$, reacts with $[RuCl_2(PPh_3)_3]$ to give $[Ru(PPh_3)([15]aneS_5)]^{2+}$; coordination of all five *S*-donor atoms was confirmed crystallographically.[1627] The complexes $[Ru([18]aneS_6)][BPh_4]_2$ ([18]aneS$_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane), $[Ru(L\text{-}S,S')_3][PF_6]_2$ (L = 1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane),[1628] and $[RuL'][PF_6]_2$ (L′ = 2,3,11,12-dibenzo-1,4,7,10,13,16-hexathiacyclooctadecane)[1629] have been prepared and structurally characterized. Ligands (**359**) and (**360**) have been incorporated into the complexes *trans*-[RuCl$_2$(**359**)$_2$], *cis*-[RuCl$_2$(**360**)$_2$], *trans*-[RuCl$_2$(**360**)$_2$], [RuCl(**359**)(**360**)(tht)]$^+$, and [RuCl$_2$(dmso)$_2$(**360**)]. The structures of the first four complexes have been determined in order to confirm preferences for arrangements of different donor groups.[1630]



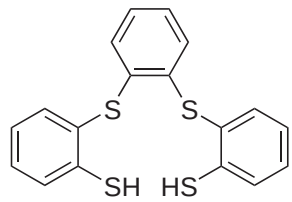
(**358**) X = O, S (**359**) (**360**)

Complex formation using the potentially tetra- or pentadentate ligands (**361**)$^{2-}$ to (**364**)$^{2-}$ has formed part of extensive work by Sellmann and co-workers. The reaction of $[RuCl_2(PPh_3)_3]$ with Li$_2$(**361**) and gaseous HCl, followed by treatment of the resulting complex with base to remove HCl, yields [Ru(PPh_3)(**361**)]. This unsaturated complex readily forms [Ru(PPh_3)(**361**)L] where L = N_3^-, NH_3, N_2H_4. The hydrazine complex can be oxidized with concomitant formation of a diazene-bridged dinuclear species, the crystal structure of which has been determined.[1631] The reaction of Na$_2$(**362**) with $[RuCl_2(dmso)_4]$ leads to [Ru(**362**)(dmso)$_2$] from which the dmso ligands

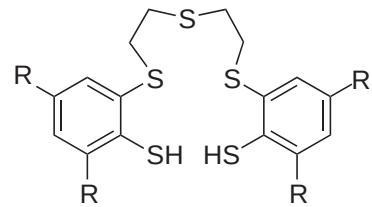
can be displaced by small ligands such as PEt_3 and PPr_3. The solid-state structure of [Ru(**362**)$(PPr_3)_2$] confirms a *cis* arrangement of the phosphine ligands. For the more sterically demanding phosphines PCy_3 and P^iPr_3, reactions with [Ru(**362**)$(dmso)_2$] yield [Ru(**362**)(dmso)-(PR_3)], the reactivity of which has been described.[1632] Reactions of [Ru(**362**)(dmso)(PR_3)] (R = Cy, ^{i}Pr) or [Ru(**362**)$(PPh_3)_2$] with $LiAlH_4$ or $NaBEt_3H$ produce hydrido complexes $[Ru(H)(PR_3)(\mathbf{362})]^-$ (R = Ph, Cy, ^{i}Pr) which have been isolated as solvated sodium or lithium complexes. The reaction of representative complexes with CD_3OD was followed by NMR spectroscopy; HD is expelled and $[Ru(D)(PR_3)(\mathbf{362})]^-$ formed. Analogous reactions with CH_3OH have been investigated. These, and reactions that illustrate the reversible uptake of H_2 by the $Ru(PR_3)$(**362**) unit, have been studied in detail.[1633] Ligand H_2(**363**) has been prepared in order to find a ligand that is related to, but more stable with respect to reductive C—S cleavage than, H_2(**362**). The complexes [Ru(PR_3)L(**363**)] (R = Et, L = PEt_3; R = Ph, L = PPh_3, CO, dmso) have been prepared and characterized, and the crystal structures of [Ru$(PEt_3)_2$(**363**)] and [Ru(PPh_3)(CO)(**363**)] have confirmed that the thiolate groups of $(\mathbf{363})^{2-}$ are mutually *trans*.[1634] Starting from $[Ru(NO)(1,2\text{-}(S)_2C_6H_4)_2]^-$ and $S(CH_2CH_2Br)_2$, it has been possible to assemble $[Ru(NO)(\mathbf{365})]^+$. The reactions of this complex with nucleophiles such as N_3^- and $LiNH_2$ have been investigated.[1635] The *tert*-butyl derivative [Ru(NO)(**366**)]Br has also been prepared. This complex reacts with $LiBEt_3H$ to yield [Ru_2(**366**)$_2$] and [Ru(**366**)Ru(NO)(L)(L′)] where H_2L and $H_2L' = 1,2\text{-}(SH)_2\text{-}3,5\text{-}^tBu_2C_6H_2$ and 2-SH-3,5-^{t}Bu$_2$ $C_6H_2SCH_2CH_2SH$.[1636]



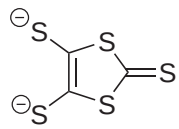
H_2(361) R = ^{t}Bu
H_2(362) R = H



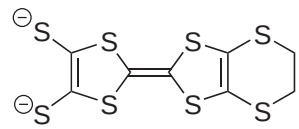
H_2(363)



H_2(364) R = H
H_2(365) R = ^{t}Bu



(366)



(367)

Ruthenium(II) complexes of general formula *cis* or *trans*-$[RuCl_2L_2]$ where L is a didentate sulfoxide ligand $RS(O)(CH_2)_nS(O)R$ (R = Me, Et, Pr, $n = 2$; R = Me, $n = 3$) have been prepared and structurally characterized. *In vitro* studies suggest that the *trans*-$[RuCl_2L_2]$ complexes accumulate in hamster ovary cells and bind to DNA to a higher degree than the *cis* complexes.[1637] In *trans*-$[RuCl_2\{(4\text{-}MeC_6H_4)S(O)C_6H_4S(O)(4\text{-}MeC_6H_4)\}_2]$, spectroscopic data are consistent with *S*-coordination.[1638] Molecular mechanics calculations have been carried out on sulfoxide complexes in this $[RuCl_2L_2]$ family to investigate the isomer preferences for *S* over *O*-bonding and *cis* vs. *trans* isomer formation.[1639]

N,N-dimethylbenzo[b]furan-2-carbothioamide, HL, forms a cyclometallated complex [RuCl-$(CO)_2(PBu_3)$(L-*C,S*)] which has been structurally characterized. An analogous synthesis using the seleno analog of HL does not lead to a corresponding cyclometallated complex.[1640] The air-stable, aryl sulfonylamido complexes [Ru$(ArSO_2NH)(Et_2dtc)(CO)(PPh_3)_2$] (Ar = 4-$MeC_6H_4$, 4-^{t}Bu$C_6H_4$, 2,4,6-^{i}Pr$_3C_6H_2$) have been prepared from $ArSO_2N_3$ and [Ru(H)$(Et_2dtc)(CO)(PPh_3)_2$]. Structural characterization of one derivative confirms that the $ArSO_2NH^-$ ligand is *N*-bonded and *trans* to the carbonyl ligand, and the Et_2dtc^- ligand is bound as the usual *S,S′* chelate. Reactions of [Ru$(ArSO_2NH)(Et_2dtc)(CO)(PPh_3)_2$] with oxidizing agents and base have been investigated, and among the products isolated and characterized is [(CO)$(Et_2dtc)(PPh_3)$Ru-$(\mu\text{-}Et_2dtc)(\mu\text{-}I)$RuI(CO)$(PPh_3)$].[1641] The reaction of [Ru$(Et_2dtc)_2(dmso)_2$] with ^{t}BuNC results in the formation of *trans*-[Ru$(Et_2dtc)_2(^tBuNC)_2$], the crystal structure of which has been determined.

The oxidation of this complex by I_2 yields $[Ru(Et_2dtc)_2(^tBuNC)_2]^+$; an analogous oxidation occurs with $[Ru(Et_2dtc)_2(PPh_3)_2]$. With I_2, $[Ru(Et_2dtc)_2(dmso)_2]$ reacts to give the mixed-valent complex $[Ru_3(Et_2dtc)_6(dmso)_2][I_3]_2$. The complex cation is best described in terms of a $\{Ru^{III}_2(Et_2dtc)_4\}^{2+}$ unit linked to a $\{Ru^{II}(Et_2dtc)_2(dmso)_2\}$ unit.[1642] Dialkylthiocarbamate complexes $[Ru(R_2dtc)(bpy)_2]^+$ and $[Ru(R_2dtc)(phen)_2]^+$ have been prepared along with the complexes $[RuL_2(PPh_3)_2]$ and $[RuL(bpy)_2]^+$ where HL is a series of 2-alkylamino-1-cyclopentene-1-dithiocarboxylic acids. Spectroscopic and electrochemical properties of the complexes have been studied.[1643] Reactions between $[Ru(EtCOCS_2)_2(PPh_3)_2]$ or $[Ru\{(CH_2)_4NCS_2\}_2(PPh_3)_2]$ and various tertiary phosphine ligands result in phosphine substitution. Preferences for *cis* and *trans* isomers are discussed, both for the Ru^{II} complexes and the Ru^{III} products of oxidation.[1644] A number of derivatives incorporating $EtOCS_2^-$, Et_2dtc^-, or $Ph_2PCSNPh^-$ ligands have been prepared starting from Ru^{II} halophosphine carbonyl or nitrosyl complexes. When the precursor is $[RuCl_2(CO)(CS)(PPh_3)_2]$, it is the CS ligand that is displaced by $EtOCS_2^-$ or Et_2dtc^-, whereas $Ph_2PCSNPh^-$ reacts to produce $[RuCl(Ph_2PCSNPh)(CO)(CS)(PPh_3)]$.[1645] Treatment of $[OsBr_2(PPh_3)_3]$ with $Na[Et_2dtc]$ yields *cis*-$[Os(Et_2dtc)_2(PPh_3)_2]$; oxidation with Ce^{IV} results in the formation of *trans*-$[Os(Et_2dtc)_2(PPh_3)_2]^+$ and reduction of this cation with hydrazine produces *trans*-$[Os(Et_2dtc)_2(PPh_3)_2]$. The isolation of the latter is possible only because isomerization to the preferred *cis* form is slow for Os^{II} in solution; *cis*-to-*trans* isomerization of the Os^{III} complex is so rapid that this species cannot be isolated.[1646] Similarly, oxidation of *cis*-$[Os(RSCS_2)_2(PPh_3)_2]$ is followed by rapid isomerization to *trans*-$[Os(RSCS_2)_2(PPh_3)_2]^+$. Reduction of this complex yields *trans*-$[Os(RSCS_2)_2(PPh_3)_2]$ which slowly isomerizes to *cis*-$[Os(RSCS_2)_2(PPh_3)_2]$. Factors influencing these isomerizations have been discussed, and comparisons have been made with related processes for the analogous Ru complexes.[1647,1648] The crystal structure of *cis*-$[Ru(PhCH_2SCS_2)_2(PPh_3)_2]$ has been determined.[1648] The reaction of $[OsBr_2(PPh_3)_3]$ with $K[ROCS_2]$ (R = Me, Et, ^{i}Pr, $PhCH_2$) gives *cis*-$[Os(ROCS_2)_2(PPh_3)_2]$. As with the previous example, oxidation of this complex with Ce^{IV} leads to the *trans* isomer, reduction of which yields *trans*-$[Os(ROCS_2)_2(PPh_3)_2]$. Representative structures have been determined; the *cis*/*trans* isomer preferences are explained in terms of poor backbonding to Os^{III} resulting in steric factors being dominant over electronic factors on going from Os^{II} to Os^{III}.[1649] Another *S,S′*-chelate that has been studied is $Ph_2PS_2^-$. A crystal structure determination of $[Ru(Ph_2PS_2)_2(CO)(PPh_3)]\cdot 0.25Et_2O$ reveals that the two dithiophosphinato ligands are mutually *cis*.[1650] The reactions of $K[R_2P(S)NP(S)R_2]$ (R = Ph, ^{i}Pr) with $[RuCl_2(PPh_3)_3]$, $[RuCl_2(dmso)_4]$, or $[RuCl_2(CO)_2]_x$ lead to $[Ru\{R_2P(S)NP(S)R_2\}_2(PPh_3)]$, *cis*-$[Ru\{Ph_2P(S)NP(S)Ph_2\}_2(dmso)_2]$, or *cis*-$[Ru\{R_2P(S)NP(S)R_2\}_2(CO)_2]$. The crystal structures of the two five-coordinate complexes $[Ru\{R_2P(S)NP(S)R_2\}_2(PPh_3)]$ have been established. Treatment of $[Ru\{^iPr_2P(S)NP(S)P^iPr_2\}_2(PPh_3)]$ with ^{t}BuNC produces *trans*-$[Ru\{^iPr_2P(S)NP(S)P^iPr_2\}_2(^tBuNC)_2]$. The complexes $[Ru\{R_2P(S)NP(S)PR_2\}_3]$ can be prepared from reactions between $RuCl_3\cdot xH_2O$ and $K[R_2P(S)NP(S)R_2]$ (R = Ph, ^{i}Pr). An interesting reaction in this series is that of $[Ru\{^iPr_2P(S)NP(S)P^iPr_2\}_2(PPh_3)]$ with pyridine which leads, not to a py complex, but to $[Ru\{^iPr_2P(S)NP(S)P^iPr_2\}_2(SO)]$. Other SO_2 and SO_4^{2-} complexes in this series have also been prepared and characterized.[1651]

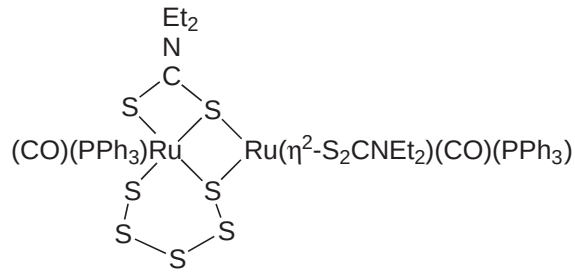
The complexes $[Bu_4N][Ru(\mathbf{366})_2]$, $[Bu_4N][Ru(\mathbf{367})_2]$, $[Ru(bpy)_2(\mathbf{366})]$ and $[Ru(bpy)_2(\mathbf{367})]$ have been prepared and their redox properties investigated. The oxidized complexes $[Bu_4N]_{0.1}[Ru(\mathbf{366})_2]$ and $[Ru(bpy)_2(\mathbf{367})][I_3]_{2.1}$ possess electrical conductivities of 1.8×10^{-3} and 2.0×10^{-4} S cm^{-1} respectively.[1652]

5.5.3.4.2 Di- and trinuclear complexes

Dinuclear complexes involving $[S_2]^{2-}$ bridging ligands include $[\{P(OEt)_3\}_2ClRu(\mu\text{-}N_2H_4)(\mu\text{-}Cl)(\mu\text{-}S_2)RuCl\{P(OEt)_3\}]$, a mixed-valent compound that exhibits both inter- and intramolecular hydrogen bonding involving the hydrazine ligand.[209] The related complex $[\{P(OMe_3\}_2ClRu(\mu\text{-}N_2H_4)(\mu\text{-}Cl)(\mu\text{-}S_2)RuCl\{P(OMe)_3\}]$ reduces O_2 and forms $[\{P(OMe_3\}_2ClRu(\mu\text{-}N_2H_4)(\mu\text{-}Cl)(\mu\text{-}S_2)RuCl\{P(OMe)_3\}][O_2]$ in which $[O_2]^-$ is coordinated to the bridging $[S_2]^{2-}$ ligand. The mechanism by which O_2 reduction takes place is discussed. Among products that have been isolated and structurally characterized in this study is the Ru^{II} complex $[\{P(OMe_3\}_2ClRu(\mu\text{-}N_2H_4)(\mu\text{-}S_2O_5)RuCl\{P(OMe)_3\}]$.[1653] A number of complexes containing a $Ru(\mu\text{-}S_2)(\mu\text{-}Cl)_2Ru$ core have been reported, and we have already mentioned the Ru^{III} complex $[\{P(OMe)_3\}_2ClRu(\mu\text{-}S_2)(\mu\text{-}Cl)_2RuCl\{P(OMe)_3\}]$.[120] This and the related Ru^{III} complexes $[\{P(OMe)_3\}_2ClRu(\mu\text{-}S_2)(\mu\text{-}Cl)_2Ru(MeCN)\{P(OMe)_3\}]^+$ and $[\{P(OMe)_3\}_2(MeCN)Ru(\mu\text{-}S_2)(\mu\text{-}Cl)_2Ru(MeCN)\{P(OMe)_3\}]^{2+}$

have been structurally characterized.[1654,1655] The complex $[\{P(OMe)_3\}_2(MeCN)_3Ru^{III}(\mu\text{-}S_2)Ru^{III}(MeCN)_3\{P(OMe)_3\}]^{4+}$ and its one-electron-reduced derivative $[\{P(OMe)_3\}_2(MeCN)_3Ru^{III}(\mu\text{-}S_2)Ru^{II}(MeCN)_3\{P(OMe)_3\}]^{3+}$ have also been prepared. The latter was the first example of a mixed-valent complex with a *trans*-MS_2M core, and ESR and PES data are reported. $[\{P(OMe)_3\}_2(MeCN)_3Ru^{III}(\mu\text{-}S_2)Ru^{II}(MeCN)_3\{P(OMe)_3\}]^{3+}$ does not exhibit an intervalence band, and is considered as a class III Robin–Day species.[1656] The Na/Hg reduction of $[\{P(OMe)_3\}_2ClRu^{III}(\mu\text{-}S_2)(\mu\text{-}Cl)_2Ru^{III}Cl\{P(OMe)_3\}]$ in thf leads initially to the solution species $[\{P(OMe)_3\}_2Cl(thf)_2Ru^{II}(\mu\text{-}S_2)\ Ru^{II}Cl(thf)_2\{P(OMe)_3\}]$, but on crystallization, the isolated product is a tetranuclear Ru^{II} species. This consists of two *trans*-$Ru^{II}SSRu^{II}$ cores, oriented parallel to one another and connected by $\mu,\eta^1,\eta^2\text{-}S_2^{2-}$,$\mu\text{-}Cl^-$ and $\mu\text{-}P(OMe)_3\text{-}P,O$ ligands.[1656] Both $[S_2]^{2-}$ and S^{2-} ligands support the Ru^{II}_2 core in the complex $[\{MeC(CH_2PPh_2)_3\}Ru(\mu\text{-}S)(\mu\text{-}S_2)Ru\{MeC(CH_2PPh_2)_3\}]^+$, isolated and characterized as the $[CF_3SO_3]^-$ salt.[1657]

Bridging polysulfide ligands feature in the complexes $[Ru_2(\mu\text{-}S_n)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ ($n = 5$ or 6). In the solid state, the structure of each complex is unsymmetrical as illustrated in structure (**368**) for the $[S_5]^{2-}$-bridged complex.[1658] These complexes react with NH_3, N_2H_4, and py (L), and in each case, the bridging mode shown in structure (**368**) opens up. Reactions with NH_3 or py lead to complexes of the type $[\{(S_2CNMe_2)(CO)(PPh_3)LRu\}_2(\mu\text{-}S_n)]$ in which the two octahedral Ru^{II} centers are remote from each other. When $[Ru_2(\mu\text{-}S_n)(\mu\text{-}S_2CNMe_2)(S_2CNMe_2)(CO)_2(PPh_3)_2]$ reacts with N_2H_4, desulfurization occurs, and the product contains a $\mu\text{-}[S_4]^{2-}$ ligand as well as a $\mu\text{-}N_2H_4$ group.[1659] The complexes $[Ru_2(S_2CNMe_2)_2(CO)_2(PPh_3)_2(\mu\text{-}SR)_2]$ (R = Et or Ph) have been prepared by reacting RSH with $[RuH(S_2CNMe_2)(CO)(PPh_3)_2]$. Treatment of these $Ru^{II}Ru^{II}$ species with HNO_3 in MeCN produces the $Ru^{IV}Ru^{IV}$ dimers $[Ru_2(S_2CNMe_2)_2(CO)_2(PPh_3)_2(\mu\text{-}SR)_2][NO_3]_4$. Structural data are presented for the Ru^{II} and Ru^{IV} PhS^- complexes, and the most significant feature is the increase in Ru—Ru separation that accompanies oxidation: 3.683(1) Å for Ru^{II}—Ru^{II}, and 2.876(2) Å for Ru^{IV}—Ru^{IV}, corresponding to Ru—Ru bond formation.[1660] Thiolate-bridged complexes of the type $[Ru_2(\mu\text{-}SR)_2(CO)_4(PPh_3)_2]$ and $[Ru_2\{\mu\text{-}S(CH_2)_nS\}(CO)_4(PPh_3)_2]$ can be synthesized by replacement of carboxylate bridges in $[Ru_2(\mu\text{-}O_2CR)_2(CO_4)(PPh_3)_2]$ (e.g., R = H). The crystal structure of $[Ru_2\{\mu\text{-}S(CH_2)_3S\}(CO)_4(PPh_3)_2]$ confirms that the dithiolate bridge is symmetrically disposed between the two Ru^{II} centers with each S atom interacting with both Ru atoms; the Ru—Ru bond length of 2.690(1) Å indicates the presence of a metal–metal bond.[1661]



(**368**)

The reaction between elemental sulfur and $[CpRu(SPh)(PPh_3)\{P(OMe)_3\}]$ yields $[Cp_2Ru_2\{P(OMe)_3\}_2S_n]$ ($n = 4$ or 6). Treatment of $[Cp_2Ru_2\{P(OMe)_3\}_2S_6]$ with PPh_3 abstracts sulfur from the bridge forming $[Cp_2Ru_2\{P(OMe)_3\}_2S_4]$. Both complexes exhibit unusual bridge structures. The Ru_2S_4 unit in $[Cp_2Ru_2\{P(OMe)_3\}_2S_4]$ has a chair conformation, reminiscent of S_6, whereas in $[Cp_2Ru_2\{P(OMe)_3\}_2S_6]$, the Ru_2S_6 unit resembles the bicyclic structure of $[S_8]^{2+}$.[1662]

An interesting reaction occurs between Ru powder and SCl_2 in a closed vessel at 140 °C. The isolated products are $[fac\text{-}Ru^{II}Cl_3(SCl_2)_3]^-[SCl_3]^+$, $[Cl(SCl_2)_3Ru^{II}(\mu\text{-}Cl)_2Ru^{II}(SCl_2)_3Cl]$, and $[(SCl_2)_3Ru^{III}(\mu\text{-}Cl)_3Ru^{II}(SCl_2)Cl_2]$ and their crystal structures have been determined. In $[RuCl_3(SCl_2)_3]^-[SCl_3]^+$, cation–anion association occurs with the chloro ligands of the anion forming unsymmetrical bridges between the Ru^{II} center and the S atom of the cation.[1663,1664]

The reaction between PhMeSO and $RuCl_3{\cdot}xH_2O$ leads to the formation of the trinuclear complex $[Ru_3(\mu\text{-}PhMeSO\text{-}S,O)_2(\mu\text{-}Cl)_4(PhMeSO\text{-}S)_4Cl_2]$. The complex (characterized spectroscopically and crystallographically) contains a linear arrangement of octahedrally coordinated Ru atoms.[1665]

5.5.3.5 Selenium- and Tellurium-donor Ligands

The Ru^{III} complex $[\{P(OMe_3\}_2ClRu(\mu\text{-}Se_2)(\mu\text{-}Cl)_2RuCl\{P(OMe)_3\}]$ has been prepared and structurally characterized; it undergoes irreversible electrochemical reduction.[1666]

The seleno- and telluroether complexes *trans*-$[RuCl_2L_2]$ and *trans*-$[RuBr_2L_2]$ have been prepared for L = $PhSeCH_2CH_2SePh$, $MeSeCH_2CH_2SeMe$, and 1,2-$(MeTe)_2C_6H_4$ from $RuCl_3 \cdot xH_2O$. Techniques used for compound characterization include ^{77}Se and ^{125}Te NMR spectroscopies. The crystal structure of *trans*-$[RuCl_2(PhSeCH_2CH_2SePh)_2]$ has been established.[1667] The tripodal ligands $MeC(CH_2SeMe)_3$ and $MeC(CH_2TeMe)_3$ (L) form the homoleptic complexes $[RuL_2]^{2+}$, isolated as the $[CF_3SO_3]^-$ salts. Structural data for the seleno derivative reveal that the lone pairs on the Se atoms are in a *syn* arrangement.[1668] When $[OsCl_2(PPh_3)_3]$ reacts with $MeSe(CH_2)_3SeMe$ (L), the product is *trans*-$[OsCl(PPh_3)(L\text{-}Se,Se)_2]^+$. Analogous reactions occur with $MeSCH_2CH_2SMe$ and with ditelluroethers. Attempts to prepare Os^{II} complexes of ditelluroethers from OsO_4/HCl/EtOH or $[OsCl_6]^{2-}$ ran into difficulties arising from ligand chlorination. These problems were overcome by using *trans*-$[OsCl_2(dmso)_4]$ as a starting material. As part of this study, the crystal structure of *trans*-$[OsCl_2\{PhTe(CH_2)_3TePh\}_2]$ was determined; it is similar to that of the Ru^{II} analog previously established.[1669]

The reaction between $[Ru(dmf)_6]Cl_3$ and 1,5,9,13-tetraselenacyclohexadecane, [16]aneSe$_4$, in EtOH at reflux yields *cis*-$[RuCl_2([16]aneSe_4)]$. The complex *cis*-$[RuCl_2([8]aneSe_2)]$ ([8]aneSe$_2$ = 1,5-diselenocyclooctane) was similarly prepared. The derivatives *cis*-$[RuBr_2([16]aneSe_4)]$ and *cis*-$[RuI_2([16]aneSe_4)]$ can be made from $[Ru(dmf)_6][CF_3SO_3]_3$ in the presence of LiBr or NaI. A *cis*-*trans* isomerization is observed when *cis*-$[RuX_2([16]aneSe_4)]$ (X = Cl, Br) is heated in nitromethane solution. The ligand [16]aneSe$_4$ also reacts with $[MCl_2(PPh_3)_3]$ (M = Ru, Os) to yield *trans*-$[MCl(PPh_3)([16]aneSe_4)]^+$; the crystal structure of *trans*-$[RuCl(PPh_3)([16]aneSe_4)][PF_6]$ has been determined.[1670]

5.5.3.6 Mixed-donor Atom Ligands

5.5.3.6.1 N,O-donors

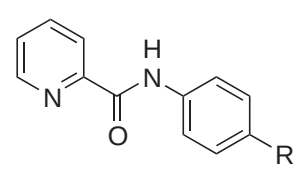
A range of complexes involving *N,O*-chelates based on 2-(2-hydroxyphenyl)pyridine (HL′) or 8-hydroxyquinoline have been reported. Ligand HL′ reacts with $[RuCl_2(bpy)_2]$ in the presence of PF_6^- to give $[Ru(bpy)_2(L'\text{-}N,O)]^+$. Electrochemical data indicate that the phenolate group stabilizes the Ru^{III} state by 0.86 V relative to $[Ru(bpy)_3]^{2+}$.[122] The reaction of $[RuCl_2(PPh_3)_3]$ with 8-hydroxyquinoline (HL) yields $[Ru(L\text{-}N,O)_2(PPh_3)_2]$ both in the *cis,trans,cis* and *trans,trans, trans* forms. Both isomers are oxidized to the *trans,trans,trans* form of $[Ru(L\text{-}N,O)_2(PPh_3)_2]^+$, and reduction of this isomer produces solely *trans,trans,trans*-$[Ru(L\text{-}N,O)_2(PPh_3)_2]$. The crystal structures of *cis,trans,cis*-$[Ru(L\text{-}N,O)_2(PPh_3)_2]$ and *trans,trans,trans*-$[Ru(L\text{-}N,O)_2(PPh_3)_2][PF_6]$ have been determined.[1671] Isomerizations of the complexes *cis* and *trans*-$[Ru(OAc)(2\text{-}MeL\text{-}N,O)_2(NO)]$ (2-MeHL = 2-methyl-8-hydroxyquinoline) have also been investigated.[1672] When $[RuCl_3(2\text{-}MeL\text{-}N,O)(NO)]^-$ reacts with excess 8-hydroxyquinoline (HL), the major product is $[RuCl(L\text{-}N,O)(2\text{-}MeL\text{-}N,O)(NO)]$ in which the *O*-donor of 2-MeL$^-$ is *trans* to the nitrosyl ligand, and the *N*-donors of the two quinoline-based ligands are mutually *trans*. The same isomer is formed when $[RuCl_3(L\text{-}N,O)(NO)]^-$ reacts with excess 2-MeHL.[1673] Three geometrical isomers of $[RuCl(2\text{-}EtL\text{-}N,O)_2(NO)]$ (2-EtHL = 2-ethyl-8-hydroxyquinoline) have been crystallographically characterized, and variable-temperature ^1H NMR spectroscopy has been used to probe the isomer preferences in solution.[1674]

Pyridine-2-carboxylic acid (picolinic acid, Hpic) reacts with the mixed-valent $[Ru_2Cl(\mu\text{-}OAc)_4]$ to yield $[Ru^{III}(pic)_3]$ and $[Ru^{II}_2(\mu\text{-}pic)_4]$. Both complexes react with PPh_3 to give the same Ru^{II} product, $[Ru(pic\text{-}N,O)_2(PPh_3)_2]$, the crystal structure of which confirms a *trans* arrangement of PPh_3 ligands.[1675] The complex $[RuX(H_2O)(pic\text{-}N,O)(PPh_3)_2]$ (X = Cl, Br) can be prepared from equimolar amounts of Hpic and $[RuX_2(PPh_3)_3]$; a 2:1 molar ratio of reagents results in the formation of $[Ru(pic\text{-}N,O)_2(PPh_3)_2]$. When treated with base, $[RuX(H_2O)(pic\text{-}N,O)(PPh_3)_2]$ loses HX and forms the dimer $[Ru_2(OH)_2(pic)_2(PPh_3)_4]$. The redox properties of the complexes have been described.[1676] Like pic$^-$, the conjugate bases of pyrazine 2-carboxylic acid, imidazole 4,5-dicarboxylic acid, and pyrazine 2,3-dicarboxylic acid all function as *N-O* chelates in complexes of type $[RuL_2(PPh_3)_2]$. The second CO_2H group of each dicarboxylic acid is non-coordinated. Structural data for the pic$^-$ and imidazole derivatives show that the PPh_3 ligands are mutually

cis.[1677] The complexes [Ru(6-CO_2bpy-*N,N′,O*)$_2$], [Ru(6-CO_2bpy-*N,N′,O*)(tpy)]$^+$, and [Ru(bpy)$_2$-(pic)-*N,O*)]$^+$ have been prepared and characterized (6-CO_2Hbpy = 2,2′-bipyridine-6-carboxylic acid). Electrochemical data show there to be a linear relationship between the redox potentials and the number of coordinated CO_2^- groups, each *O*-donor leading to a 0.4 V decrease in $E(Ru^{II}/Ru^{III})$. [Ru(6-CO_2bpy-*N,N′,O*)(tpy)]$^+$ and [Ru(bpy)$_2$(pic)-*N,O*]$^+$are luminescent.[1678]

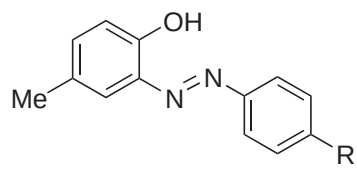
Salts of a number of α-amino acids, HL, have been reacted with [MH(Cl)(CO)(PPh_3)$_3$] (M = Ru, Os) to give complexes of type [MH(CO)(L-*N,O*)(PPh_3)$_2$], structurally characterized for M = Ru and HL = L-proline. For M = Ru, a second preparative route involves reaction of HL with [Ru(CO)$_3$(PPh_3)$_2$]. Direct reaction of HL with [RuH(Cl)(CO)(PPh_3)$_3$] results in the formation of [RuCl(CO)(L-*N,O*)(PPh_3)$_2$].[1679] The peptide diglycine can potentially act as an *N,O,N′,O′*-donor; similarly, triglycine could utilize an *N,O,N′,O′,N″,O″*-donor set. The reactions of diglycine and triglycine with [$RuCl_2(PPh_3)_3$] lead to mononuclear and dinuclear complexes respectively. The deprotonated glygly ligand binds as an *N,N′,O* bischelate in [RuL(PPh_3)$_2$-(MeOH)]. In contrast, the longer tripeptide supports a diruthenium complex [$Ru_2L_2(PPh_3)_4$], exhibiting an *N*(amino),*N*(peptide),*O*(peptide),*O*(carboxyl) binding mode. Each ligand is tridentate to one Ru^{II} center and monodentate (*O*) to the other.[1680]

The ligands **369** react with [$RuCl_2(dmso)_4$] to yield [$RuCl_2$(dmso)$_2$(**369**-*N,O*)], characterized by spectroscopic and electrochemical methods.[1681] Complexes in the families [Ru^{II}(bpy)(**370**)$_2$][1682] and [Ru^{III}(acac)(**370**)$_2$][1683] have been reported. The complexes [Ru(bpy)(**370**)$_2$] undergo a reversible Ru^{II}/Ru^{III} oxidation followed by an irreversible Ru^{III}/Ru^{IV} process; the bpy-centered one-electron reduction is also observed. Chemical oxidation of the complexes [Ru(bpy)(**370**)$_2$] gives [Ru(bpy)(**370**)$_2$]$^+$ (isolated as the iodides), the electronic and ESR spectroscopic properties of which have been described.[1682] The crystal structure of [Ru(acac)(**371**)$_2$] has been established, and the electrochemical and chemical redox reactions of [Ru(acac)(**370**)$_2$] and [Ru(acac)(**371**)$_2$] generate Ru^{II} and Ru^{IV} species that have been characterized by spectroscopic and electrochemical techniques.[1683]



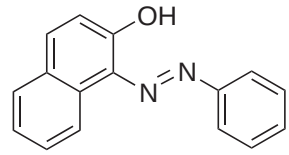
R = H, Me, OMe, Cl, NO_2

(**369**)



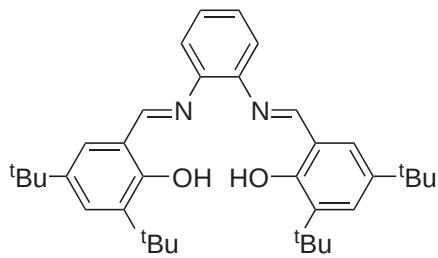
R = H, Me, OMe, Cl, NO_2

(**370**)

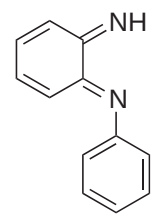


(**371**)

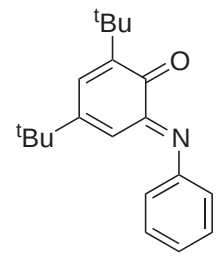
The Schiff-base complex [Ru(**372**)(CO)] has been prepared from H_2(**372**) and $Ru_3(CO)_{12}$ in toluene. By utilizing the vacant coordination site in [Ru(**372**)(CO)], a range of mononuclear and dinuclear complexes (e.g., [Ru(**372**)(CO)(py)] and [{Ru(**372**)(CO)}$_2$(μ-4,4′-bpy)] can be prepared. Choice of bridging ligand allows control over the electronic communication between the metal centers in the dinuclear species.[1684] The aniline derivative [$RuCl_2(PhNH_2)_2$(**373**)][896] reacts with 3,5-di-*tert*-butylcatchol to yield [$RuCl_2$(**373**)(**374**)] via oxidative coupling of the catechol and coordinated $PhNH_2$. The crystal structure of [$RuCl_2$(**373**-*N,N′*)(**374**-*N,O*)] has been determined, and bond parameters are consistent with an Ru^{II} rather than Ru^{III} species.[1685]



H_2(372)



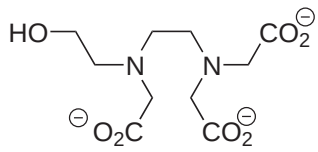
(**373**)



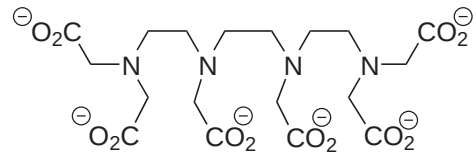
(**374**)

In Section 5.5.2.5.1, we summarized Ru^{III} complexes of $edta^{4-}$ and related ligands. Related Ru^{II} complexes include those containing ligand (**375**). Detailed solution ^1H and ^{19}F NMR

spectroscopic studies have been used to investigate the reactions between $[Ru(\mathbf{375})(H_2O)]^-$ and 5-substituted (X = F, Cl, Br, I, CO_2H) uracils and uridines. These give derivatives in which the pyrimidine nucleobases are bound in an η^2 mode (C=C) which competes with donation through atom N(3). The η^2 mode has previously been observed for the coordination of related uridine and cytidine ligands to $[Ru(\mathbf{375})]^-$.[1686] The η^2 binding of the nucleobases has been compared with that of various alkenes, and equilibrium constants for the formation of $[Ru(\mathbf{375})L]^-$ have been determined. The largest value of K for L = alkene was observed for methyl vinyl ketone.[1687] Reactions between pyrimidine (pyr), 4-Mepyr or 4,6-Me_2pyr, and $[Ru(\mathbf{375})(H_2O)]^-$ proceed through a kinetically controlled substitution at atom N(1), followed by linkage isomerization to the η^2-bound pyrimidine ligand. Isomer distributions have been investigated using NMR spectroscopy, and it has been confirmed that dissociation of one CO_2^- group of ligand (**375**) occurs as the η^2-pyrimidine mode is established.[1688] Addition of appropriate amounts of pyrimidine to $[Ru(\mathbf{375})(H_2O)]^-$ leads eventually to $[Ru(\mathbf{375})(pyr)_2]^-$, with the addition of the second equivalent of pyr being rate-limited by the dissociation of one CO_2^- donor group from ligand (**375**). The two pyrimidine ligands in $[Ru(\mathbf{375})(pyr)_2]^-$ are distinct, the first being rigidly bound and the second being fluxional.[1689] Related reactions using pyridazine as the incoming *N*-heterocycle have also been investigated; addition of the second equivalent of pyridazine is far faster than that of pyrimidine, pyrazine, or pyridine, indicating base-assisted dissociation of the carboxylate arm of ligand (**375**).[1690] Further investigations of these systems have utilized $[Ru(\mathbf{375})(D_2O)]^-$. Pyrazine reacts with $[Ru(\mathbf{375})(D_2O)]^-$ in D_2O to give a mixture of isomers and a pyz-bridged diruthenium complex. The distribution and interconversion of the isomers (one of which contains a fluxional pyz ligand) has been monitored by solution ^1H and ^{13}C NMR spectroscopies.[1691] With 2,3-Me_2pyz, $[Ru(\mathbf{375})(H_2O)]^-$ reacts to give $[Ru(\mathbf{375})(2,3\text{-}Me_2pyz)]^-$ or $[\{Ru(\mathbf{375})\}_2(\mu\text{-}2,3\text{-}Me_2pyz)]^{2-}$ depending on the stoichiometry of the reaction. Electrochemical data have been reported for the complexes, and in the oxidized dinuclear species, there is only weak electronic coupling between the Ru centers.[1692] The properties of the complexes $[Ru(\mathbf{375})L]^-$ where L = 2,2′-dipyridylamine or *N,N,N′,N′*-tetrakis(2-pyridyl)adipamide have been studied using NMR spectroscopic and electrochemical techniques. Even when there is an excess of 2,2′-dipyridylamine, only one equivalent of the ligand binds to the Ru^{II} center. The pK_a of $[Ru(\mathbf{375})(HL)]$ (HL = 2,2′-dipyridylamine) is ≈5.[1693] The complexes $[Ru(\mathbf{375})L]^{n-}$ (L = NO^+, $n = 0$; L = NO, $n = 1$; L = NO^-, $n = 2$) result from reactions of $[Ru(\mathbf{375})(H_2O)]^-$ with gaseous NO or $[NO_2]^-$. Values of ν(NO) provide information about the relative back-donation from Ru^{II} to the $NO^{n\pm}$ ligand. For the ^{14}N and ^{15}N labeled complexes respectively, $\nu(NO) = 1{,}846$ and $1{,}827\,cm^{-1}$ for L = NO^+, 1,858 and $1{,}842\,cm^{-1}$ for L = NO, and 1,383 and $1{,}370\,cm^{-1}$ for L = NO^-. ^{15}N NMR spectra have been recorded for complexes containing coordinated $^{15}NO^{n\pm}$ and $^{15}NO_2^-$.[1694] A detailed electrochemical investigation of the reactions between NO and $[Ru_2(\mathbf{376})_2(H_2O)_2]^{2-}$ or $[Ru_2(\mathbf{376})(bpy)(H_2O)]^{2-}$ in aqueous solution has been carried out.[1695]



(375)



(376)

The free *N*-donor atoms in $[Ru(bpz)_3]^{2+}$ enter the coordination sphere of $[Ru(edta)]^{2-}$ to enable the formation of the supramolecular complex $[Ru(bpz)_3\{Ru(edta)\}_6]^{10-}$ which has been characterized in solution. In the electronic spectrum of this complex, the MLCT bands of the central Ru^{II} are hidden by absorptions assigned to the edta-bound Ru^{II} centers. Resonance Raman spectra of $[Ru(bpz)_3\{Ru(edta)\}_6]^{10-}$ have been recorded and assigned. On going from $[Ru(bpz)_3]^{2+}$ to $[Ru(bpz)_3\{Ru(edta)\}_6]^{10-}$, the luminescence of the former is partially quenched.[1696]

Dinuclear Ru^{II} complexes with *N,O*-donor ligands include $[Ru_2(\mu\text{-L-}N,O)_4]$ (HL = 2-chloro-6-hydroxypyridine) which is prepared from $[Ru_2(OAc)_4Cl]$ and molten HL. Reduction of the intermediate compound $[Ru_2L_4Cl]$ with Zn in the presence of thf yields $[Ru_2L_4(thf)]$. Both $[Ru_2L_4]$ and its thf adduct have been structurally characterized. Abstraction of Cl^- from $[Ru_2L_4Cl]$ results in the formation of $[\{Ru_2L_4\}_2][BF_4]_2$.[1697] The dinuclear complex $[Ru_2(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-L-}N,O)_2(PPh_3)_4]$ in which HL is succinimide, forms in the reaction of HL with $[RuH(Cl)(PPh_3)_3]$. If the reaction is carried out in the presence of excess NEt_3, $[Ru_2(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-L-}N,O)_2(PPh_3)_3(CO)]$ can be isolated. Further CO-for-PPh_3 substitution yields

$[Ru_2(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-L-}N,O)_2(PPh_3)_2(CO)_2]$.[1698] The reactions of $[Ru_2(CO)_4(MeCN)_4L_2]^{2+}$ (L = tertiary phosphine) with $NaNO_2$ or $NaNO_3$ in methanol afford the complexes $[Ru_2(CO)_4(\mu\text{-}NO_2\text{-}N,O)_2L_2]$ or $[Ru_2(CO)_4(\mu\text{-}NO_3\text{-}O,O)_2L_2]$. Isomers of $[Ru_2(CO)_4(\mu\text{-}NO_2)_2L_2]$ arise from head-to-head or head-to-tail arrangements of the $\mu\text{-}NO_2^-$ groups. The reactivities of the two complexes have been explored.[1699]

5.5.3.6.2 N,P-donors

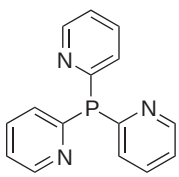
The simplest *P,N*-donor described in this section is $Me_2NCH_2CH_2PPh_2$. It reacts with $RuCl_3 \cdot xH_2O$ in the presence of Zn to give $[Ru(Me_2NCH_2CH_2PPh_2\text{-}P,N)_2Cl_2]$, an alternative route to which is the reaction between the ligand and $[RuCl_2(PPh_3)_3]$. The reactivity of $[Ru(Me_2NCH_2CH_2PPh_2\text{-}P,N)_2Cl_2]$ has been investigated. For example, it reacts with CO to give $[Ru(Me_2NCH_2CH_2PPh_2\text{-}P,N)(Me_2NCH_2CH_2PPh_2\text{-}P)(CO)Cl_2]$, and it loses Cl^- when treated with $NaBPh_4$. The crystal structure of $[Ru(Me_2NCH_2CH_2PPh_2\text{-}P,N)_2Cl][BPh_4]$ has been determined, confirming the five-coordinate geometry. The sixth coordination site is readily occupied, e.g., by CO or MeCN.[1700] $[Ru(Me_2NCH_2CH_2PPh_2\text{-}P,N)_2Cl_2]$ undergoes a reversible one-electron oxidation in CH_2Cl_2 solution, but in MeOH, a two-step ionization/solvolysis process involving opening of the chelate ring is observed.[1701] The crystal structures of $[Ru(Me_2NCH_2CH_2PPh_2\text{-}P,N)_2Cl_2]$ (*trans*-Cl, *cis*-P)[1701] and $[Ru(H)Cl_2\{P(4\text{-}MeC_6H_4)_3\}_3(2\text{-}PPh_2C_6H_4NMe_2\text{-}P,N)]$ (*trans*-Cl, *cis*-P)[1702] have been determined. The latter five-coordinate complex reversibly binds H_2 and N_2 forming η^2–H_2 and σ–N_2 complexes respectively.[1702]

2-Diphenylphosphinopyridine (2-Ph_2Ppy) has been incorporated into the complex $[Ru(2\text{-}Ph_2Ppy)_3Cl]^+$. Spectroscopic data indicate that two ligands are *P,N* chelates and the third is monodentate. From chlorinated solvent solutions of $[Ru(2\text{-}Ph_2Ppy)_3Cl]Cl$, it is possible to isolate *cis*-$[Ru(2\text{-}Ph_2Ppy)_2Cl_2]$. Carbon monoxide displaces Cl^- in $[Ru(2\text{-}Ph_2Ppy)_3Cl]^+$ to yield $[Ru\text{-}(2\text{-}Ph_2Ppy)_3(CO)]^{2+}$, and with $Ag[CF_3CO_2]$, $[Ru(2\text{-}Ph_2Ppy)_3Cl]Cl$ reacts to give $[Ru(2\text{-}Ph_2Ppy)_3(CF_3CO_2)][CF_3CO_2]$ as the main product.[1703] The complexes $[Ru(L\text{-}P,N)_2X_2]$ (L = 2-$Ph_2PCH_2CH_2$py; X = Cl, Br, I) have been prepared and their solution properties studied by UV–vis and multinuclear NMR spectroscopies and conductivity measurements. Dissociation of X^- gives five-coordinate species that dimerize to $[Ru_2(L\text{-}P,N)_4(\mu\text{-}X)_2]^{2+}$, although this process is dependent on the size of the halide ligand.[1704] Analogous Os^{II} complexes have also been characterized. The complexes $[Os(L\text{-}P,N)_2X_2]$ (L = 2-$Ph_2PCH_2CH_2$py; X = Cl, Br) react with CO to give $[Os(L\text{-}P,N)(L\text{-}P)(CO)X_2]$ or $[Os(L\text{-}P,N)_2(CO)X]^+$. The CO ligand lies *trans* to a *P*-donor atom, but isomerization to a *cis* arrangement occurs on heating. In solution, $[Os_2(L\text{-}P,N)_4\ (\mu\text{-}X)_2]^{2+}$ dissociates to $[Os(L\text{-}P,N)_2X]^+$. In MeCN, the complex $[Os(L\text{-}P,N)_2(MeCN)_2]^{2+}$ is formed and undergoes substitution reactions with py, PMe_2Ph, or $P(OEt)_3$.[1705] 2,6-Bis(diphenylphosphinomethyl)pyridine, L, reacts with $[RuCl_2(PPh_3)_3]$ in MeCN to produce *mer*-$[RuCl_2(PPh_3)(L\text{-}P,N,P')]$ and $[RuCl(MeCN)(PPh_3)(L\text{-}P,N,P')]Cl$.[1706] The same ligand has been incorporated into the complexes $[Ru(OAc)_2(L\text{-}P,N,P')]$, $[Ru(OAc)_2(L\text{-}P,N,P')(PPh_3)]$, $[RuH(X)(L\text{-}P,N,P')(PPh_3)]$ (X = Cl, OAc), and $[RuH_2(L\text{-}P,N,P')(PPh_3)]$. A determination of the crystal structure of $[RuH(Cl)(L\text{-}P,N,P')(PPh_3)]$ confirms a *mer* configuration for the tridentate ligand. Deuterium exchange reactions have been carried out with the hydrido complexes and intermediate dihydrogen complexes have been proposed.[1707] The ligand $PrN(CH_2CH_2PPh_2)_2$ (L) coordinates to Ru^{II} in a *mer* configuration in the complex $[RuCl_2L(PPh_3)]$; the PPh_3 ligand is *trans* to the *N*-donor atom of L.[1708]

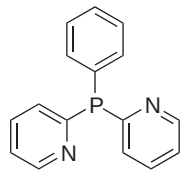
The reaction between ligand (**377**) and $[RuCl_2(PPh_3)_3]$ in benzene leads to the formation of $[RuCl_2(\mathbf{377}\text{-}N,N',N'')(PPh_3)]$, the non-coordinated P atom in which oxidizes to give the corresponding phosphine oxide compound.[1709] $[RuCl_2(377\text{-}N,N',N'')(PPh_3)]$ can also be obtained from (**377**) and $[RuCl_2(PPh_3)_3]$ in $CDCl_3$, but a change in conditions alters the reaction pathway in favor of $[RuCl_2(\mathbf{377}\text{-}N,P,N')(PPh_3)]$. The related complex $[RuCl_2(\mathbf{378}\text{-}N,P,N')(PPh_3)]$ has also been prepared and both $[RuCl_2(\mathbf{377}\text{-}N,P,N')(PPh_3)]$ and $[RuCl_2(\mathbf{378}\text{-}N,P,N')(PPh_3)]$ have been structurally characterized.[1710]

The syntheses and structures of *trans*-$[RuCl_2(\mathbf{379}\text{-}P,N,N',P')]$ and the related saturated derivative have been reported;[1711,1712] the C_2-symmetric complex is a highly efficient catalyst precursor for the asymmetric transfer hydrogenation of aromatic ketones, e.g., acetophenone.[1711] The reaction of $[Ru(OAc)_2(PPh_3)_2]$ with ligand (**380**) yields *trans*-$[Ru(OAc)_2(\mathbf{380}\text{-}P,N,N',P')]\cdot 2H_2O$ when the reaction is carried out in CH_2Cl_2; in toluene at reflux, the product is hydrated *trans*-$[RuCl_2(\mathbf{380}\text{-}P,N,N',P')]$ which has been structurally characterized.[1713,1714] The latter can also be prepared from $[RuCl_2(dmso)_4]$ and (**380**), and this route is also used to synthesize

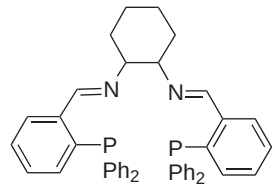
trans-[$RuCl_2$(**381**-*P,N,N′,P′*)]. The complex *trans*-[$RuCl_2$(**380**-*P,N,N′,P′*)] catalyzes the hydrogenation of acrylic acid to propionic acid.[1714]



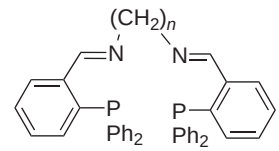
(**377**)



(**378**)

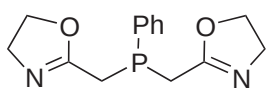


(**379**)

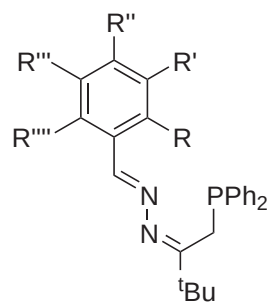


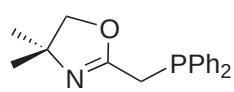
(**380**) *n* = 2
(**381**) *n* = 3

Treatment of [$RuCl_2(PPh_3)_3$] with $LiN(SiMe_2CH_2PPh_2)_2$ generates [$RuCl(PPh_3)${$N(SiMe_2CH_2PPh_2)_2$-*P,N,P′*}]. This adds H_2 producing two isomers of [$RuH(Cl)(PPh_3)${$NH(SiMe_2CH_2PPh_2)_2$-*P,N,P′*}]. The five-coordinate [$RuCl(PPh_3)${$N(SiMe_2CH_2PPh_2)_2$-*P,N,P′*}] undergoes orthometallation when it reacts with MeLi, Me_3SiCH_2Li or $H_2C{=}CHCH_2MgCl$, forming [$Ru(C_6H_4PPh_2)${$N(SiMe_2CH_2PPh_2)_2$-*P,N,P′*}]. Orthometallation also occurs when [$RuCl(PPh_3)${$N(SiMe_2CH_2PPh_2)_2$-*P,N,P′*}] reacts with PEt_3.[1715] Ligand **382** acts as an *N,P,N′* donor in the complexes *fac*-[$RuCl_2$(dmso)(**382**)], *fac*-[$RuCl_2(PPh_3)$(**382**)], and [$Ru(\eta^6$-$C_6H_6)$(**382**)]$^{2+}$, while in [$RuCl(\eta^6$-$C_6H_6)$(**382**)]$^+$ one oxazoline ring is pendent as confirmed by X-ray diffraction studies. All four complexes catalyze the transfer hydrogenation reactions between propan-2-ol and ketones.[1716] The catalytic properties of Ru^{II} complexes containing ligand (**383**) have also been explored. Attempts to prepare hydrido complexes containing ligand (**383**) from the reactions between [$RuH(Cl)(PPh_3)_3$] and [$RuH(OAc)(PPh_3)_3$] and (**383**) have been unsuccessful, and during investigations of other possible routes to hydrido species, the unexpected deprotonation of the CH_2 group of the CH_2PPh_2 chain in (**383**) was observed in the formation of [Ru(OAc-*O,O′*)(**383**-*N,P*){(**383**–H)-*N,P*}].[1717]



(**382**)

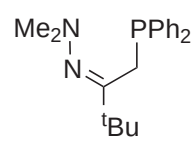




(**383**)

R = R'''' = F; R' = R'' = R''' = H
R = R' = R'' = R''' = R'''' = F
R = Cl; R ' = R'' = R''' = H; R'''' = F
R = F; R = R' = R'' = R''' = H
R = R' = F; R'' = R''' = R'''' = H

(**384**)



(**385**)

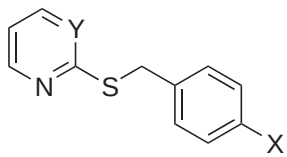
The syntheses of ligands (**384**) have been described starting from (*Z*)-$PPh_2CH_2C(^tBu){=}NNH_2$. Reactions between (**384**) and [$RuCl_2(PPh_3)_3$] yield *mer,trans*-[$RuCl_2(PPh_3)$(**384**-*P,N,R*)] where R is the halo substituent labeled in structure (**384**). The complexes have been characterized by multinuclear NMR spectroscopy.[1718] An extension of this work involves complex formation using (**385**) and related ligands.[1719]

5.5.3.6.3 N,S-donors

Thiobenzamide reacts with [$MCl_2(PPh_3)_3$] or [$MH(X)(CO)(PPh_3)_3$] (M = Ru, Os; X = H, Cl) to yield [M{$S(NH)CPh$}$_2(PPh_3)_2$] and [MX{$S(NH)CPh$}$(CO)(PPh_3)_2$]; an *N,S*-chelate mode has been

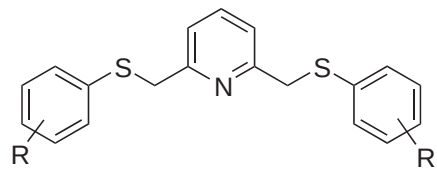
confirmed in the crystal structure of $[Os\{S(NH)CPh\}_2(PPh_3)_2]$. Related chemistry involving thiobenzoic acid has also been described.[1720] The complexes $[RuL_2Cl_2]$, $[RuL_2Br_2]$, $[RuL_2Cl(PPh_3)]^+$, and $[RuL(bpy)Cl_2]$, where L = 1-amino-2-thiomethylbenzene, have been prepared and characterized. The *N,S*-donor ligand resists demethylation on heating in dmf to reflux and this behavior contrasts with that observed for related complexes of Ni^{II}, Pd^{II}, Pt^{II}, and Cu^{II}.[1721]

The complex $[Ru(CO)_2(2\text{-Spy-}N,S)_2]$ has been prepared from $Ru_3(CO)_{12}$ and pyridine-2-thiol (2-SHpy). Spectroscopic data are consistent with the *S*-donor atoms being mutually *trans,* and a *cis* arrangement of CO ligands. Differences in the reaction patterns of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ with 2-SHpy are discussed.[1722] The complex $[Ru(CO)_2(2\text{-Spy})_2]$ has also been prepared by the reductive carbonylation of $RuCl_3 \cdot xH_2O$ followed by treatment with 2-SHpy. When 2-SHpy is replaced by quinoline-2-thione (quinSH), the major product is $[RuCl_2(CO)_2(quinSH)_2]$ rather than $[Ru(CO)_2(quinS)_2]$.[1723] Related phosphine Ru^{II} complexes containing the conjugate bases of 2-SHpy or 1-hydroxypyridine-2-thione have also been studied,[1724] and the crystal structure of $[Ru(dppb)(2\text{-Spy})_2]$ has been determined.[1725] In the latter, the S atoms are *trans* to each other, and this is also observed in the structure of $[Ru(\eta^4\text{-nbd})(2\text{-Spy})_2]$ (nbd = bicyclo[2.2.1]hepta-1,4-diene); the S—Ru—S bond angle of 149.9(1)° is similar to those in related compounds.[1726] Several related ligands including those in structures (**386**) have been prepared and characterized, and incorporated into complexes of type $[Ru(L\text{-}N,N')_2(\mathbf{386}\text{-}N,S)]^{2+}$ (L = di-2-pyridyl sulfide (dps) or di-2-pyrimidinyl sulfide). NMR spectroscopy has been used to study exchange between diastereomers arising from inversion at sulfur.[1727] The complexes $[Ru(dps\text{-}N,N')_2Cl_2]$ react with dps or 2-(6-methylpyridyl) 2-pyridyl sulfide (L) to yield $[Ru(dps\text{-}N,N')_2(L\text{-}N,S)]^{2+}$, crystallographically confirmed for L = dps. Multinuclear NMR spectroscopy has been used to investigate the solution behavior of these complexes.[1728] 6-(2-Thienyl)-2,2′-bipyridine (HL) exhibits two bonding modes in the complex $[Ru(HL\text{-}N,N')(HL\text{-}N,N',S)Cl]^+$; preference for the *N,N′ mode* is observed in the Ru^{III} complex $[Ru(LH)(py)Cl_3]$.[1729] The pyridine-based ligands (**387**) have been prepared. They react with $[RuCl_2(PPh_3)_3]$ and $[RuCl_2(dmso)_4]$ to yield $[RuCl_2L(\mathbf{387})]$ (L = PPh_3 or dmso). Isomer preferences have been discussed, and the conclusions are supported by structural data for three representative complexes.[1730]



Y = CH; X = Me, Cl
Y = N; X = Me, Cl

(**386**)



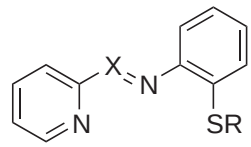
R = H, 4-OMe, 4-Cl, 4-NO_2,
2-CO_2Me, 3-CO_2Me, 4-CO_2Me

(**387**)

A series of complexes of general type $[Ru(bpy)_2(L\text{-}N,S)]^+$ where HL is pyrimidine-2-thione or a related ligand has been prepared and spectroscopically characterized. The existence of linkage isomerism and electronic factors influencing the latter have been described; for $[Ru(bpy)_2L][ClO_4]$ where HL = 4-methylpyrimidine-2-thione, a crystal structure determination confirms that L^- binds through atoms S(2) and N(3).[1731] As part of an investigation of Ru^{II} mercaptopurine riboside complexes, the structure of $[Ru(L\text{-}N,S)_2(PPh_3)_2]Cl_2$ (L = 9-β-D-ribofuranosyl-6-mercaptopurine) has been determined. This represents both the first X-ray diffraction study of a ruthenium–nucleoside complex and the first structurally characterized metal complex containing a 6-mercaptopurine riboside.[1732]

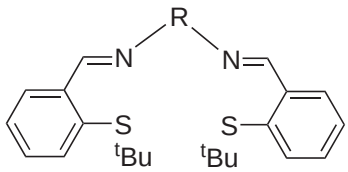
Ligand $(\mathbf{388})^-$ functions as an *N,N′,S* bischelate in the complexes $[Ru(\mathbf{388})(PPh_3)X]$ (X = Cl, Br), $[Ru(\mathbf{388})(PPh_3)_2Cl]$, $[Ru(\mathbf{388})(PPh_3)L]^+$ (L = 1-Meim, 2-Meim), $[Ru(\mathbf{388})(PPh_3)L_2]^+$ (L = im, 1-Meim, H_2O), and $[Ru(\mathbf{388})(PPh_3)L]^+$ (L = bpy, phen) which have been characterized by spectroscopic and electrochemical methods. It is proposed that the five-coordinate complexes among this group are stabilized by pπ donation involving the sulfur atom of $(\mathbf{388})^-$.[1733] As part of a study of Ru^{II} complexes containing ligand (**389**), the crystal structures of *cis*-$[Ru(\mathbf{389}\text{-}N,N',S)(PPh_3)Cl_2]$ and $[Ru(389\text{-}N,N',S)(PPh_3)(bpy)][ClO_4]_2$ have been determined.[1734] Coordinated ligand $(\mathbf{390})^-$ has been prepared starting from $[RuCl_2L_2]$ or $[OsBr_2L_2]$ (L = 2-(2-chlorophenylazo)pyridine) and K[S_2COEt] or Na[S_2CNEt_2]. The complexes that result are $[Ru(\mathbf{390}\text{-}N,N',S)_2]$ and $[Os(\mathbf{390}\text{-}N,N',S)_2]$. Spectroscopic data are consistent with a *mer* configuration of each ligand,[1735] and this

has been confirmed in the crystal structure of [Os(**390**-*N,N′,S*)$_2$].[1736] The rate of reaction between K[S_2COR] and [$OsBr_2L_2$] depends on R: Et > Me > ^{i}Pr > ^{i}Bu > Pr > Bu > Bz.[1736]

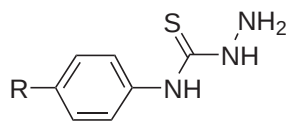


H (**388**) X = CH; R = H
(**389**) X = CH; R = Me
H (**390**) X = N; R = H

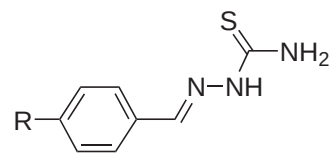
Complexes of type [$RuCl_2$(L-*S,S,S′,N′*)] and [RuCl(MeCN)(L-*S,S,S′,N′*)]$^+$ where L is a Schiff base ligand (**391**) have been prepared and characterized (including one representative crystal structure determination) along with compounds containing related P_2N_2- and O_2N_2-donor ligands.[143] A family of thiosemicarbazide complexes of type [$Ru(bpy)_2L$]$^{n+}$ has been made in which L is in either the keto (structure (**392**) and $n = 2$) or enolate ($n = 1$) forms. In both, the ligand functions as an *N,S* chelate.[1737] The conjugate bases of ligands (**393**) form a series of Ru^{II} and Os^{II} complexes of type [$M(bpy)_2$(**393**)]$^+$ and have been isolated and characterized as the perchlorate salts. In MeCN solution, the complexes exhibit intense MLCT absorptions in the visible region. The related complexes [$M(bpy)_2L$][ClO_4] (M = Ru, Os; HL = $Me_2C{=}NNHC(S)NH_2$}) have also been studied. Structural data for [Ru(bpy)(**393**)]$^+$ and [$Ru(bpy)_2L$]$^+$ show that (**393**)$^-$ coordinates through the S and hydrazinic N atoms giving a rather strained four-membered chelate ring, whereas L^- binds through S and the imine *N*-donors.[1738]



R = various spacers
(**391**)

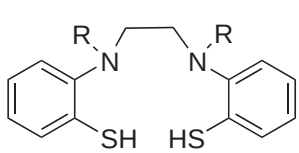


R = Me, Cl, Br, MeO
(**392**)

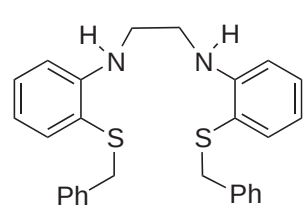


R = H, Me, Cl, NO_2, MeO
H(**393**)

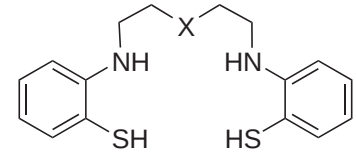
The complexes [Ru(**394**)(NO)(PPh_3)]$^+$ and [Ru_2(**394**)$_2$($NO)_2$] are formed when ligand (**394**)$^{2-}$ reacts with [$RuCl_3$(NO)($PPH_3)_2$]. The pathway of the reactions depends on solvent and concentration of H^+, and treatment of the mononuclear complex with base converts it to the dinuclear species. The effects of protonating and deprotonating the N atoms in the coordinated N_2S_2-donor ligand have been explored.[1739] The reaction of H_2(**395**) with $RuCl_3{\cdot}xH_2O$, LiOMe and CO produces [Ru(**395**)$(CO)_2$] in which each pair of CO ligands, *S*-donors, and NMe groups are *cis*.[1740] The complexes [Ru(**394**)($PPr_3)_2$], [Ru(**394**)(CO)(PPr_3)], [Ru(**394**)(CO)(PCy_3)], and [RuBr(**396**)(PPh_3)]$^+$ are among a series in which the Ru^{II} center lies within an S_2N_2PX environment. A five-coordinate Ru^{IV} complex [RuL(PCy_3)] has also been reported in which L^{4-} is derived from H_2(**394**); [RuL(PCy_3)] may be reversibly converted into the Ru^{II} complex [Ru(**394**)(CO)(PCy_3)].[1741] The complexes [Ru(**397**)(CO)(PCy_3)], [Ru(**397**)($PPr_3)_2$], [Ru(**397**)(PR_3)] (R = Pr, Ph), and [RuL(NO)] (in which L^{3-} is derived by the deprotonation of one NH group in (**397**)$^{2-}$) have been prepared in an effort to achieve electron-rich ruthenium complexes. When heated in solution, [Ru(**397**)($PPr_3)_2$] loses PPr_3 to give [Ru(**397**)(PPr_3)]. However, [Ru(**397**)(CO)(PCy_3)] (in which it is proposed that (**397**)$^{2-}$ is tetradentate) is stable enough to withstand heating, and neither CO nor PCy_3 is expelled.[1742] Ligand H_2(**398**) is related to H_2(**397**) by replacement of the central S atom by an NH group. Reaction of the conjugate base of H_2(**398**) with [$RuCl_2(PPh_3)_3$] in thf at reflux results in the formation of [Ru(**398**-*S,N,N′,N″,S′*)(PPh_3)]. It is proposed that the complex possesses C_s symmetry, partly on the basis of the crystal structure of the *S*-methylated derivative.[1743] Ligand **399**$^{2-}$ is pentadentate in [Ru(**399**)(NO)]$^+$. Treatment of this complex with $NaBH_4$ leads to the formation of [Ru(**399**)(HNO)] and represents the first example of hydride addition to coordinated NO^+ to give an *N*-bound HNO ligand.[1744]



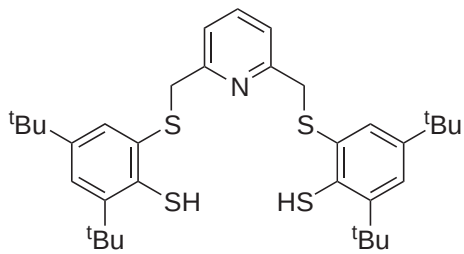
H_2 (394) R = H
H_2 (395) R = Me



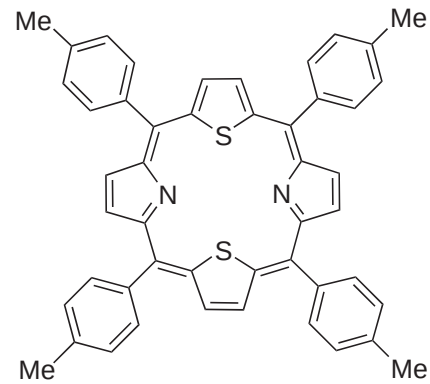
(396)



H_2 (397) X = S
H_2 (398) X = NH



H_2 (399)



(400)

Encapsulation of Ru^{2+} in an N_3S_3-donor set has been achieved in the complex $[RuL]^{2+}$ in which L is $MeC(CH_2SCH_2CH_2NHCH_2)_3CH$. The complex has been crystallographically characterized.[1745]

The first example of a metal complex of the dithiaporphyrin (**400**) has been reported. Ligand (**400**) reacts with $[Ru(cod)Cl_2]$ to give *trans*-$[RuCl_2$(**400**)$]$ which has been characterized in solution using ^1H NMR spectroscopy and electrochemical methods, and in the solid state by X-ray diffraction. The latter reveals that the two thiophene rings in coordinated ligand (**400**) are tilted out of the mean porphyrin plane.[1746]

5.5.3.6.4 P,O- and P,S-donors

In many cases, the driving force behind studies of Ru^{II} or Os^{II} complexes containing phosphine ligands incorporating *O*-donors is potential application in catalysis. A common feature of many of the *P,O*-bound ligands described in this section is their partial lability, with the conversion of a *P,O*- to *P*-coordinated ligand as another Lewis base such as CO or RNC displaces the *O*-donor.

The ligand $Ph_2PCH_2CH_2OMe$, L, forms the octahedral complex *trans*-$[RuCl_2$(L-*P,O*)$_2]$ and this has been used as a starting material for the preparation of a series of Ru^{II} complexes which include $[RuCl$(L-*P,O*)$_2$(L-*P*)$]^+$, *trans*-$[RuCl_2$(L-*P,O*)(L-*P*)$_2]$, and $[Ru$(L-*P,O*)$_3]^{2+}$. The solution dynamic behavior of these species has been discussed.[1747] In $[RuCl_2$(L-*P,O*)$_2]$ (L = $Ph_2PCH_2CH_2OMe$, $Ph_2PCH_2C_4H_7O_2$, and $Cy_2PCH_2CH_2OMe$) the *O*-donors interact only weakly with the metal center. As a result, reactions with small molecules such as SO_2, MeCN, and ^{t}BuNC occur readily, being accompanied by a change in the coordination mode of the phosphine ligands.[1748] The ligand $Ph_2PCH_2C_3H_5O$ (L) can be prepared by treating $LiPPh_2$ with 2-chloromethyloxetane. It reacts with $[RuCl_2(PPh_3)_3]$ to yield *trans*-$[RuCl_2$(L-*P,O*)$_2]$. On reaction with CO, the product is *trans*-$[RuCl_2(CO)$(L-*P,O*)(L-*P*)$]$, the solution fluxional properties of which have been investigated by ^{31}P NMR spectroscopy.[1749] These solution studies have been extended to a wider group of *trans*-$[RuCl_2(CO)$(L-*P,O*)(L-*P*)$]$ complexes containing different phosphine-based *P,O*-donor ligands.[1750,1751] The reactions between $RuCl_3 \cdot xH_2O$ or $[RuCl_2(PPh_3)_3]$ and $RP(CH_2CH_2OMe)_2$ or $RP(CH_2CO_2Me)$ (R = ^{i}Pr, ^{t}Bu; all ligands represented by L) result in the formation of $[RuCl_2$(L-*P,O*)$_2]$. As with previous examples of this type of complex, the weak

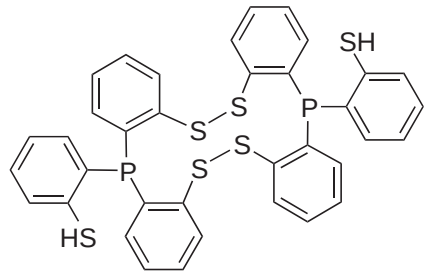
association of the O atom with the Ru^{II} center allows facile reactions with small molecules, e.g., CO, PhC≡CH. When $[RuCl_2\{^tBuP(CH_2CH_2OMe)_2\text{-}P,O\}_2]$ is treated with $AgPF_6$, Cl^- is abstracted and a *P,O,O′*-coordination mode for the ligand is achieved.[1752]

The reaction of $[RuCl_2(dmso)_4]$ with $Ph_2P\{2,6\text{-}(MeO)_2C_6H_3\}$ (L) gives rise to *trans,cis,cis*-$[RuCl_2(L\text{-}P,O)_2]$. During reactions involving $PhP\{2,6\text{-}(MeO)_2C_6H_3\}_2$, the ligand is demethylated. Further reactions in this series have also been investigated, including that between $P\{2,6\text{-}(MeO)_2C_6H_3\}_3$ and $[RuCl_2(dmso)_4]$.[1753] Related studies have explored *P,O* chelate formation with $Ph_2P(2\text{-}MeOC_6H_4)$, $Ph_2P(2\text{-}EtOC_6H_4)$, and $Ph_2P(2\text{-}MeOCH_2CH_2C_6H_4)$ in complexes of type $[Ru(bpy)_2(L\text{-}P,O)]$. For the methoxy- and ethoxyphenyl derivatives, the complexes are subject to dealkyation.[1754] With the aim of developing potential catalysts with hydrophilic and hydrophobic arms, eight new ligands containing polyether and aliphatic chains have been prepared, e.g., $PhRP(CH_2CH_2O)_3R'$ (R = isopentyl, R′ = Me; R = octyl, R′ = H). Reactions of these ligands with $RuCl_3 \cdot xH_2O$ gave mixtures of products which were not separated. More success was achieved starting from $[RuCl_2(PPh_3)_3]$. Multinuclear NMR spectroscopy was used to characterize the products, and in one case, an X-ray diffraction study was carried out showing that $[RuCl_2(PPh_3)\{Ph(CH_2CH_2CHMe_2)P(CH_2CH_2O)_3Me\text{-}P,O,O'\}]$ possesses a *trans* and *mer* arrangements of Cl^- and tridentate ligand donor atoms respectively.[1755] In the latter complex, the *P,O,O′*-ligand is partially labile in that one *O*-donor is displaced when the complex reacts with CO. The catalytic activity of systems containing these ligands and $RuCl_3$ with respect to the hydrogenation of 3-methyl-2-butenol has been investigated and the most efficient catalysts contain long polyether chains.[1756]

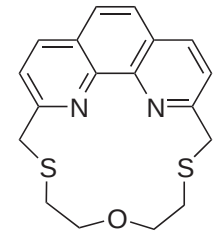
Reactions between $[RuCl_2(PPh_3)_3]$ or $RuCl_3 \cdot xH_2O$ and the phosphino diester $^tBuP(CH_2CO_2Me)_2$ result in the formation of isomers of $[RuCl_2\{^tBuP(CH_2CO_2Me)_2\text{-}P,O\}_2]$. The crystal structure of one isomer confirms *trans*-Cl and *cis*-P atoms. Removal of Cl^- generates $[RuCl\{^tBuP(CH_2CO_2Me)_2\text{-}P,O\}\{^tBuP(CH_2CO_2Me)_2\text{-}P,O,O'\}]^+$ from which, after treatment with K^tBu or $NaN(SiMe_3)_2$, an enolate complex (structurally characterized) can be obtained. The reactivities of these systems have been studied in detail.[1757] The complex $[(\eta^6\text{-Mes})OsCl_2\{^tBuP(CH_2CO_2Me)_2]$ undergoes chloride abstraction when treated with $AgPF_6$, and the monocationic product so formed is deprotonated on the ligand by K^tBu to give $[(\eta^6\text{-Mes})Os\{^tBuP(CH\text{-}CO_2Me)_2]$. Apart from containing the η^6-mesityl group, the coordination sphere in this complex contains three- and five-membered chelate rings involving the *P*-donor and either one CH^- group or an O-donor.[1758] Dissolution in MeOH of NH_4PF_6 and $[RuCl_2(Ph_2PCH_2CO^tBu\text{-}P,O)_2]$ results is slow abstraction of Cl^-. Subsequent reaction of the product with CO gives $[RuCl(CO)(Ph_2PCH_2\text{-}CO^tBu\text{-}P,O)_2][PF_6]$. When CO reacts with $[RuCl_2(Ph_2PCH_2CO^tBu\text{-}P,O)_2]$, the product is $[RuCl_2\text{-}(CO)(Ph_2PCH_2CO^tBu\text{-}P,O)(Ph_2PCH_2CO^tBu\text{-}P)]$, and heating this complex under CO leads to the formation of *cis,cis,trans*-$[RuCl_2(CO)_2(Ph_2PCH_2CO^tBu\text{-}P)_2]$. Reaction of $NOBF_4$ with $[RuCl_2(Ph_2PCH_2CO^tBu\text{-}P,O)_2]$ gives $[RuCl_2(NO)(Ph_2PCH_2CO^tBu\text{-}P,O)(Ph_2PCH_2CO^tBu\text{-}P)]^+$, deprotonation of which produces a Ru^{IV} phosphino enolate complex.[1759] Reactions between $[RuCl_2(PPh_3)_3]$ and Ph_2PCH_2COPh yield *trans,mer*-$[RuCl_2(Ph_2PCH_2COPh\text{-}P,O)(PPh_3)_2]$, *trans,cis,-cis*-$[RuCl_2(Ph_2PCH_2COPh\text{-}P,O)_2]$, or *trans,mer*-$[RuCl_2(Ph_2PCH_2COPh\text{-}P,O)(Ph_2PCH_2COPh\text{-}P)]$ depending on the stoichiometry of the reaction. The solution dynamic properties, reactivity, and catalytic behavior of these complexes have been explored, and among the structurally characterized products is $[Na(15\text{-crown-}5)\cdot H_2O][mer\text{-}Ru(Ph_2PCHCOPh\text{-}P,O)_3]$ in which the initial ligand has been deprotonated.[1760]

Ligands that are *P,S*-donors include $[Ph_2PC(S)NPh]^-$. This reacts with $[RuCl_2(PPh_3)_3]$ to give $[Ru(Ph_2PC(S)NPh\text{-}P,S)_2(PPh_3)_2]$ from which the PPh_3 ligands can be displaced by, for example, dppe. A range of related complexes including $[RuCl(Ph_2PCSNPh\text{-}P,S)(CO)(CS)(PPh_3)]$ have also been prepared and characterized.[1645] Reactions between the ligands $Ph_2PCH_2CH_2SR$ (R = Me, Et, Cy) and *cis*-$[RuCl_2(dmso)_4]$ result in the formation of the *cis,cis,cis*, *cis,cis,trans*, and *trans,cis,cis* isomers of $[RuCl_2(Ph_2PCH_2CH_2SR\text{-}P,S)_2]$. Halide exchange starting from the appropriate isomer gives a route to *cis,cis,trans*-$[RuI_2(Ph_2PCH_2CH_2SR\text{-}P,S)_2]$. Treatment of $[RuCl_2(Ph_2PCH_2CH_2SR\text{-}P,S)_2]$ with CO displaces Cl^- or one *S*-donor to give $[RuCl\text{-}(CO)(Ph_2PCH_2CH_2SR\text{-}P,S)_2]^+$ or $[RuCl_2(CO)(Ph_2PCH_2CH_2SR\text{-}P,S)(Ph_2PCH_2CH_2SR\text{-}P)]$ respectively, and Cl^- can also be displaced by MeCN to give $[Ru(MeCN)_2(Ph_2PCH_2CH_2\text{SR-}P,S)_2]^{2+}$.[1761]

The reaction of $[OsCl_2(PPh_3)_3]$ with $P(C_6H_4\text{-}2\text{-}SH)_3$ results unexpectedly in the formation of $[Os(\mathbf{401}\text{-}P,P',S,S',S'',S''')]$ in which the macrocyclic ligand results from oxidative coupling of two molecules of the original tertiary phosphine. A crystal structure determination of the complex confirms that the *P*-donors are mutually *cis*, and only one of each of the disulfide S atoms is involved in coordination to the metal center.[1762]



H_2(401)



(402)

5.5.3.6.5 S,O- and N,O,S-donors

The synthesis and characterization of the complexes $[RuL(H_2O)]$ and $[Ru_2L(H_2O)_2]$ in which H_4L is ethane-1,1′,2,2′-tetra(thioglycolic acid) have been reported. It is proposed from spectroscopic data that each complex contains five-coordinate Ru^{II} and that H_2L^{2-} acts as an S_2O_2-donor, while L^{4-} utilizes eight donor atoms. $[RuL(H_2O)]$ and $[Ru_2L(H_2O)_2]$ react with CO, PPh_3, or NO^+, and the site of addition is proposed to be *trans* to the aqua ligand in each case.[1763]

The mono 4-(4-tolyl)thiosemicarbazone of 2,6-diacetylpyridine (H_2L) reacts with $RuCL_3{\cdot}xH_2O$, $[RuCl_2PPh_3)_3]$ and $[Ru(NH_3)_5Cl]Cl$ to give a number of complexes that include *trans*-$[Ru(L\text{-}S,N,N',O)(PPh_3)_2]^+$, the perchlorate salt of which has been crystallographically characterized.[1764] Macrocycle (**402**) forms the Ru^{II} complex $[Ru(\mathbf{402}\text{-}N,N',S,O,S')(PPh_3)][PF_6]_2$ which has been structurally characterized; the PPh_3 ligand is *trans* to the *O*-donor atom. The conformations of ligand (**402**) and its N_2S_3 analog have been studied by calculation and, in solution, the coordinated (**402**) adopts the same conformation as in the solid state.[1765]

5.5.3.7 Mononuclear Complexes with Cyanide or Fluoride Ligands

The solid-state structures of the Ru^{II} cyano derivatives $GdKRu(CN)_6{\cdot}4H_2O$ and $TbKRu(CN)_6{\cdot}4H_2O$ contain eight-coordinate Gd^{III} and Tb^{III}, rspectively. The coordination sphere of each metal center comprises six cyano N atoms and two aqua ligands. Each octahedral Ru^{II} center is thereby linked to the lanthanoid metals through μ-CN^- ligands to give an infinite array, cavities within which are occupied by K^+ ions.[1766] The solid-state structures of $Na_4M(CN)_6{\cdot}10H_2O$ (M = Ru, Os) consist of layers of $[M(CN)_6)]^{4-}$ ions, intercalated by layers that contain Na^+ and H_2O molecules.[1767]

The preparation and characterization of $K_3[Os(CN)_5(NH_3)]{\cdot}2H_2O$ have been described. This complex is a useful starting material for the synthesis of other $[Os^{II}(CN)_5L]^{n-}$ species (e.g., L = py, pyz) and $[Os(CN)_5(H_2O)]^{3-}$ can be obtained by the controlled aquation of $[Os(CN)_5(NH_3)]^{3-}$. The kinetics of these ligand displacements have been investigated and mechanisms for the processes have been discussed.[1768] The UV–vis spectrum of each complex in the series $[Os^{II}(CN)_5L]^{n-}$ in which L is py, pyz, $Mepz^+$, or derivatives thereof, exhibits an intense, asymmetric MLCT absorption, split by spin–orbit coupling, and the effects of the electronic properties of L on the spectra have been examined. Redox properties of the complexes and the kinetics of the dissociation of pyz from $[Os(CN)_5(pyz)]^{3-}$ have also been reported.[1769]

Xenon difluoride reacts with $Ru_3(CO)_{12}$ in anhydrous HF to generate *cis*-$[RuF_2(CO)_4]$. Minor products of the reaction are $[RuF(CO)_5]^+$, *mer*- and *fac*-$[RuF_3(CO)_3]^-$, $[\{RuF(CO)_4\}_2(\mu\text{-}F)]^+$, $[Ru_2(CO)_7F_4]$, $[F_2(CO)_3Ru(\mu\text{-}F)Ru(CO)_5]^+$, and the polymeric $[RuF_2(CO)_3]_n$. When HF was removed from the reaction mixture under vacuum, $[\{RuF_2(CO)_3\}_4]$ was isolated.[1770] Analogous fluorination of $Os_3(CO)_{12}$ provides a route to *cis*-$[OsF_2(CO)_4]$ and smaller amounts of $[OsF(CO)_5]^+$, $[Os_2F_4(CO)_7]$, and $[Os_2F_3(CO)_8]^+$; $[\{OsF_2(CO)_3\}_4]$ is formed in a similar manner to $[\{RuF_2(CO)_3\}_4]$.[1771] The tetramers $[\{MF_2(CO)_3\}_4]$ (M = Ru, Os) react with Lewis bases, L, (e.g., PR_3) to give mononuclear $[MF_2(CO)_2L_2]$ which are air and moisture stable. Spectroscopic data are consistent with *cis,cis,trans*-$[MF_2(CO)_2L_2]$, and confirmed in the crystal structures of $[RuF_2(CO)_2(PEtPh_2)_2]$, $[OsF_2(CO)_2(PPh_3)_2]$, and $[OsF_2(CO)_2(PCy_3)_2]$. In each of these derivatives, the PR_3 ligands are bent towards the F^- ligands, and exhibit $H_{phosphine}$—F hydrogen bonds.[1772]

Additional structural data are available for *cis,cis,trans*-$[RuF_2(CO)_2(PPh_3)_2]$.[1773] The reaction between XeF_2 and $[M(CO)_3(PPh_3)_3]$ (M = Ru, Os) in CH_2Cl_2 results in the formation of M^{II} fluoroacyl derivatives. The Ru^{II} complex is not stable at 298 K and loses CO to give $[RuF_2(CO)_2(PPh_3)_2]$.[1773] *cis,cis,trans*-$[OsF_2(CO)_2(PPh_3)_2]$ (M = Ru, Os) can also be made by treating $[MH_2(CO)_2(PPh_3)_2]$ with anhydrous HF (see Section 5.5.4).

5.5.4 DINUCLEAR COMPLEXES OF M^{III} AND M^{II} CONTAINING HALO-BRIDGES

Dinuclear Ru^{II} and Os^{II} complexes containing halo bridges include a number of fluoro carbonyl complexes, described in the last section.[1770,1771] The reactions between anhydrous HF and $[MH_2(CO)_2(PPh_3)_2]$ (M = Ru, Os) produce *cis,cis,trans*-$[MF_2(CO)_2(PPh_3)_2]$, but when the precursor is $[MH_2(CO)(PPh_3)_3]$, the dinuclear complexes $[M_2(CO)_2(PPh_3)_4(\mu\text{-}F)_3]^+$ result. Initially, these form as the $[HF_2]^-$ salts, but are better isolated as the air-stable $[BPh_4]^-$ salts.[1774]

The formation of $[HP^tBu_2Me][Cl(P^tBu_2Me)(CO)Ru(\mu\text{-}Cl)_3Ru(CO)(P^tBu_2Me)Cl]$ starting from H_2 and $[RuCl_2(CO)(P^tBu_2Me)_2]$ has been described; the reaction pathway involves the intermediate production of $[RuHCl(CO)(P^tBu_2Me)_2]$ and HCl. The structure of $[Cl(P^tBu_2Me)(CO)Ru(\mu\text{-}Cl)_3Ru(CO)(P^tBu_2Me)Cl]^-$ has been confirmed crystallographically.[1775] UV–vis and $^{31}P\{^1H\}$ NMR spectroscopic and stopped-flow kinetics methods have been used to investigate the reaction of H_2 and $[Cl(dppb)Ru(\mu\text{-}Cl)_2Ru(dppb)Cl]$ which reversibly gives $[(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3Ru(dppb)Cl]$.[1776] The chloro-bridged dinuclear complexes $[Cl(dppb)Ru(\mu\text{-}Cl)_2(\mu\text{-}D_2O)Ru(dppb)Cl]$, $[(\eta^2\text{-}H_2)(dppb)Ru(\mu\text{-}Cl)_3Ru(dppb)Cl]$, and $[Cl(dppb)Ru(\mu\text{-}Cl)_3Ru(dppb)Cl]^-$ have been structurally characterized, and a ^{31}P CP/MAS NMR spectroscopic study of $[Cl(dppb)Ru(\mu\text{-}Cl)_2(\mu\text{-}D_2O)Ru(dppb)Cl]$ has also been carried out.[1777] Starting from $[RuCl_2(PPh_3)L]$ or $[Ru_2Cl_2L_2(\mu\text{-}Cl)_2]$ where L = dppb, diop (**24**) or binap (**25**), a series of RCN (R = Me, Ph) derivatives has been prepared. By altering the conditions, various species can be isolated and hese include $[RuClL(RCN)_3]^+$, $[RuCl_2L(RCN)_2]$, $[Ru_2L_2(RCN)_2(\mu\text{-}Cl)_3]^+$, and $[Ru_2L_2(RCN)Cl(\mu\text{-}Cl)_3]$.[1778]

A series of related chloro-bridged $Ru^{II}Ru^{II}$, $Ru^{II}Ru^{III}$, and $Ru^{III}Ru^{III}$ complexes has been described by Cotton *et al.* Two salts of $[Ru_2(\mu\text{-}Cl)_3(PBu_3)_6]^+$ were structurally characterized, the Ru—Ru distance being 3.412(1) Å in the BPh_4^- salt and 3.395(1) Å in the $[RuCl_4(PBu_3)_2]^-$ salt. The mixed-valent complex $[Ru_2(\mu\text{-}Cl)_3Cl_2(PBu_3)_4]$ exists in two isomeric forms which differ in the distribution of the terminal ligands. Structural data show that where the ligands are unsymmetrically distributed with respect to the metal centers, there is no Ru—Ru bonding interaction; valence trapping is observed. In complexes such a $[Ru_2(\mu\text{-}Cl)_3Cl_2(PMe_2Ph)_4]$ and $[Ru_2(\mu\text{-}Cl)_3Cl_2(PMe_3)_4]$ where there are one chloro and two PR_3 ligands per metal center, the odd electron is delocalized and a weak Ru—Ru bonding interaction is evidenced. In the $Ru^{III}Ru^{III}$ complex $[Ru_2Cl_6(PEt_3)_2]$, structural data are consistent with the absence of a Ru—Ru bond.[1779] The crystal structure of the mixed-valent complex $[Cl_2(PPh_3)Ru(\mu\text{-}Cl)_3(PPh_3)_2(CO)]$ has also been reported, and the compound is formulated as a valence-trapped species on the basis that no intervalence CT transition is observed. EPR spectroscopic data confirm the presence of an Ru^{III} center.[1780] A related, but symmetrical, complex is $[Cl(PPh_3)(CO)Ru(\mu\text{-}Cl)_3(PPh_3)(CO)Cl]$.[1781]

The prototype triruthenium complex with a structure consisting of three face-sharing octahedra is $[Ru_3Cl_{12}]^{4-}$. The related complexes $[(PMe_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mu\text{-}Cl)_3Ru(PMe_3)_2Cl]$ and $[(PEt_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mu\text{-}Cl)_3Ru(PEt_3)_2Cl]$ have been prepared and structurally characterized, and other members of this family have also been described. The one-electron oxidation product $[(PEt_3)_2ClRu(\mu\text{-}Cl)_3Ru(\mu\text{-}Cl)_3Ru(PEt_3)_2Cl]^+$ has been isolated and fully characterized as the SbF_6^- salt.[1782] Extension of this work leads to species in which all the terminal ligands are replaced by PR_3 ligands, e.g., $[(PEt_3)_3Ru(\mu\text{-}Cl)_3Ru(\mu\text{-}Cl)_3Ru(PEt_3)_3]^+$.[1783]

The anions $[Ru_2X_9]^{n-}$ where X = Cl, Br, and $n = 1$, 2, 3, or 4, have been investigated by spectroelectrochemistry. The $Ru^{II}Ru^{III}$ complexes exhibit delocalization of electronic charge, the $Ru^{III}Ru^{III}$ species has a strong Ru—Ru bonding interaction, and the more oxidized systems exhibit no metal–metal bonding interaction.[1784]

The reaction of $RuCl_3 \cdot xH_2O$ with PEt_3 under carefully controlled conditions yields $[Ru^{III}{}_2Cl_6(PEt_3)_4]$. However, isolation of the complex is not easy and attempts to recrystallize it resulted in the formation of $[Ru_2Cl_6(PEt_3)_3]$. The results of an ESR spectroscopic investigation lead to the conclusion that $[Ru_2Cl_6(PEt_3)_4]$ contains no Ru—Ru bond.[1785]

5.5.5 DINUCLEAR COMPLEXES CONTAINING CARBOXYLATE AND RELATED BRIDGING LIGANDS

Rather than being segregated by oxidation state, dinuclear systems containing bridging RCO_2^- ligands are described together. Many related complexes exist that contain M_2^{4+}, M_2^{5+}, and M_2^{6+} cores, as well as more highly oxidized species, and Ru-containing complexes predominate over those centered on Os. We start the section with a look at complexes that formally contain Ru^I. The reaction of $Ru_3(CO)_{10}(MeCN)_2$ (or $Ru_3(CO)_{12}$ in $MeCN/CH_2Cl_2$) with CF_3CO_2H results in the formation of $[Ru_2(CO)_4(MeCN)_2(\mu\text{-}O_2CCF_3)_2]$ which has been structurally characterized. The MeCN ligands are in axial sites, with each CO *trans* to a μ-carboxylate *O*-donor atom; the Ru—Ru bond length is 2.683(1) Å.[1786] Two related complexes are $[Ru_2(CO)_4(pz)_2(\mu\text{-}O_2CMe)_2]$ and $[Ru_2(CO)_4(3,5\text{-}Me_2pz)_2(\mu\text{-}O_2CMe)_2]$, the crystal structures of which have been established. As expected, the pyrazole ligands occupy axial sites.[1787] Structural determinations of $[Ru_2(CO)_4(PPh_3)_2(\mu\text{-}O_2CR)_2]$ for R = Me, Ph, and CF_3 have been carried out and from a comparison of data for a range of similar complexes it is concluded that the axial, rather than equatorial, ligands are primarily responsible for variations in the Ru—Ru bond lengths.[1788] In another structural study that focuses on $[Ru_2(CO)_4(PR_3)_2(\mu\text{-}O_2CMe)_2]$ for R = ^{n}Bu, ^{t}Bu, and ^{i}Pr, a correlation has been made between the P–Ru-Ru–P torsion angle and the catalytic activity of the complexes with respect to alkene hydrogenation.[1789] Reactions of $[Ru_2(CO)_4(PPh_3)_2\text{-}(\mu\text{-}O_2CH)_2]$ with RCH_2OH (various R groups) in toluene at reflux proceed with oxidation of the alcohol to yield $[Ru_2(CO)_4(PPh_3)_2(\mu\text{-}O_2CR)_2]$. In some cases, unstable alkoxide derivatives of the type $[Ru_2(R'O)_2(CO)_4(PPh_3)_2]$ are formed.[1790] The complexes $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2]_n$ and $[Ru_2(CO)_4(MeCN)_2(\mu\text{-}O_2CR)_2]$ (R = H, Me, Et) react with 2-Ph_2Ppy, 6-Ph_2Pbpy, or 2-Ph_2Pquin (quin = quinoline) in alcohol solvent to give bis-axially substituted derivatives in which the phosphine ligands are monodentate, occupying axial sites. With changes in the reaction conditions, it is possible to prepare $[Ru_2(CO)_4(\mu\text{-}O_2CR)\{\mu\text{-}(2\text{-}Ph_2Ppy)\}_2]^+$ (structurally characterized, axial sites occupied with CO ligands), $[Ru_2(CO)_4(\mu\text{-}O_2CR)\{\mu\text{-}(2\text{-}Ph_2Pquin)\}_2]^+$, and $[Ru_2(CO)_2\text{-}(\mu\text{-}O_2CR)\{\mu\text{-}(2\text{-}Ph_2Pbpy)\}_2]^+$ (crystallographically confirmed, axial sites unoccupied).[1791] Bridging ligands can be introduced to connect the $[Ru_2(CO)_4(\mu\text{-}O_2CR)_2]$ units into polymeric species, as is observed in the reactions of $[Ru_2(CO)_4(\mu\text{-}O_2CMe)_2]_n$ or $[Ru_2(CO)_4(MeCN)_2(\mu\text{-}O_2CMe)_2]$ with equimolar amounts of ligands such as $Ph_2PCH_2CH_2AsPh_2$, $Ph_2PCH_2P(S)Ph_2$, $Ph_2P(S)CH_2P(S)Ph_2$, $R_2P(CH_2)_nPR_2$, $R_2As(CH_2)_nAsR_2$, and $RSCH_2SR$ (R = Me, Ph; n = 1–4). With a twofold excess of $Ph_2PCH_2P(S)Ph_2$ or dppm, discrete molecules with the axial sites occupied by monodentate phosphine ligands are produced, and analogous Os-containing complexes have also been prepared.[1792] Related to the dinuclear carboxylate-bridged species described above is the complex $[Ru_2(CO)_4(\mu\text{-}2\text{-}Opy\text{-}N,O)_2(2\text{-}HOpy\text{-}N)_2]$ in which molecules of 2-hydroxypyridine occupy the axial sites and the deprotonated ligand takes a bridging role.[1793] Compared to those observed for RCO_2^- and 2-Opy^-, a rather different bridging mode is adopted by the $C_6Cl_4O_2^{2-}$ ligand in $[Ru_2(CO)_4(PPh_3)_2(\mu\text{-}O_2C_6Cl_4)_2]$. Here, one *O*-donor is associated with both Ru centers while the second coordinates only to one Ru atom. The complex $[Ru_2(CO)_4(PPh_3)_2\text{-}(\mu\text{-}O_2C_6Cl_4)_2]$ reacts with 4,4′-bpy with the concomitant opening of the catecholate bridges and the formation of $[(CO)_2(PPh_3)(C_6Cl_4O_2\text{-}O,O')Ru(\mu\text{-}4,4'\text{-bpy})Ru(C_6Cl_4O_2\text{-}O,O')(PPh_3)(CO)_2]$. When treated with $[NO][PF_6]$, this complex undergoes ligand-centered oxidation to yield the corresponding bis(semiquinone) species.[1794]

Now we move to complexes which contain a Ru_2^{4+} or Ru_2^{5+}core. A number of Ru_2^{4+} complexes contain bridging aqua ligands, for example, $[Ru_2(MeCO_2\text{-}O)_2(Sb^iPr_3)_4(\mu\text{-}H_2O)\text{-}(\mu\text{-}O_2CMe)_2]$,[1795] $[Ru_2(CF_3CO_2\text{-}O)_2(cod)_2(\mu\text{-}H_2O)(\mu\text{-}O_2CCF_3)_2]$,[1796] and $[Ru_2(CF_3CO_2\text{-}O)_2\text{-}\{PCy_2(C_6H_9)\}_2(\mu\text{-}H_2O)(\mu\text{-}O_2CCF_3)_2]$.[1797] In the latter, the dehydrogenated cyclohexyl substituents enter into π-bonding interactions with the Ru^{II} centers. By introducing a potential bridging ligand such as pyrazine the Ru_2 units can be linked together as is exemplified by the formation of $[Ru_2\{\mu\text{-}O_2C(CH_2)_6Me\}_4(\mu'\text{-pyz})]_n$. With an asymmetrical ligand such as 4-cyanopyridine, however, preferential coordination by the pyridine N atom results in the formation of discrete molecules $[Ru_2\{\mu\text{-}O_2C(CH_2)_6Me\}_4(4\text{-NCpy})_2]$ in which the 4-NCpy ligands are monodentate and occupy axial sites. In solution, both the pz and 4-NCpy ligands are labile, giving rise to a number of species. Treatment of $[Ru_2\{\mu\text{-}O_2C(CH_2)_6Me\}_4]$ with either TCNE or benzoquinone results in redox reactions.[1798]

Our discussion of mixed-valent diruthenium complexes begins with $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2]^+$ and $[Ru_2(\mu\text{-}O_2CMe)_4(\mu'\text{-pyz})^+]_n$; in the latter, the pyrazine molecules bridge between Ru_2^{5+} units. The magnetic properties of $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2]^+$ can be rationalized in terms of noninteracting spin 3/2 dimers undergoing large zero-field splitting. In the pyrazine-bridged system there is an

additional intermolecular antiferromagnetic exchange interaction.[1799] Similar magnetic behavior is seen for $[Ru_2(\mu\text{-}O_2CMe)_4(\mu'\text{-}4,4'\text{-bpy})^+]_n$ and $[Ru_2(\mu\text{-}O_2CMe)_4(\mu'\text{-dabco})^+]_n$.[1800] Strong zero-field splitting has also been observed in $[Ru_2(\mu\text{-}O_2CR)_4X]$ where R is a long aliphatic chain or RCO_2^- is dialkoxy or trialkoxybenzoate, and X = Cl or dodecyl sulfate. The crystal structure of one of this family of complexes, $[Ru_2(\mu\text{-}O_2C^nBu)_4Cl]$, has been determined. Magnetic susceptibility measurements in the columnar mesophase of the mesomorphic members of the series are consistent with there being no significant structural changes at the crystal–liquid crystal transition.[1801] Another polymeric system is $[Ru_2(\mu\text{-}O_2CR)_4(\mu'\text{-}O_2CR)]_n$ where $R = CH_2(CH_2)_6CH{=}CH(CH_2)_5Me$. Experimental data for this polymer support the existence of a hexagonal discotic mesophase, and this was the first example of room-temperature mesomorphism in a mixed-valent metallomesogen.[1802]

The mixed-valent complex $[Ru_2(\mu\text{-}O_2C^tBu)_4(thf)_2]^+$ has been prepared and the hydroxide has been structurally characterized; as expected the thf ligands occupy axial sites.[1803] The reactions of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with $^tBuCO_2H$ or Me_2CHCO_2H in aqueous MeOH result in the formation of $[Ru_2Cl(\mu\text{-}O_2C^tBu)_4(H_2O)]$ and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(H_2O)]$. Recrystallization from thf leads to exchange of aqua ligands by thf; these adducts then lose thf to form $[Ru_2Cl(\mu\text{-}O_2C^tBu)_4]$ and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4]$, respectively. The crystal structures of $[Ru_2Cl(\mu\text{-}O_2C^tBu)_4(H_2O)]$ and $[Ru_2Cl(\mu\text{-}O_2CCHMe_2)_4(thf)]$ have been determined; both are discrete molecules with Cl^- and H_2O or thf axial ligands.[1804] The complex $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ reacts with indole-2-carboxylic acid, *N*-methyl-pyrrole-2-carboxylic acid, furan-2-carboxylic acid, thiophene-2-carboxylic acid, and benzofuran-2-carboxylic acid to give $[Ru_2Cl(\mu\text{-}O_2CR)_4]$. Each R group contains a potential donor atom in the α position, but the RCO_2^- ligands retain an *O,O′*-bonding mode as seen for simpler carboxylate groups. However, when $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ reacts with quinoline-2-carboxylic acid (Hquin), the *N*-donor atom comes into play and the products are $[Ru^{II}_2(quin\text{-}N,O)_4]$ and $[Ru^{III}(quin\text{-}N,O)_3]$, formed as a result of disproportionation. The structures of the new $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ complexes vary, and both molecular and polymeric species are observed depending on R.[1806] Another example of cleavage of the mixed-valent system is seen in the reaction of $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ with pyridine-2-carboxylic acid (2-CO_2Hpy) in aqueous methanol. The products are $[Ru^{II}_2(2\text{-}CO_2py)_4]$ and $[Ru^{III}(2\text{-}CO_2py\text{-}N,O)_3]\cdot H_2O$, and the crystal structure of the latter has been established.[1805] Molecular species are obtained when Et_2HCCO_2H, EtMeHC-CO_2H, or PhMeHCCO_2H react with $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ in MeOH/H_2O solvent. The reactivities of the products, $[Ru_2Cl\ (\mu\text{-}O_2CR)_4]$, and of $[Ru_2Cl(\mu\text{-}O_2CMe)_2(\mu\text{-}O_2C^tBu)_2]$ have been investigated, e.g., the introduction of axial ligands such as SCN^- and Ph_3PO.[1807] When the complexes $[Ru_2Cl(\mu\text{-}O_2CR)_4]$ (R = Me, Ph, 2-ClC_6H_4, 4-$^tBuC_6H_4$, ^{i}Pr, ^{t}Bu, $CHEt_2$) are reduced with Zn amalgam in thf, the products are $[Ru_2(\mu\text{-}O_2CR)_4]$. In solvents such as MeOH or thf, adducts are formed in which both axial sites are occupied. Substitution of these axial ligands by Ph_3PO yields $[Ru_2(\mu\text{-}O_2CR)_4(Ph_3PO)_2]$. The presence of a reducing agent is not required in order to form $[Ru_2(\mu\text{-}O_2CCOPh)_4(thf)_2]$; this results when $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ reacts with $PhCOCO_2H$. The crystal structure of $[Ru_2(\mu\text{-}O_2CCOPh)_4(thf)_2]$ has been determined (Ru–Ru = 2.2756(8) Å).[1808] In the solid state, $[Ru_2Cl\{\mu\text{-}(Z)\text{-}O_2CCMe{=}CHEt\}_4]$ is polymeric with bridging chloro ligands between Ru_2^{5+} units. However, dissolution results in collapse of the polymeric structure. $[Ru_2Cl\{\mu\text{-}(Z)\text{-}O_2CCMe{=}CHEt\}_4]$ reacts with Ph_3PO in CH_2Cl_2 or AgSCN in thf to give, respectively, $[Ru_2Cl\{\mu\text{-}(Z)\text{-}O_2CCMe{=}CHEt\}_4(Ph_3PO)]$ (monomeric) or $[Ru_2\{\mu\text{-}(Z)\text{-}O_2CCMe{=}CHEt\}_4(SCN)]$ (polymeric in the solid state). Silver tetrafluoroborate reacts with $[Ru_2Cl\{\mu\text{-}(Z)\text{-}O_2CCMe{=}CHEt\}_4]$, abstracting Cl^- and forming $[Ru_2\{\mu\text{-}(Z)\text{-}O_2CCMe{=}CHEt\}_4][BF_4]$.[1809] In aqueous solution, $[Ru_2Cl(\mu\text{-}O_2CMe)_4]$ reacts in the presence of Ag_2SO_4 an NH_4PF_6 to generate $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2][PF_6]$, the aqua ligands in which are displaced by dmso or dmf. Structural data are presented for $[Ru_2(\mu\text{-}O_2CMe)_4(H_2O)_2][PF_6]\cdot 3H_2O$, $[Ru_2(\mu\text{-}O_2CMe)_4(dmf)_2][PF_6]$ (with and without dmf solvate), and $[Ru_2(\mu\text{-}O_2CMe)_4(dmso)_2][PF_6]$. Only very small changes in the Ru—Ru bond length are observed across this series of complexes, and electronic spectroscopic, electrochemical data, and the constant values of μ_{eff} are consistent with there being little change to the π*- and δ*-orbital energies.[1810] A system that falls between the end points of the discrete dinuclear and polymeric structures is $[\{Ru_2(\mu\text{-}O_2C^tBu)_4\}_2(\mu\text{-TCNQ})(H_2O)_2]^{2+}$. The structure of the BF_4^- salt has been determined and confirms that the TCNQ ligand binds axially to each of two Ru_2^{5+} cores, the second axial sites of which are occupied by an aqua ligand. There is weak antiferromagnetic coupling between the Ru_2^{5+} units.[1811]

Three nitroxide derivatives of Ru_2^{5+} species have been reported. The first contains the $[Ru_2(\mu\text{-}O_2C^tBu)_4L_2]^+$ ion where L = 2,2,6,6-tetramethylpiperidine-1-oxyl. A relatively large antiferromagnetic coupling is observed between the Ru_2^{5+} core and the nitroxide radical.[1812] The second example is $[Ru_2(\mu\text{-}O_2C^tBu)_4L^+]_n$ where L = 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy-3-oxide.

Ligand L bridges between Ru_2^{5+} units, with an *O*-coordinated NO group occupying each axial site. As the temperature decreases, the magnetic moment of the complex decreases. Both zero-field splitting and the coupling between the Ru_2^{5+} core and the nitroxide radical contribute significantly to the magnetic behavior.[1813,1814] In the related complex $[Ru_2(\mu\text{-}O_2C^tBu)_4L^+]_n$ where L = 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-1-oxy-3-oxide, the two donor sites for L are the pyridine N atom and one of the nitroxide groups. Magnetic data show that the Ru_2^{5+} units and the nitroxide radicals are ferromagnetically coupled.[1815]

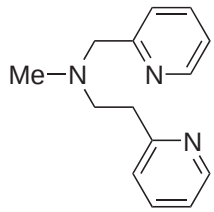
The adamantyl derivatives $[Ru_2(\mu\text{-}O_2CC_{10}H_{15})_4(MeOH)_2]$ and $[Ru_2(\mu\text{-}O_2CC_{10}H_{15})_3(\mu\text{-}CO_3)(MeOH)_2]$ have been prepared by treating $K_3[Ru_2(CO_3)_4]\cdot 4H_2O$ with $C_{10}H_{15}CO_2H$. Reduction clearly accompanies the conversion of $[Ru_2(CO_3)_4]^{3-}$ to $[Ru_2(\mu\text{-}O_2CC_{10}H_{15})_4(MeOH)_2]$, and this constitutes part of the disproportionation process $2Ru_2^{5+} \rightarrow Ru_2^{4+} + 2Ru^{3+}$.[1816]

Reactions between PPh_3 and $[Ru_2Cl(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}X)_4]$ (X = H, Me, Cl, NO_2, OMe) in aqueous acetonitrile result in the formation of the mixed-valent $[Ru_2Cl(H_2O)(MeCN)(PPh_3)_2(O_2CC_6H_4\text{-}4\text{-}X)_4]$ and the all-Ru^{II} complex $[Ru_2(H_2O)(MeCN)_2(PPh_3)_2(O_2CC_6H_4\text{-}4\text{-}X)_4]$. The crystal structure of a representative $Ru^{II}Ru^{III}$ derivative confirms the distribution of ligands to be $[(PPh_3)Cl(4\text{-}MeOC_6H_4CO_2\text{-}O)Ru^{III}(\mu\text{-}H_2O)(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}OMe)_2Ru^{II}(MeCN)(4\text{-}MeOC_6H_4CO_2\text{-}O)(PPh_3)]$. The spectroscopic and electrochemical properties of the complexes have been investigated. The mixed-valent complexes disproportionate in solution, giving $Ru^{II}{}_2(\mu\text{-}H_2O)$ and $Ru^{III}{}_2(\mu\text{-}O)$ species.[1817] The reaction of Ph_3P with the mixed-valent $[Ru_2(\mu\text{-}O_2CMe)_4(thf)_2]^+$ leads to the Ru^{II} and Ru^{III} species $[Ru(O_2CMe)_2(PPh_3)]$ and $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2(MeCO_2\text{-}O,O')_2(PPh_3)_2]$.[1818] Cleavage of the Ru—Ru bond has also been observed in the reactions of $[Ru_2(\mu\text{-}O_2CMe)_4(thf)_2]^+$ with $C_6H_{11}NC$ to give $[Ru(C_6H_{11}NC)_6]^{2+}$, and with SCN^- to give $[Ru(NCS)_6]^{3-}$. Similarly, $[Ru_2(\mu\text{-}L)_4(thf)]^+$ (HL = 2-Cl-6-HOpy)[1819] reacts with PMe_3 to give the mononuclear complex $[Ru(L\text{-}N,O)(PMe_3)_4]^+$.[1820] The structural parameters of $[Ru_2(\mu\text{-}L)_4(thf)][BF_4]$ (HL = 2-Cl-6-HOpy and all L^- ligands in a head-to-head arrangement) have been compared with those of $[Ru_2(\mu\text{-}L)_4(thf)]$. On going from the Ru_2^{4+} to Ru_2^{5+} core, there is a 0.005(1) Å increase in the Ru—Ru bond length.[1819] The same bridging ligand L^- features in the complexes $[Ru_2(\mu\text{-}L)_3(\mu\text{-}O_2CMe)Cl]$ and $[Ru_2(\mu\text{-}L)_3(\mu\text{-}O_2CMe)][CF_3SO_3]$, the latter being formed from the former by treatment with $AgCF_3SO_3$. Chloride abstraction from $[Ru_2(\mu\text{-}L)_3(\mu\text{-}O_2CMe)Cl]$ using $[Ag(MeCN)_4][BF_4]$ yields $[Ru_2(\mu\text{-}L)_3(\mu\text{-}O_2CMe)(MeCN)][BF_4]$. Using wet AgX (X = BF_4 or CF_3SO_3) to remove Cl^- from $[Ru_2(\mu\text{-}L)_4Cl]$ leads to the formation of $[Ru_2(\mu\text{-}L)_4(H_2O)][X]$. The role of weakly coordinating anions as axial ligands has been explored in these and related systems.[1821] Just as a head-to-head arrangement of *N,O*-donors was observed in $[Ru_2(\mu\text{-}L)_4(thf)]^+$ (HL = 2-Cl-6-HOpy),[1819] a similar arrangement of the two *N,O*-ligands has been confirmed in $[Ru_2Cl(\mu\text{-}L')_2(\mu\text{-}O_2CMe)_2]$ where HL′ = 5-methyl-7-phenyl-1,8-naphthyridin-2-one. Reduction of $[Ru_2Cl(\mu\text{-}L')_2(\mu\text{-}O_2CMe)_2]$ to $[Ru_2(\mu\text{-}L')_2(\mu\text{-}O_2CMe)_2]$ leads to a change in the bonding mode of L'^- from *N,O* to *N,N′*, and a switching of ligand orientations such that the phenyl substituents become remote from one another. On going to $[Ru_2(\mu\text{-}L')_4]$ and $[Ru_2(\mu\text{-}L')_4(H_2O)]$, steric interactions between the Ph substituents in the bridging ligand appear to play a role in controlling the mode of ligand coordination.[1822]

We now focus on Ru^{III} dimers containing oxo-bridging ligands which constitute a well-established group of compounds. A driving force for their study is the relationship to the active center of methemerythrin, and model complexes such as $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6]^{2+}$ and $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_2(bpy)_2]^{2+}$ have been prepared and characterized. From the crystal structure of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6][PF_6]_2$, the Ru—Ru bond length of 3.251(2) Å indicates that no Ru–Ru bonding interaction is present, a feature that is typical of this group of complexes. Substitution reactions carried out with $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6]^{2+}$ reveal that the pyridine *trans* to the oxo ligand is ≈10 times more labile than those py ligands in *cis* positions.[1823] Resonance Raman spectra of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_6][PF_6]_2$ have provided insight into the excited-state geometry of the complex.[1824] An electrochemical investigation of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(bpy)_2(1\text{-}Meim)_2]^{2+}$ has shown that, in MeCN, the redox potentials for the $Ru^{III}Ru^{III}/Ru^{III}Ru^{II}$ and $Ru^{III}Ru^{II}/Ru^{II}Ru^{II}$ couples become more positive in the presence of strong acid. In the presence of weaker acids, the oxidations tend to a single, two-electron process.[1825] The complexes $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(py)_4L_2]^{2+}$ (L = py or various imidazole derivatives), $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(bpy)_2L_2]^{2+}$ (L = py, im, 1-Meim, bim), and $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(phen)_2L_2]^{2+}$ (L = py, im, bim) have been prepared and characterized. Each complex exhibits an intense absorption in the visible region, assigned to a transition between π-orbitals associated with the $Ru(d\pi - O_{oxo}(p\pi))$ interaction. Electrochemical properties have also been examined.[1826] The

lability of the ligands *trans* to the μ-oxo ligand in complexes with the $Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)^{2+}$ core has been the subject of a kinetic study of the exchange of 4-picoline with dmso. Changes in ^1H NMR spectra of dmso-d_6 solutions of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(4\text{-pic})_6]^{2+}$ at different temperatures have been monitored, and used to obtain kinetic data. Exchange at one Ru center influences the reactivity at the second metal center.[1827] The synthesis and structure of $[Ru_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)(MeCN)_4(PPh_3)_2][ClO_4]_2$ have been reported; MeCN ligands occupy sites *trans* to the μ-oxo ligand.[1828] Asymmetry is introduced to this type of complex in $[(en)(PPh_3)Ru(\mu\text{-}O_2CC_6H_4\text{-}4\text{-}X)_2(\mu\text{-}O)Ru(MeCO_2\text{-}O,O')(PPh_3)]^+$ (X = OMe, Me). The complexes exhibit intense absorptions in the visible region, assigned to a CT transition involving the $Ru(d\pi) \rightarrow O_{oxo}(p\pi)$ orbitals.[1829]

Tridentate terminal ligands have been used to prepare a number of derivatives with bridging oxo ligands. The preparation, characterization, and redox properties of $[Ru_2(\mathbf{403})_2(\mu\text{-}O_2CMe)_2(\mu\text{-}O)][ClO_4]_2\cdot 4H_2O$ have been described.[1830] Related to ligand (**403**) is tris(2-pyridylmethyl)amine (tpa). This has been incorporated into the $Ru^{III}{}_2$ species $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CR)(tpa)_2]^{3+}$ (R = Me, Et, Pr, Ph) and $[Ru_2(\mu\text{-}O)(\mu\text{-}Cl)_2(tpa)_2]^{2+}$ which were prepared from $[RuCl_2(tpa)]^+$.[1831] 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me_3tacn) has been used as a terminator ligand in $[Ru_2(Me_3tacn)_2(acac)_2(\mu\text{-}O)]^{2+}$ and the mixed-valent $[Ru_2(Me_3tacn)_2(acac)_2(\mu\text{-}O)]^{3+}$. Hydrogen-bonded association of the bridging hydroxy group with H_2O (O—H—O = 2.496(6) Å) is observed in $[Ru_2(Me_3tacn)_2(acac)_2(\mu\text{-}O_2H_3)]^{3+}$.[1832] Related complexes have utilized 1,4,7-triazacyclononane (tacn) and 1,2-bis(1,4,7-triazacyclononan-1-yl)ethane (dtne). Useful precursors in this chemistry are $[Ru(tacn)Cl_3]$, $[Ru_2Cl_6(\mu\text{-dtne})]$ and $[Ru_2Br_6(\mu\text{-dtne})]$, and from these, hydroxy and oxo species that include $[Ru_2(\mu\text{-dtne})(\mu\text{-}OH)_2(\mu\text{-}O_2CPh)]^{3+}$, $[Ru_2(tacn)_2(\mu\text{-}OH)_2(\mu\text{-}CO_3)]^{2+}$, and the mixed-valent $[Ru_2(\mu\text{-dtne})_2(\mu\text{-}O)_2(\mu\text{-}CO_3)]^+$ have been prepared. Electrochemically generated $Ru^{IV}{}_2(\mu\text{-}OH)_2$ species have also been studied.[1833] Heterometallic complexes containing tacn and Me_3tacn terminating ligands have also been reported. These are of the general type $[LRu(\mu\text{-}O)(\mu\text{-}O_2CMe)_2ML']^{2+}$ where M = Co, V, Mn, Fe, or Cr, and each complex undergoes a reversible, one-electron oxidation. In acidic media, protonation of the μ-O atom occurs to give isolable hydroxy species. Magnetic and ESR spectroscopic data for the complexes have been reported, and the assignment of the metal oxidation states and the strong spin-exchange coupling that some of the complexes exhibit have been discussed in detail.[1834]



(**403**)

Triruthenium complexes supported by a μ_3-oxo ligand include $[Ru_3(\mu_3\text{-}O)(\mu\text{-}O_2CMe)_6(H_2O)_3]^+$, crystallographically characterized as both the hydrated tetrafluoroborate[1835] and perchlorate[1836] salts. During crystallization of the latter, a solution color change from blue–green to purple was observed and interpreted as oxidation of the $Ru^{III}{}_3$ to $Ru^{III}{}_2Ru^{IV}$ species.[1836] The heterometallic $[Ru_2Co(\mu_3\text{-}O)(\mu\text{-}O_2CMe)_6L_3]$ (L = H_2O or py) has also been synthesized, and low-temperature ESR spectroscopic data are consistent with there being no inter-metal interactions.[1837] A general method of introducing the heterometal to such systems has been described.[1838]

5.5.6 RUTHENIUM AND OSMIUM COMPLEXES CONTAINING HYDRIDE AND DIHYDROGEN LIGANDS

No attempt has been made in this section to assign formal oxidation states to the Ru and Os metal centers since ambiguities clearly arise when considering "classical" hydride and "non-classical" dihydrogen ligands. There are differences when comparing apparently similar compounds of Ru and Os, so, for example, $[OsH_6L_2]$ (L = tertiary phosphine) complexes generally contain hydrido ligands (classical) while $'[RuH_6L_2]'$ might be expected to be formulated as $[RuH_2(\eta^2\text{-}H_2)_2L_2]$. A pertinent review that appeared in 1998 covers the chemistry of bis(dihydrogen) complexes of ruthenium.[1839] The survey includes the synthesis, characterization, and

reactivity of $[RuH_2(H_2)_2(PCy_3)_2]$,[1839] the crystal structure of which has been determined confirming that the H_2 ligands are *cis* to each other and lie in the equatorial plane, each *trans* to a hydrido ligand.[1840] The thermal decomposition of solid $[RuH_2(H_2)_2(PCy_3)_2]$ occurs, first by transformation into $[RuH_3(\eta^3\text{-}C_6H_8PCy_2)(PCy_3)]$ and $[RuH(\eta^3\text{-}C_6H_8PCy_2)(\eta^2\text{-}C_6H_9PCy_2)]$, followed by loss of C_6H_6.[1841] When $[RuH_2(H_2)_2(PCy_3)_2]$ reacts with $(R_2SiH)_2X$ (R = Ph, X = O; R = Me, X = O, C_6H_4, CH_2CH_2, $CH_2CH_2CH_2$, $OSiMe_2O$), the products are the complexes $[RuH_2\{\eta^2\text{-}HSiR_2)_2X\}(PCy_3)_2]$ in which each η^2 interaction involves an Si—H bond. During these reactions, the PCy_3 groups go from being mutually *trans* in $[RuH_2(H_2)_2(PCy_3)_2]$ to *cis*.[1842]

The hexahydride $[OsH_6(PCy_3)_2]$ may be made by $LiAlH_4$ reduction of $[OsO_2Cl_2(PCy_3)_2]$. Bis(diphenylphosphino)methane reacts with $[OsH_6(PCy_3)_2]$ to give $[OsH_4(PCy_3)_2(\text{dppm-}P)]$ along with smaller amounts of $[OsH_4(PCy_3)(\text{dppm-}P,P')]$.[1843] The complex $[OsH_6(P^iPr_3)_2]$ reacts with PPh_2H, liberating H_2 and forming $[OsH_4(PPh_2H)(P^iPr_3)_2]$. Continued treatment with PPh_2H results in the formation of $[OsH_2(PPh_2H)_3(P^iPr_3)]$. The complex $[OsH_5(PPh_2H)(P^iPr_3)_2]^+$ can be obtained by protonating $[OsH_4(PPh_2H)(P^iPr_3)_2]$ using HBF_4, and this cation reacts with PPh_2H to yield H_2 and $[OsH_3(PPh_2H)_2(P^iPr_3)_2]^+$. An X-ray diffraction study of $[OsH_5(PPh_2H)\text{-}(P^iPr_3)_2][BF_4]$ confirms the basic structure; from the results of calculations on the model complex $[OsH_5(PH_3)_3]^+$, it is concluded that going from the classical pentahydride to a structure involving a coordinated H_2 molecule is an easy process, both in terms of kinetics and thermodynamics.[1844] Treating $[OsH_6(P^iPr_3)_2]$ with 2-HSpy (pyridine-2-thiol) produces $[OsH_3(P^iPr_3)_2(\text{2-Spy-}N,S)]$, a structural determination of which confirms that the *trans* arrangement of the P^iPr_3 is retained; hydrido ligands form a triangular arrangement and are nonbonded. Hydrogen atom site-exchange in solution has been investigated.[1845] 2,2′-Biimidazole (H_2biim) reacts with $[OsH_6\text{-}(P^iPr_3)_2]$ to yield $[OsH_3(Hbiim)(P^iPr_3)_2]$, and from this, the heterometallic complexes $[(P^iPr_3)_2H_3Os(\mu\text{-biim})M(cod)]$ (M = Rh, Ir) have been prepared. In each complex, the P^iPr_3 ligands are mutually *trans*, and this arrangement is retained throughout a number of pyrazole derivatives that have prepared and characterized. The ^1H NMR spectra of $[OsH_3(Hbiim)(P^iPr_3)_2]$ and $[(P^iPr_3)_2H_3Os(\mu\text{-biim})M(cod)]$ (M = Rh, Ir) show coupling features in the hydride region that have been interpreted in terms of quantum mechanical exchange coupling within the OsH_3 unit.[1846] These effects have been further explored in the $[OsH_3X(P^iPr_3)_2]$ (X = Cl, Br, I) systems, and, among other conclusions, it is found that the magnitude of quantum exchange coupling is sensitive to the identity of X^-.[1847] The use of NMR measurements (T_1 relaxation times[1848] and deuterium quadrupole coupling constants) to distinguish between classical and nonclassical hydrogen bonding modes has been the topic of a range of investigations.[1849–1852] An assessment of the 'T_1 criterion' has been made based on measurements of T_1 for $[OsH_4\{P(4\text{-}MeC_6H_4)_3\}_3]$ and a series of deuterated analogs along with the results of associated calculations. Some important conclusions were drawn from this study. First, dipole–dipole interactions (which in η^2-H_2 complexes can shorten the longitudinal relaxation times T_1 to <0.03 s) make the greatest contribution to hydride relaxation for many polyhydride complexes. It was also found that T_1(min) can be calculated using internuclear distances determined from diffraction data but it is essential that dipole–dipole interactions with metal and ligand nuclei are included in the calculations. Finally, for some complexes, it was not possible to distinguish between classical and nonclassical hydrides from the observed T_1(min) values.[1849] Complementary NMR spectroscopic studies have been carried out on $[RuH_4(PPh_3)_3]$.[1850] The dihydrido complex $[OsH_2Cl_2(P^iPr_3)_2]$ reversibly binds H_2, giving $[OsH_4Cl_2(P^iPr_3)_2]$, the crystal structure of which has been determined, giving the skeletal geometry of the complex. Solution ^1H NMR spectroscopic data and T_1(min) measurements provide evidence for bonding interactions between the H ligands in $[OsH_4Cl_2(P^iPr_3)_2]$.[1853] Further studies of this system have been extended to the reactions of H_2 with the series of complexes $[OsH_2(X)(Y)(P^iPr_3)_2]$ where X and Y are Cl, Br, and I, and an X-ray diffraction study of $[OsH_4Br_2(P^iPr_3)_2]$ has been carried out. Use has again been made of T_1(min) measurements and J(HD) coupling constants to distinguish between classical and nonclassical hydride ligands.[1854]

Kinetics investigations of the dissociation of H_2 from $[RuH_3(PPh_3)_3]^-$, $[RuH_4(PPh_3)_3]$, $[RuH_5(PPh_3)_3]^+$, $[OsH_4\{P(4\text{-}MeC_6H_4)_3\}_3]$, and $[OsH_5\{P(4\text{-}MeC_6H_4)_3\}_3]^+$ have shown that (i) on going from an Ru to corresponding Os hydride, H_2 dissociates more slowly, and (ii) the rate increases with increasing protonation. Dihydrogen dissociation from $[OsH_3\{P(4\text{-}MeC_6H_4)_3\}_3]^-$ was too slow to allow data to be recorded.[1855]

A wide range of complexes in the family $[RuH(H_2)L_4]^+$ is now known, and examples include $[RuH_3(dppf)_2]^+$,[1856] $[RuH_3L\{PhP(CH_2CH_2PPh_2)_2\}]^+$ (e.g., L = CO, PMe_2Ph),[1857] $[RuH\text{-}(H_2)(dppe)_2]^+$,[1858,1859] $[RuH(H_2)(Et_2PCH_2CH_2PEt_2)_2]^+$,[1858] $[RuH(H_2)(PMe_2Ph)_4]^+$,[1860] $[RuH(H_2)\text{-}\{(4\text{-}RC_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}4\text{-}R)_2\}_2]^+$ (R = OMe, CF_3).[1861] The crystal structure of $[RuH(H_2)(dppe)_2][BF_4]$ has been determined by X-ray (at 123 K) and neutron (at 12 K) diffraction

techniques. The coordination environment of the Ru atom is distorted octahedral, with the η^2-H_2 group (H—H = 0.83(8) Å, corrected to ≈0.94 Å) lying *trans* to the H^- ligand; the P—Ru—P bond angle is 167.9(4)°.[1859] Methods of synthesis of these compounds vary, and a few examples are selected here. The complex $[RuH(H_2)(PMe_2Ph)_4]^+$ can be prepared by the reaction of $[RuH(PMe_2Ph)_5]^+$ with H_2 in thf,[1860] while $[RuH(H_2)\{(4\text{-}RC_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}4\text{-}R)_2\}_2]^+$ (R = OMe, CF_3) has been made by HBF_4 protonation of the corresponding $[RuH_2L_4]$ species.[1861] The derivatives $[RuH_3L\{PhP(CH_2CH_2PPh_2)_2\}]^+$ (e.g., L = CO, PMe_2Ph) were produced in the reactions of $[RuCl_2L\{PhP(CH_2CH_2PPh_2)_2\}]$ with $NaBH_4$ in EtOH at reflux, followed by HBF_4 protonation.[1857] The related complex $[RuH(H_2)Cl(CO)(P^iPr_3)_2]$ results when H_2 adds to $[RuHCl(CO)(P^iPr_3)_2]$, and the equilibrium that is established between the two hydrido species lies in favor of $[RuH(H_2)Cl(CO)(P^iPr_3)_2]$ at low temperatures.[1862] The solution behavior of $[RuH(H_2)(PMe_2Ph)_4]^+$ has been investigated by ^1H and ^{31}P NMR spectroscopies and four different dynamic processes have been identified, which include H ligand exchange and isomerization.[1860] In contrast to $[RuH(\eta^2\text{-}H_2)L_4]^+$ complexes, the corresponding osmium trihydrides tend to contain "classical" hydride ligands. For example, $[OsH_3(dippe)_2][BPh_4]$ (dippe = $^iPr_2PCH_2CH_2$-P^iPr_2) is formed when *cis*-$[OsCl_2(dippe)_2]$ reacts with $NaBH_4$ in the presence of $NaBPh_4$ in EtOH. Deprotonation of $[OsH_3(dippe)_2]^+$ yields *cis*-$[OsH_2(dippe)_2]$. The cationic monohydride $[OsH(dippe)_2]^+$ has been detected in solution; it has a high affinity for O_2, forming *trans*-$[OsH(O_2)(dippe)_2]^+$, isolated as the BPh_4^- salt.[1863] Further examples of the differences between Os and Ru trihydrides come in a study of the complexes $[MH_3(PR_3)_4]^+$ where M = Ru or Os, and R = Me or Et. From the results of solution NMR spectroscopic studies, it is concluded that $[RuH_3(PEt_3)_4]^+$ exhibits isomerism involving a distorted octahedral *cis*-$[RuH(H_2)(PR_3)_4]^+$ species and a trihydride-capped tetrahedral complex. On the other hand, $[OsH_3(PMe_3)_4]^+$ exists in solution as two classical hydrido isomers: a pentagonal bipyramidal *cis*-$[OsH_3(PMe_3)_4]^+$ in equilibrium with a trihydride-capped tetrahedral species. In contrast to the isomerism displayed by $[RuH_3(PEt_3)_4]^+$, $[RuH_3(PMe_3)_4]^+$ favors only the *cis*-$[RuH(H_2)(PR_3)_4]^+$ form, but like all the other species studied, is fluxional in solution.[1864] This one study alone demonstrates the complexity of the "classical"/"nonclassical" interface, and the authors note that the presence of four monodentate phosphine ligands in complexes of type $[MH_3L_4]^+$ results in properties that are quite different from those of similar complexes containing, for example, didentate ligands.

The anionic complexes $[MH_3(CO)(PR_3)_2]^-$ (M = Ru, R = ^{i}Pr, Ph; M = Os, R = ^{i}Pr) and $[MH_5(P^iPr_3)_2]^-$ (M = Ru, Os) can be isolated in the presence of crown ethers from the reactions of KH with $[MHCl(CO)(PR_3)_2]$ (R = ^{i}Pr or Ph). The crystal structures of $[K(18\text{-crown-}6)]^+$ and $[K(1\text{-aza-}18\text{-crown-}6)]^+$ salts of *mer*-$[OsH_3(CO)(P^iPr_3)_2]^-$ have been established. The choice of cation has an effect on the extent of hydrogen bonding in the solid-state lattice.[1865] Protonation of $[K(18\text{-crown-}6)][RuH_5(P^iPr_3)_2]$ yields $[RuH_2(\eta^2\text{-}H_2)_2(P^iPr_3)_2]$, although this complex is unstable with respect to loss of H_2, forming $[(P^iPr_3)_2HRu(\mu\text{-}H)_3RuH_2(P^iPr_3)_2]$. Comparative studies have been carried out with PCy_3 and PPh_3-containing complexes.[1866] When $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ is protonated with $HBF_4.Et_2O$ in the presence of MeC_6H_5, H_2 elimination occurs and the final product is the monohydride $[(\eta^6\text{-}C_6H_5Me)RuH(PCy_3)_2][BF_4]$. However, changing the protonating agent to RCO_2H results in the isolation of $[RuH(\eta^2\text{-}H_2)(CO_2R)(PCy_3)_2]$.[1867]

The reactions of $[RuH_2(PPh_3)_4]$ or $[OsH_4(PPh_3)_3]$ with $SiHR_3$ (M = Os, R = *N*-pyrrole, Et, Ph; M = Ru, R = *N*-pyrrole) yield $[MH_3(SiR_3)(PPh_3)_3]$, in which the three hydrides are involved in 3-center M–H–Si interactions.[1868] A separate study has shown that $[RuH_3(SMeCl_2)(PPh_3)_3]$ results from the reaction of $[RuCl_2(PPh_3)_3]$ with $SiHMeCl_2$, and again, M–H–Si interactions are observed.[1869]

Osmium complexes containing η^2-H_2 are exemplified by $[OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2]$ (R = Cy, ^{i}Pr) which results from the displacement by H_2 (24 bar pressure) of O_2 from $[OsHCl(O_2)$-$(CO)(PR_3)_2]$. The phosphine ligands in $[OsHCl(\eta^2\text{-}H_2)(CO)(PR_3)_2]$ exchange slowly (relative to the NMR spectroscopic timescale) with other bulky PR_3 ligands and, for example, such exchange by an associative process allows access to the complex $[OsHCl(\eta^2\text{-}H_2)(CO)(PCy_3)(P^iPr_3)]$.[1870] Short T_1(min) values have provided evidence for the presence of η^2-H_2 ligands in $[Os(\eta^2$-$H_2)(PPh_3)_2(bpy)(CO)]^{2+}$, $[Os(\eta^2\text{-}H_2)(PMePh_2)_2(bpy)(CO)]^{2+}$, $[Os(\eta^2\text{-}H_2)(PPh_3)_2(phen)(CO)]^{2+}$, and $[Ru(\eta^2\text{-}H_2)(PPh_3)_2(bpy)(CO)]^{2+}$. These species are strong acids, indicating that heterolytic cleavage can readily occur, but on the other hand, the H_2 ligand is so tightly bound that exchange with D_2 does not take place. Differences in properties between the Ru and Os complexes are reflected by the differing stabilities of $[Os(\eta^2\text{-}H_2)(PPh_3)_2(bpy)(CO)]^{2+}$ and its Ru analog in solution at 298 K.[1871] The related complex $[Os(\eta^2\text{-}H_2)(CO)(2\text{-}Spy)(PPh_3)_2]^+$ (2-HSpy = pyridine-2-thiol) is also a strong acid ($pK_a \approx -1$) but is stable with respect to elimination of H_2.[1872] In the series of complexes *trans*-$[M(\eta^2\text{-}H_2)(CN)L_2]^+$ and *trans*-$[M(\eta^2\text{-}H_2)(CNH)L_2]^{2+}$ (M = Fe, Ru, Os;

L_2 = dppm, dppe, dppp, depe), all of which are strong acids, the Ru species are unstable with respect to H_2 loss while the Fe and Os cations are more robust. When $[Ru(\eta^2\text{-}H_2)(CN)L_2]^+$ and $[Ru(\eta^2\text{-}H_2)(CNH)L_2]^{2+}$ lose H_2, the coordination site is taken by the $CF_2SO_3^-$ counter-ion, as confirmed by the crystal structure of *trans*-$[Ru(CF_3SO_3)(CN)L_2]$.[1873] The complex $[Os(\eta^2\text{-}H_2)Cl(H_2biim)(P^iPr_3)_2]Cl$ (H_2biim = 2,2′-biimidazole) forms when $[OsH_2Cl_2(P^iPr_3)_2]$ reacts with H_2biim. Treatment of $[Os(\eta^2\text{-}H_2)Cl(H_2biim)(P^iPr_3)_2]^+$ with $NaBPh_4$ results in mono-deprotonation of the coordinated H_2biim ligand, and reactions in which $Hbiim^-$ is then utilized as a bridging ligand have been explored.[1874] This is related to reactions of $[OsH_3(Hbiim)(P^iPr_3)_2]$ described earlier.[1846] The solid-state structure of $[Os(\eta^2\text{-}H_2)Cl(H_2biim)(P^iPr_3)_2]Cl$ has been studied in detail along with that of $[(\eta^5\text{-}C_5Me_5)Ru(\eta^2\text{-}H_2)(dppm][BF_4]$.[1875] The complexes $[MCl(\eta^2\text{-}H_2)(dppp)_2]^+$ (M = Ru, Os) can be prepared by the addition of H_2 to the coordinatively unsaturated $[MCl(dppp)_2]^+$, and the crystal structure of $[OsCl(\eta^2\text{-}H_2)(dppp)_2]^+$ has been determined. The reaction of H_2 with $[OsHCl(dppp)_2]$ yields the classical hydrido species $[OsH_3(dppp)_2]^+$, also obtained by protonation ($HBF_4{\cdot}Et_2O$) of $[OsH_2(dppp)_2]$.[1876]

The protonation of *trans*-$[RuH(dppe)_2L]^+$ with $HBF_4{\cdot}Et_2O$ gives $[Ru(\eta^2\text{-}H_2)(dppe)_2L]^{2+}$ in which L = $PF(OMe)_2$, $PF(OEt)_2$ or $PF(O^iPr)_2$.[1877,1878] The relationship between the cone angles of the phosphite ligands and the stability of the hydride and dihydrogen complexes has been explored.[1878] The phosphite complexes $[MHXL_4]$ where M = Ru, Os; X = Cl, Br, I, SEt, N_3; L = $P(OEt)_3$, $P(OEt)_2Ph$, $P(OEt)Ph_2$, have been prepared by reaction of $[MH_2L_4]$ with CF_3SO_3Me followed by treatment with an excess of X^-. Protonation of $[MHXL_4]$ leads to the formation of $[M(\eta^2\text{-}H_2)XL_4]^+$ when X = Cl, Br, I, SEt, but when $X = N_3$, the protonation product contains classical hydride ligands. If the protonation is carried out under an atmosphere of H_2, $[M(\eta^2\text{-}H_2)HL_4]^+$ can be isolated.[1879] The complex $[Ru(\eta^2\text{-}H_2)H(dmpe)_2]^+$ is formed when weak organic acids are used to protonate $[RuH_2(dmpe)_2]$. Over the range 220–300 K, hydrogen exchange is observed between the complex and the protonating agent, a process that involves all the Ru-bound H atoms. The H_2 ligand is relatively weakly bound and reactions with RSH occur to give thiolate complexes; reaction with PhSH results in the formation of *trans*-$[Ru(SPh)_2(dmpe)_2]$.[1880] $[RuH_2(dmpe)_2]$ was prepared by the reduction of *trans*-$[RuCl_2(dmpe)_2]$ with Na in 2-propanol,[1880] and the reduction of *cis*-$[RuCl_2(dppm)_2]$ using KOH in EtOH or 2-propanol has also been studied. The reaction produces *cis*/*trans*-$[RuH_2(dppm)_2]$ in high yield. Changes in reaction conditions can tip the reaction path in favor of the formation of *trans*-$[RuHCl(dppm)_2]$.[1881] The complexes $[OsH_2Cl_2(P^iPr_3)_2]$ (structurally characterized) and $[OsH_2Cl_2(P^tBu_2Me)_2]$ can be prepared from $OsCl_3{\cdot}xH_2O$ and the appropriate phosphine in 2-propanol at reflux. Lewis bases such as CO and PMe_3 displace H_2 from $[OsH_2Cl_2(P^tBu_2Me)_2]$ to give $[Os(CO)_2Cl_2(P^tBu_2Me)_2]$ and $[Os(PMe_3)_2Cl_2(P^tBu_2Me)_2]$, respectively.[1882] A method for the enhancement of ^1H NMR spectroscopic signals by para-hydrogen-induced polarization has been described, and has been applied to aid the detection of isomers of $[Ru(CO)_2H_2(PPh_3)_2]$ and $[Ru(CO)_3H_2(PPh_3)]$.[1883]

The kinetics of the reactions of thiols, CO, and PPh_3 with *cis,cis,trans*-$[RuH_2(CO)_2(PPh_3)_2]$ have been investigated. The rate-determining step in each case is the initial dissociation of H_2, leading to the conclusion that the activated complex contains an η^2-H_2 ligand. A comparative study of the reaction of $[RuH_2(dppm)_2]$ with thiols has also been described.[1884]

There are several hydrido complexes that also contain coordinated N_2. The reversible reaction of N_2 with $[RuH_2(H_2)_2(PCy_3)_2]$ results in the formation of $[RuH_2(N_2)_2(PCy_3)_2]$, and reactions between $[RuH_2(H_2)(Ph_3SiH)(PCy_3)_2]$ or $[RuH_2(H_2)(Ph_3GeH)(PCy_3)_2]$ with N_2 yield $[RuH_2(N_2)_2(PCy_3)_2]$.[252] The preparations of $[OsH(N_2)L_4]^+$ (L = $PPh_2(OMe)$, $PPh_2(OEt)$, $PPh_2(O^iPr)$, $PPh(OEt)_2$) have also been described.[1885]

We end this section with a number of dinuclear complexes containing bridging hydrido ligands. The reactions between $[ReH_6L_2]^-$ (L = $PMePh_2$, $AsPh_3$ PPh_3 or L_2 = dppe) and $[RuHCl(CO)(PPh_3)_{3-x}\{P(O^iPr)_3\}_x]$ yield the complexes containing an $Re(\mu\text{-}H)_3Ru$ core.[1886] Metal complexes containing the ferrocene-based ligands $CpFe\{\eta^5\text{-}C_5H_3\text{-}1\text{-}(CHMeNMe_2)\text{-}2\text{-}PR_2\}$ (R = ^{i}Pr, Ph) have been investigated as homogeneous catalysts. These ligands, L, have been incorporated into the dinuclear hydrido complexes $[L_2(\eta^2\text{-}H_2)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)RuH(PPh_3)_2]$. For the complex with $L = CpFe\{\eta^5\text{-}C_5H_3\text{-}1\text{-}(CHMeNMe_2)\text{-}2\text{-}P^iPr_2\}$, a multinuclear NMR spectroscopic study shows there to be fast exchange between η^2-H_2 and μ-H at 293 K, along with a slower exchange process involving the terminal hydrido ligand. When the ^{i}Pr groups are replaced by Ph, both exchange processes are fast on the NMR timescale.[1887] The complex $[(PPh_3)_2HRu(\mu\text{-}Cl)_2(\mu\text{-}H)RuH(PPh_3)_2][dma]$ (dma^+ = *N,N*-dimethylacetamidinium ion) has been prepared and structurally characterized. In solution, H^+ transfer from dma^+ to the complex anion results in the formation of $[(PPh_3)_2(\eta^2\text{-}H_2)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)RuH(PPh_3)_2]$.[1888]

5.5.7 RUTHENIUM(0) AND OSMIUM(0)

The majority of Ru^0 and Os^0 complexes are classed as organometallic species and therefore fall outside the remit of this review. However, a number of complexes in which M—C bonds are not the main features of interest are discussed below.

Crystals of $[Ru(bpy)_3]$ have been grown on a Pt cathode from a solution containing $[Ru(bpy)_3]^{2+}$, and the complex has been structurally characterized. A comparison of the structural parameters of $[Ru(bpy)_3]$ and $[Ru(bpy)_3]^{2+}$ does not lead to a firm conclusion concerning the location of the negative charge added to the system during the reduction process.[1889]

The osmium(0) complex $[Os(PMe_3)_5]$ has been prepared by treating $[OsCl_2(PMe_3)_4]$ with a tenfold excess of PMe_3 in the presence of Na and naphthalene in thf. In solution, $[Os(PMe_3)_5]$ is fluxional on the NMR spectroscopic timescale. Protonation of $[Os(PMe_3)_5]$ with triflic acid gives $[OsH(PMe_3)_5]^+$.[1890] The isolation of $[Ru(CO)_2(P^tBuMe_2)_2]$ from the Mg reduction of $[RuCl_2(CO)_2(P^tBuMe_2)_2]$ has been described. The structure of this complex is unexpected and is best described as being derived from a trigonal bipyramidal ligand array with one equatorial site vacant (a disphenoidal structure); the CO ligands occupy equatorial positions. The reactivity of $[Ru(CO)_2(P^tBuMe_2)_2]$ (e.g., with CO, MeNC, O_2, CS_2, C_2H_4, H_2, Cl_2, MeCl, and MeOH) has been investigated.[1891]

The 16-electron complex $[Os(NO)Cl(P^iPr_3)_2]$ has been prepared and an X-ray diffraction study confirms a square planar structure with *trans*-P^iPr_3 ligands.[1892] The complexes $[Os(NO)Cl(P^iPr_3)_2]$ and $[Os(NO)Cl(P^iPr_2Ph)_2]$ form in near quantitative yields from the reactions of $[Os(NO)Cl(PPh_3)_3)$ with P^iPr_3 or P^iPr_2Ph. As expected, these 16-electron complexes readily react with, for example, CO and H_2. A range of reactions has been investigated.[1893] The complexes $[Ru(NO)Cl(P^iPr_3)_2]$ and $[Ru(NO)Cl(P^iPr_2Ph)_2]$ have also been reported. They are formed by the reduction (with Cu/Zn) of $[Ru(NO)Cl_3(PPh_3)_2]$ followed by phosphine exchange. The crystal structure of $[Ru(NO)Cl(P^iPr_3)_2]$ has been determined, confirming a square planar geomsetry. Reactions of $[Ru(NO)Cl(P^iPr_3)_2]$ include those with HCl, O_2, and CO.[1894]

ACKNOWLEDGEMENTS

The area of ruthenium and osmium coordination chemistry is vast and I am grateful to Professor Edwin Constable for carrying out the initial search of the literature and generating a database of over 12,000 references from which to start the "pruning" process.

5.5.8 REFERENCES

1. Schröder, M.; Stephenson, T. A. *Comprehensive Coordination Chemistry*, Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., eds. Pergamon, Oxford, 1987, Vol. 4, pp 277–518.
2. Griffith, W. P. *Comprehensive Coordination Chemistry*, Wilkinson, G.; Gillard, R. D.; McCleverty, J. A., eds. Pergamon, Oxford, 1987, Vol. 4, pp 519–633.
3. Constable, E. C.; Housecroft, C. E. *Coord. Chem. Rev.* **1993**, *124*, 183–216.
4. Ward, M. D. *Coord. Chem. Rev.* **1993**, *124*, 1–38.
5. Wong, W.-T. *Coord. Chem. Rev.* **1994**, *131*, 45–94.
6. Bailey, P. J. *Coord. Chem. Rev.* **1995**, *138*, 87–119.
7. Chan, S.; Wong, W.-T. *Coord. Chem. Rev.* **1995**, *138*, 219–296.
8. Ward, M. D. *Coord. Chem. Rev.* **1995**, *146*, 99–113.
9. Wong, W.-Y.; Wong, W.-T. *Coord. Chem. Rev.* **1995**, *146*, 307–384.
10. Cargill Thompson, A. M. W. *Coord. Chem. Rev.* **1996**, *152*, 157–173.
11. Au, Y.-K.; Wong, W.-T. *Coord. Chem. Rev.* **1997**, *162*, 417–475.
12. Lee, S.-M.; Wong, W.-T. *Coord. Chem. Rev.* **1997**, *164*, 415–482.
13. Ward, M. D. *Coord. Chem. Rev.* **1997**, *164*, 483–502.
14. Hui, J. W.-S.; Wong, W.-T. *Coord. Chem. Rev.* **1998**, *172*, 389–436.
15. Charmant, J. P. H. *Coord. Chem. Rev.* **1998**, *172*, 437–456.
16. Rard, J. A. *Chem. Rev.* **1985**, *85*, 1–39.
17. Rotzinger, F. P. *J. Phys. Chem. A* **1999**, *103*, 9345–9348.
18. McGarvey, B. R.; Batista, N. C.; Bezerra, C. W. B.; Schultz, M. S.; Franco, D. W. *Inorg. Chem.* **1998**, *37*, 2865–2872.
19. Boggs, S. E.; Clarke, R. E.; Ford, P. C. *Inorg. Chim. Acta* **1997**, *247*, 129–130.
20. de Paula, A. S. A. T.; Mann, B. E.; Tfouni, E. *Polyhedron* **1999**, *18*, 2017–2026.
21. Alves, J. J. F.; Franco, D. W. *Polyhedron* **1996**, *15*, 3299–3307.
22. Alves, J. J. F.; Plepis, A. M. D.; Davanzo, C. U.; Franco, D. W. *Polyhedron* **1993**, *12*, 2215–2219.

23. Ando, I.; Fujimoto, H.; Nakayama, K.; Ujimoto, K.; Kurihara, H. *Polyhedron* **1991**, *10*, 1139–1141.
24. Ando, I.; Ishimura, D.; Mitsumi, M.; Ujimoto, K.; Kurihara, H. *Polyhedron* **1992**, *11*, 2335–2340.
25. Ando, I.; Ishimura, D.; Ujimoto, K.; Kurihara, H. *Inorg. Chem.* **1994**, *33*, 5010–5014.
26. Medina, A. N.; Gandra, F. G.; Baesso, M. L.; Lima, J. B.; McGarvey, B. R.; Franco, D. W. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 2105–2111.
27. Chou, M. H.; Szalda, D. J.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1994**, *33*, 1674–1684.
28. Derezende, N. M. S.; Martins, S. D.; Marinho, L. A.; Dossantos, J. A. V.; Tabak, M.; Perussi, J. R.; Franco, D. W. *Inorg. Chim. Acta* **1991**, *182*, 87–92.
29. Mazzetto, S. E.; Rodrigues, E.; Franco, D. W. *Polyhedron* **1993**, *12*, 971–975.
30. Anderson, C.; Beauchamp, A. L. *Can. J. Chem.* **1995**, *73*, 471–482.
31. Chatlas, J.; Vaneldik, R.; Keppler, B. K. *Inorg. Chim. Acta* **1995**, *233*, 59–63.
32. Anderson, C.; Beauchamp, A. L. *Inorg. Chem.* **1995**, *34*, 6065–6073.
33. Anderson, C.; Beauchamp, A. L. *Inorg. Chim. Acta* **1995**, *233*, 33–41.
34. Hartmann, M.; Einhauser, T. J.; Keppler, B. K. *Chem. Commun.* **1996**, 1741–1742.
35. Peti, W.; Pieper, T.; Sommer, M.; Keppler, B. K.; Giester, G. *Eur. J. Inorg. Chem.* **1999**, 1551–1555.
36. Pieper, T.; Sommer, M.; Galanski, M.; Keppler, B. K.; Giester, G. *Z. Anorg. Allg. Chem.* **2001**, *627*, 261–265.
37. La Chance-Galang, K. J.; Doan, P. E.; Clarke, M. J.; Rao, U.; Yamano, A.; Hoffman, B. M. *J. Am. Chem. Soc.* **1995**, *117*, 3529–3538.
38. Batista, A. A.; Polato, E. A.; Queiroz, S. L.; Nascimento, O. R.; James, B. R.; Rettig, S. J. *Inorg. Chim. Acta* **1995**, *230*, 111–117.
39. Lay, P. A.; Sargeson, A. M. *Inorg. Chim. Acta* **1992**, *200*, 449–460.
40. Clark, T.; Robinson, S. D.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1992**, 3199–3202.
41. Lee, S. Y.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1990**, *29*, 2480–2482.
42. Nazeeruddin, M. K.; Zakeeruddin, S. M.; Kalyanasundaram, K. *J. Phys. Chem.* **1993**, *97*, 9607–9612.
43. Ferrere, S.; Gregg, B. A. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2827–2833.
44. Pruchnik, F. P.; Galdecka, E.; Galdecki, Z.; Kowalski, A. *Polyhedron* **1999**, *18*, 2091–2097.
45. Pal, P. K.; Drew, M. G. B.; Datta, D. *New J. Chem.* **2002**, *26*, 24–27.
46. Wong, K. Y.; Che, C. M.; Yip, W. H.; Wang, R. J.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1992**, 1417–1421.
47. Seyler, J. W.; Fanwick, P. E.; Leidner, C. R. *Inorg. Chem.* **1992**, *31*, 3699–3700.
48. I engo, E.; Mestroni, G.; Geremia, S.; Calligaris, M.; Alessio, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3361–3371.
49. Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Greedan, J. E.; Crutchley, R. J. *Inorg. Chem.* **1991**, *30*, 3234–3236.
50. Aquino, M. A. S.; Bostock, A. E.; Crutchley, R. J. *Inorg. Chem.* **1990**, *29*, 3641–3644.
51. Chronister, C. W.; Binstead, R. A.; Ni, J. F.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 3814–3815.
52. Lei, Y. B.; Hurst, J. K. *Inorg. Chim. Acta* **1994**, *226*, 179–185.
53. Lei, Y. B.; Hurst, J. K. *Inorg. Chem.* **1994**, *33*, 4460–4467.
54. Hurst, J. K.; Zhou, J. Z.; Lei, Y. B. *Inorg. Chem.* **1992**, *31*, 1010–1017.
55. Nazeeruddin, M. K.; Rotzinger, F. P.; Comte, P.; Grätzel, M. *J. Chem. Soc., Chem. Commun.* **1988**, 872–874.
56. Iyun, J. F.; Ayoko, G. A.; Lohdip, Y. N. *Polyhedron* **1992**, *11*, 2389–2394.
57. Lai, Y. K.; Wong, K. Y. *J. Electroanal. Chem.* **1995**, *380*, 193–200.
58. Dunandsauthier, M. N. C.; Deronzier, A.; Navarro, M. *Chem. Commun.* **1996**, 2165–2166.
59. Navarro, M.; Collomb, M. N.; Deronzier, A. *J. Electroanal. Chem.* **2002**, *520*, 150–156.
60. Ishitani, O.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 2167–2168.
61. Sudha, C.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1996**, 3289–3292.
62. Grover, N.; Ciftan, S. A.; Thorp, H. H. *Inorg. Chim. Acta* **1995**, *240*, 335–338.
63. Lebeau, E. L.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 6476–6484.
64. Geselowitz, D. A.; Kutner, W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2015–2023.
65. Polam, J. R.; Porter, L. C. *J Coord Chem* **1993**, *28*, 297–304.
66. Hinckley, C. C.; Matusz, M.; Robinson, P. D. *Acta Crystallogr., Sect. C* **1988**, *44*, 1829–1831.
67. Hinckley, C. C.; Matusz, M.; Kibala, P. A.; Robinson, P. D. *Acta Crystallogr., Sect. C* **1987**, *43*, 1880–1882.
68. Champness, N. R.; Levason, W.; Pletcher, D.; Spicer, M. D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2201–2207.
69. Champness, N. R.; Levason, W.; Pletcher, D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1992**, 3243–3247.
70. Champness, N. R.; Frampton, C. S.; Levason, W.; Preece, S. R. *Inorg. Chim. Acta* **1995**, *233*, 43–50.
71. Baxley, G. T.; Miller, W. K.; Lyon, D. K.; Miller, B. E.; Nieckarz, G. F.; Weakley, T. J. R.; Tyler, D. R. *Inorg. Chem.* **1996**, *35*, 6688–6693.
72. Khan, M. M. T.; Ramachandraiah, G.; Shukla, R. S. *Polyhedron* **1992**, *11*, 3075–3081.
73. Diamantis, A. A.; Moritz, P. S. *Aust. J. Chem.* **1993**, *46*, 221–231.
74. El-Hendawy, A. M. *Polyhedron* **1990**, *9*, 2309–2314.
75. Judd, R. J.; Cao, R. H.; Biner, M.; Armbruster, T.; Burgi, H. B.; Merbach, A. E.; Ludi, A. *Inorg. Chem.* **1995**, *34*, 5080–5083.
76. Alessio, E.; Balducci, G.; Lutman, A.; Mestroni, G.; Calligaris, M.; Attia, W. M. *Inorg. Chim. Acta* **1993**, *203*, 205–217.
77. Chattopadhyay, S.; Bag, N.; Basu, P.; Lahiri, G. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1990**, 3389–3392.
78. Basuli, F.; Das, A. K.; Mostafa, G.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **2000**, *19*, 1663–1672.
79. Kaziro, R.; Hambley, T. W.; Binstead, R. A.; Beattie, J. K. *Inorg. Chim. Acta* **1989**, *164*, 85–91.
80. Reynolds, P. A.; Cable, J. W.; Sobolev, A. N.; Figgis, B. N. *J. Chem. Soc., Dalton Trans.* **1998**, 559–569.
81. Figgis, B. N.; Reynolds, P. A.; Murray, K. S.; Moubaraki, B. *Aust. J. Chem.* **1998**, *51*, 229–234.
82. Satsu, Y.; Endo, A.; Shimizu, K.; Sato, G. P.; Ono, K.; Watanabe, I.; Ikeda, S. *Chem. Lett.* **1986**, 585–588.
83. Tang, J. S.; Shimizu, K.; Osteryoung, R. A. *Inorg. Chem.* **1992**, *31*, 2328–2333.
84. Hasegawa, T.; Lau, T. C.; Taube, H.; Schaefer, W. P. *Inorg. Chem.* **1991**, *30*, 2921–2928.
85. Majumdar, P.; Falvello, L. R.; Tomas, M.; Goswami, S. *Chem.–Eur. J.* **2001**, *7*, 5222–5228.
86. Knowles, T. S.; Howlin, B. J.; Jones, J. R.; Povey, D. C.; Amodio, C. A. *Polyhedron* **1993**, *12*, 2921–2924.
87. Kasahara, Y.; Hoshino, Y.; Shimizu, K.; Sato, G. P. *Chem. Lett.* **1990**, 381–384.

88. Kobayashi, T.; Nishina, Y.; Shimizu, K.; Sato, G. P. *Chem. Lett.* **1988**, 1137–1140.
89. Hoshino, Y.; Takahashi, R.; Shimizu, K.; Satô, G. P.; Aoki, K. *Inorg. Chem.* **1990**, *29*, 4816–4820.
90. Hoshino, Y.; Hagihara, Y. *Inorg. Chim. Acta* **1999**, *292*, 64–72.
91. Baird, I. R.; Rettig, S. J.; James, B. R.; Skov, K. A. *Can. J. Chem.* **1999**, *77*, 1821–1833.
92. Tamura, J.; Satsu, Y.; Fukuhara, D.; Shimizu, K.; Sato, G. P. *Inorg. Chim. Acta* **1995**, *236*, 37–42.
93. Haga, M.; Isobe, K.; Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 3795–3799.
94. Boone, S. R.; Pierpont, C. G. *Polyhedron* **1990**, *9*, 2267–2272.
95. Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 1511–1516.
96. Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1992**, *31*, 2020–2029.
97. Da Silva, R. S.; Tfouni, E.; Lever, A. B. P. *Inorg. Chim. Acta* **1995**, *235*, 427–430.
98. Kelson, E. P.; Henling, L. M.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1993**, *32*, 2863–2873.
99. Filipek, K. *Inorg. Chim. Acta* **1995**, *231*, 237–239.
100. Higashijima, M. *Chem. Lett.* **1999**, 1093–1094.
101. Calligaris, M.; Bresciani-Pahor, N.; Srivastava, R. S. *Acta Crystallogr., Sect. C* **1993**, *49*, 448–451.
102. Jaswal, J. S.; Rettig, S. J.; James, B. R. *Can. J. Chem.* **1990**, *68*, 1808–1817.
103. Alessio, E.; Balducci, G.; Calligaris, M.; Costa, G.; Attia, W. M.; Mestroni, G. *Inorg. Chem.* **1991**, *30*, 609–618.
104. Alessio, E.; Milani, B.; Mestroni, G.; Calligaris, M.; Faleschini, P.; Attia, W. M. *Inorg. Chim. Acta* **1990**, *177*, 255–265.
105. Rack, J. J.; Gray, H. B. *Inorg. Chem.* **1999**, *38*, 2–3.
106. Geremia, S.; Alessio, E.; Todone, F. *Inorg. Chim. Acta* **1996**, *253*, 87–90.
107. Yapp, D. T. T.; Jaswal, J.; Rettig, S. J.; James, B. R.; Skov, K. A. *Inorg. Chim. Acta* **1990**, *177*, 199–208.
108. Fairlie, D. P.; Wickramasinghe, W. A.; Byriel, K. A.; Taube, H. *Inorg. Chem.* **1997**, *36*, 2242–2243.
109. Cruz-Garritz, D.; Sosa, P.; Torrens, H.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1989**, 419–423.
110. Hills, A.; Hughes, D. L.; Richards, R. L.; Arrovo, M.; Cruz-Garritz, D.; Torrens, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1281–1284.
111. Moreno-Esparza, R.; Torrens, H.; Arroyo, M.; Brianso, J. L.; Miravitlles, C.; Rius, J. *Polyhedron* **1995**, *14*, 1601–1606.
112. Arroyo, M.; Bernes, S.; Brianzo, J. L.; Mayoral, E.; Richards, R. L.; Rius, J.; Torrens, H. *Inorg. Chem. Commun.* **1998**, *1*, 273–276.
113. Abasq, M. L.; Pickett, C. J.; Richards, R. L.; Arroyo, M.; Chamizo, J. A.; Calderon, A.; Sosa, P.; Torrens, H. *Polyhedron* **1996**, *15*, 3623–3629.
114. Johnson, M. D.; Nickerson, D. *Inorg. Chem.* **1992**, *31*, 3971–3974.
115. Sellmann, D.; Geck, M.; Knoch, F.; Moll, M. *Inorg. Chim. Acta* **1991**, *186*, 187–198.
116. Maiti, R.; Shang, M. Y.; Lappin, A. G. *J. Chem. Soc., Dalton Trans.* **2002**, 244–251.
117. Schneider, R.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4935–4939.
118. See references in ref. 117.
119. Sellmann, D.; Heinemann, F. W.; GottschalkGaudig, T. *Z Naturforsch., Sect B* **1999**, *54*, 1122–1124.
120. Matsumoto, T.; Matsumoto, K. *Chem. Lett.* **1992**, 559–562.
121. Ghatak, N.; Chakravarty, J.; Bhattacharya, S. *Polyhedron* **1995**, *14*, 3591–3597.
122. Holligan, B. M.; Jeffery, J. C.; Norgett, M. K.; Schatz, E.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1992**, 3345–3351.
123. Bardwell, D. A.; Black, D.; Jeffery, J. C.; Schatz, E.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2321–2327.
124. El-Hendawy, A. M. *Polyhedron* **1991**, *10*, 2137–2143.
125. Das, A. K.; Peng, S. M.; Bhattacharya, S. *J. Chem. Soc., Dalton Trans.* **2000**, 181–184.
126. Hariram, R.; Santra, B. K.; Lahiri, G. K. *J.Organometal. Chem.* **1997**, *540*, 155–163.
127. Pattanayak, S.; Pramanik, K.; Bag, N.; Ghosh, P.; Chakravorty, A. *Polyhedron* **1997**, *16*, 2951–2956.
128. Roy, B. K.; Mallick, T. K.; Ghosh, B. K. *Polyhedron* **1992**, *11*, 1829–1835.
129. Hursthouse, M. B.; Mazid, M. A.; Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1993**, 2835–2839.
130. Khan, M. M. T.; Srinivas, D.; Kureshy, R. I.; Khan, N. H. *Polyhedron* **1991**, *10*, 2559–2565.
131. Khan, M. M. T.; Mizra, S. A.; Shaikh, Z. A.; Sreelatha, C.; Paul, P.; Shukla, R. S.; Srinivas, D.; Rao, A. P.; Abdi, S. H. R.; Bhatt, S. D.; Ramachandraiah, G. *Polyhedron* **1992**, *11*, 1821–1827.
132. Nakajima, K.; Ando, Y.; Mano, H.; Kojima, M. *Inorg. Chim. Acta* **1998**, *274*, 184–191.
133. Chatterjee, D. *Coord. Chem. Rev.* **1998**, *168*, 273–293.
134. Okamoto, K.; Hidaka, J.; Iida, I.; Higashino, K.; Kanamori, K. *Acta Crystallogr., Sect. C* **1990**, *46*, 2327–2329.
135. Chatterjee, D.; Bajaj, H. C. *J. Chem. Soc., Dalton Trans.* **1995**, 3415–3417.
136. Bajaj, H. C.; Das, A.; vanEldik, R. *J. Chem. Soc., Dalton Trans.* **1998**, 1563–1568.
137. Chatterjee, D.; Mitra, A.; Hamza, M. S. A.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **2002**, 962–965.
138. Khan, M. M. T.; Naik, R. M. *Polyhedron* **1989**, *8*, 463–467.
139. Khan, B. T.; Annapoorna, K. *Inorg. Chim. Acta* **1990**, *176*, 241–246.
140. Khan, B. T.; Annapoorna, K. *Polyhedron* **1991**, *10*, 2465–2470.
141. Rein, F. N.; Toma, H. E. *Polyhedron* **1998**, *17*, 1439–1448.
142. Chatterjee, D.; Ward, M. S.; Shepherd, R. E. *Inorg. Chim. Acta* **1999**, *285*, 170–177.
143. Chatterjee, D. *J. Chem. Soc., Dalton Trans.* **1996**, 4389–4392.
144. Araki, K.; Shu, C. F.; Anson, F. C. *Inorg. Chem.* **1991**, *30*, 3043–3047.
145. Khan, M. M. T.; Hussain, A.; Moiz, M. A. *Polyhedron* **1992**, *11*, 687–689.
146. Wanat, A.; Schneppensieper, T.; Karocki, A.; Stochel, G.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **2002**, 941–950.
147. Davies, N. A.; Wilson, M. T.; Slade, E.; Fricker, S. P.; Murrer, B. A.; Powell, N. A.; Henderson, G. R. *Chem. Commun.* **1997**, 47–48.
148. Khan, M. M. T.; Venkatasubramanian, K.; Shirin, Z.; Bhadbhade, M. M. *J. Chem. Soc., Dalton Trans.* **1992**, 885–890.
149. Vilaplana-Serrano, R.; Basallote, M. G.; Ruiz-Valero, C.; Gutierrez-Puebla, E.; Gonzalez-Vilchez, F. *J. Chem. Soc., Chem. Commun.* **1991**, 100–101.

150. Khan, M. M. T.; Bhadbhade, M. M.; Venkatasubramanian, K.; Siddiqui, M. R. H. *Acta Crystallogr., Sect. C* **1992**, *48*, 1202–1204.
151. Jolley, J.; Campbell, C. J.; Castiñeiras, A.; Yanovsky, A. I.; Nolan, K. B. *Polyhedron* **1998**, *18*, 49–55.
152. Rocha, R. C.; Araki, K.; Toma, H. E. *Inorg. Chim. Acta* **1999**, *285*, 197–202.
153. Forlano, P.; Cukiernik, F. D.; Poizat, O.; Olabe, J. A. *J. Chem. Soc., Dalton Trans.* **1997**, 1595–1599.
154. Bajaj, H. C.; Das, A. *Polyhedron* **1997**, *16*, 3851–3855.
155. Chatterjee, D. *Polyhedron* **1999**, *18*, 1767–1771.
156. Chatterjee, D.; Bajaj, H. C. *J. Chem. Soc., Dalton Trans.* **1993**, 1065–1067.
157. Khan, M. M. T.; Bajaj, H. C.; Shirin, Z.; Venkatasubramanian, K. *Polyhedron* **1992**, *11*, 1059–1066.
158. Tanase, T.; Yamada, Y.; Tanaka, K.; Miyazu, T.; Kato, M.; Lee, K.; Sugihara, Y.; Mori, W.; Ichimura, A.; Kinoshita, I.; Yamamoto, Y.; Haga, M.; Sasaki, Y.; Yano, S. *Inorg. Chem.* **1996**, *35*, 6230–6239.
159. Mikata, Y.; Takeshita, N.; Miyazu, T.; Miyata, Y.; Tanase, T.; Kinoshita, I.; Ichimura, A.; Mori, W.; Takamizawa, S.; Yano, S. *J. Chem. Soc., Dalton Trans.* **1998**, 1969–1972.
160. Zhang, S. S.; Shepherd, R. E. *Inorg. Chem.* **1994**, *33*, 5262–5270.
161. Pramanik, A.; Bag, N.; Chakravorty, A. *Inorg. Chem.* **1993**, *32*, 811–815.
162. Hector, A. L.; Levason, W.; Weller, M. T.; Hope, E. G. *J. Fluorine Chem.* **1997**, *84*, 161–165.
163. Appelbaum, L.; Heinrichs, C.; Demtschuk, J.; Michman, M.; Oron, M.; Schafer, H. J.; Schumann, H. *J. Organometal. Chem.* **1999**, *592*, 240–250.
164. Duff, C. M.; Schmid, R. A. *Inorg. Chem.* **1991**, *30*, 2938–2941.
165. Duff, C. M.; Heath, G. A. *J. Chem. Soc., Dalton Trans.* **1991**, 2401–2411.
166. Bell, I. M.; Clark, R. J. H.; Humphrey, D. G. *J. Chem. Soc., Dalton Trans.* **1999**, 1307–1310.
167. al Dulaimi, J. P.; Clark, R. J. H.; Humphrey, D. G. *J. Chem. Soc., Dalton Trans.* **1997**, 2535–2536.
168. Gheller, S. F.; Heath, G. A.; Hockless, D. C. R.; Humphrey, D. G.; McGrady, J. E. *Inorg. Chem.* **1994**, *33*, 3986–3989.
169. Wohnrath, K.; de Araujo, M. P.; Dinelli, L. R.; Batista, A. A.; Moreira, I. D.; Castellano, E. E.; Ellena, J. *J. Chem. Soc., Dalton Trans.* **2000**, 3383–3386.
170. Kang, H. W.; Moran, G.; Krausz, E. *Inorg. Chim. Acta* **1996**, *249*, 231–235.
171. Macartney, D. H. *Inorg. Chem.* **1991**, *30*, 3337–3342.
172. Kukushkin, Y. N.; Bavina, M. V.; Zinchenko, A. V.; Belsky, V. K.; Kukushkin, V. Y. *Polyhedron* **1997**, *16*, 2429–2433.
173. Fogg, D. E.; Rettig, S. J.; James, B. R. *Can. J. Chem.* **1995**, *73*, 1084–1091.
174. Fogg, D. E.; James, B. R. *Inorg. Chem.* **1997**, *36*, 1961–1966.
175. Rezvani, A. R.; Crutchley, R. J. *Inorg. Chem.* **1994**, *33*, 170–174.
176. Mosher, P. J.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **2001**, *40*, 550–553.
177. Martinez, M. S.; de Oliveira, E. C.; Tfouni, E. *J. Photochem. Photobiol. A* **1999**, *122*, 103–108.
178. da Rocha, Z. N.; Tfouni, E. *Polyhedron* **1992**, *11*, 2375–2381.
179. Tfouni, E. *Coord. Chem. Rev.* **2000**, *196*, 281–305.
180. Carlos, R. M.; Neumann, M. G.; Tfouni, E. *Inorg. Chem.* **1996**, *35*, 2229–2234.
181. Moscherosch, M.; Waldhor, E.; Binder, H.; Kaim, W.; Fiedler, J. *Inorg. Chem.* **1995**, *34*, 4326–4335.
182. Steiger, B.; Anson, F. C. *J. Porphyr. Phthalocya.* **1999**, *3*, 159–165.
183. Shin, Y. G. K.; Brunschwig, B. S.; Creutz, C.; Newton, M. D.; Sutin, N. *J. Phys. Chem.* **1996**, *100*, 1104–1110.
184. Zhang, L. T.; Ondrechen, M. J. *Inorg. Chim. Acta* **1994**, *226*, 43–51.
185. Shin, Y. K.; Szalda, D. J.; Brunschwig, B. S.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1997**, *36*, 3190–3197.
186. Ritchie, J. E.; Murray, R. W. *J. Phys. Chem. B* **2001**, *105*, 11523–11528.
187. Sun, J. F.; Stanbury, D. M. *Inorg. Chem.* **1998**, *37*, 1257–1263.
188. Chou, M. H.; Brunschwig, B. S.; Creutz, C.; Sutin, N.; Yeh, A.; Chang, R. C.; Lin, C. T. *Inorg. Chem.* **1992**, *31*, 5347–5348.
189. Plotkin, S.; Haim, A. *Inorg. Chim. Acta* **1998**, *270*, 189–196.
190. Mao, W. L.; Qian, Z.; Yen, H. J.; Curtis, J. C. *J. Am. Chem. Soc.* **1996**, *118*, 3247–3252.
191. McNamara, M. A.; Clarke, M. J. *Inorg. Chim. Acta* **1992**, *195*, 175–185.
192. Yoon, D. I.; Belanger, S.; Hupp, J. T.; Stern, C. L. *Acta Crystallogr., Sect. C* **1998**, *54*, 1427–1431.
193. Ando, I.; Ishimura, D.; Mitsumi, M.; Ujimoto, K.; Kurihara, H. *Inorg. Chim. Acta* **1996**, *249*, 201–205.
194. Ando, I.; Ishimura, D.; Ujimoto, K.; Kurihara, H. *Inorg. Chem.* **1996**, *35*, 3504–3508.
195. Johnson, M. D.; Reinsborough, V. C.; Ward, S. *Inorg. Chem.* **1992**, *31*, 1085–1087.
196. Elliott, M. G.; Zhang, S. G.; Shepherd, R. E. *Inorg. Chem.* **1989**, *28*, 3036–3043.
197. Katz, N. E.; Fagalde, F. *Inorg. Chem.* **1993**, *32*, 5391–5393.
198. Franco, D. W. *Coord. Chem. Rev.* **1992**, *119*, 199–225.
199. Mazzetto, S. E.; Plicas, L. M. D.; Tfouni, E.; Franco, D. W. *Inorg. Chem.* **1992**, *31*, 516–519.
200. Mazzetto, S. E.; Tfouni, E.; Franco, D. W. *Inorg. Chem.* **1996**, *35*, 3509–3513.
201. Mazzetto, S. E.; Gehlen, M. H.; Franco, D. W. *Inorg. Chim. Acta* **1997**, *254*, 79–83.
202. Liu, T. Y.; Chen, Y. J.; Tai, C. C.; Kwan, K. S. *Inorg. Chem.* **1999**, *38*, 674–679.
203. Heaton, B. T.; Jacob, C.; Page, P. *Coord. Chem. Rev.* **1996**, *154*, 193–229.
204. Cheng, T. Y.; Ponce, A.; Rheingold, A. L.; Hillhouse, G. L. *Angew Chem Int Ed* **1994**, *33*, 657–659.
205. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Pelizzi, G.; Ugo, P. *Inorg. Chem.* **1996**, *35*, 6245–6253.
206. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bergano, M.; Bordignon, E.; Pelizzi, G. *Inorg. Chem.* **1998**, *37*, 479–489.
207. Albertin, G.; Antoniutti, S.; Bacchi, A.; Bordignon, E.; Dolcetti, P. M.; Pelizzi, G. *J. Chem. Soc., Dalton Trans.* **1997**, 4435–4444.
208. Coia, G. M.; Devenney, M.; White, P. S.; Meyer, T. J.; Wink, D. A. *Inorg. Chem.* **1997**, *36*, 2341–2351.
209. Kawano, M.; Hoshino, C.; Matsumoto, K. *Inorg. Chem.* **1992**, *31*, 5158–5159.
210. Buys, I. E.; Field, L. D.; George, A. V.; Hambley, T. W.; Purches, G. R. *Aust. J. Chem.* **1995**, *48*, 27–34.
211. Siebald, H. G. L.; Fabre, P. L.; Dartiguenave, M.; Dartiguenave, Y.; Simard, M.; Beauchamp, A. L. *Polyhedron* **1996**, *15*, 4221–4225.
212. Leising, R. A.; Kubow, S. A.; Takeuchi, K. J. *Inorg. Chem.* **1990**, *29*, 4569–4574.

213. Freedman, D. A.; Janzen, D. E.; Mann, K. R. *Inorg. Chem.* **2001**, *40*, 6009–6016.
214. Ooyama, D.; Nagao, N.; Nagao, H.; Miura, Y.; Hasegawa, A.; Ando, K.; Howell, F. S.; Mukaida, M.; Tanaka, K. *Inorg. Chem.* **1995**, *34*, 6024–6033.
215. Blake, A. J.; Gould, R. O.; Johnson, B. F. G.; Parisini, E. *Acta Crystallogr., Sect. C* **1992**, *48*, 982–984.
216. Puig-Molina, A.; Muller, H.; Le Quere, A. M.; Vaughan, G.; Graafsma, H.; Kvick, A. *Z. Anorg. Allg. Chem.* **2000**, *626*, 2379–2387.
217. Albores, P.; Chaia, Z. D.; Baraldo, L.; Castellano, E. E.; Piro, O. E. *Acta Crystallogr., Sect. C* **2002**, *58*, M235–M236.
218. Ooyama, D.; Nagao, N.; Howell, F. S.; Mukaida, M.; Nagao, H.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2897–2904.
219. Ooyama, D.; Nagao, N.; Nagao, H.; Sugimoto, Y.; Howell, F. S.; Mukaida, M. *Inorg. Chim. Acta* **1997**, *261*, 45–52.
220. Guida, J. A.; Ramos, M. A.; Piro, O. E.; Aymonino, P. J. *J. Mol. Struct.* **2002**, *609*, 39–46.
221. Goodman, M. S.; de Marco, M. J.; Haka, M. S.; Toorongian, S. A.; Fridmann, J. *J. Chem. Soc., Dalton Trans.* **2002**, 117–120.
222. Bezerra, C. W. B.; da Silva, S. C.; Gambardella, M. T. P.; Santos, R. H. A.; Plicas, L. M. A.; Tfouni, E.; Franco, D. W. *Inorg. Chem.* **1999**, *38*, 5660–5667.
223. Borges, S. S.; da, S.; Davanzo, C. U.; Castellano, E. E.; Z.-Schpector, J.; Silva, S. C.; Franco, D. W. *Inorg. Chem.* **1998**, *37*, 2670–2677.
224. Gomes, M. G.; Davanzo, C. U.; Silva, S. C.; Lopes, L. G. F.; Santos, P. S.; Franco, D. W. *J. Chem. Soc., Dalton Trans.* **1998**, 601–607.
225. Lopes, L. G. F.; Gomes, M. G.; Borges, S. da S. S.; Franco, D. W. *Aust. J. Chem.* **1998**, *51*, 865–866.
226. Nagao, H.; Nishimura, H.; Funato, H.; Ichikawa, Y.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Inorg. Chem.* **1989**, *28*, 3955–3959.
227. Togniolo, V.; da Silva, R. S.; Tedesco, A. C. *Inorg. Chim. Acta* **2001**, *316*, 7–12.
228. Di Salvo, F.; Crespo, A.; Estrin, D. A.; Doctorovich, F. *Tetrahedron* **2002**, *58*, 4237–4244.
229. Nagao, H.; Nagao, N.; Yukawa, Y.; Ooyama, D.; Sato, Y.; Oosawa, T.; Kuroda, H.; Howell, F. S.; Mukaida, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1273–1284.
230. Nagao, H.; Ito, K.; Tsuboya, N.; Ooyama, D.; Nagao, N.; Howell, F. S.; Mukaida, M. *Inorg. Chim. Acta* **1999**, *290*, 113–119.
231. Togano, T.; Kuroda, H.; Nagao, N.; Maekawa, Y.; Nishimura, H.; Howell, F. S.; Mukaida, M. *Inorg. Chim. Acta* **1992**, *196*, 57–63.
232. Tomizawa, H.; Miki, E.; Mizumachi, K.; Ishimori, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1809–1815.
233. Toma, H. E.; Silva, D. D.; Saika, J. J. *J. Chem. Res., S* **1996**, 456–457.
234. Ooyama, D.; Nagao, H.; Ito, K.; Nagao, N.; Howell, F. S.; Mukaida, M. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2141–2149.
235. Ooyama, D.; Miura, Y.; Kanazawa, Y.; Howell, F. S.; Nagao, N.; Mukaida, M.; Nagao, H.; Tanaka, K. *Inorg. Chim. Acta* **1995**, *237*, 47–55.
236. Hirano, T.; Kuroda, M.; Takeda, N.; Hayashi, M.; Mukaida, M.; Oi, T.; Nagao, H. *J. Chem. Soc., Dalton Trans.* **2002**, 2158–2162.
237. Suzuki, Y.; Tomizawa, H.; Miki, E. *Inorg. Chim. Acta* **1999**, *290*, 36–43.
238. Miki, E.; Harada, K.; Kamata, Y.; Umehara, M.; Mizumachi, K.; Ishimori, T.; Nakahara, M.; Tanaka, M.; Nagai, T. *Polyhedron* **1991**, *10*, 583–589.
239. Miki, K.; Tomizawa, H.; Ikezawa, H.; Miki, E. *Inorg. Chim. Acta* **1997**, *257*, 3–10.
240. Ikezawa, H.; Miki, E.; Mizumachi, K.; Ishimori, T.; Nagai, T.; Tanaka, M. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 89–97.
241. Fergusson, J. E.; Robinson, W. T.; Coll, R. K. *Inorg. Chim. Acta* **1991**, *181*, 37–42.
242. Paul, B. C.; Sarker, S. C.; Poddar, R. K. *J. Coord. Chem.* **1993**, *28*, 245–249.
243. Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1992**, 1111–1116.
244. Bagatin, I. A.; Santos, R. H. D.; Franco, D. W.; Magalhaes, A.; Ferreira, A. G. *Inorg. Chim. Acta* **2002**, *333*, 109–115.
245. Souza, D. H. F.; Oliva, G.; Teixeira, A.; Batista, A. A. *Polyhedron* **1995**, *14*, 1031–1034.
246. Bhattacharyya, R.; Saha, A. M.; Ghosh, P. N.; Mukherjee, M.; Mukherjee, A. K. *J. Chem. Soc., Dalton Trans.* **1991**, 501–510.
247. Roncaroli, F.; Baraldo, L. M.; Slep, L. D.; Olabe, J. A. *Inorg. Chem.* **2002**, *41*, 1930–1939.
248. Oomura, K.; Ooyama, D.; Satoh, Y.; Nagao, N.; Nagao, H.; Howell, F. S.; Mukaida, M. *Inorg. Chim. Acta* **1998**, *269*, 342–346.
249. Roesky, H. W.; Pandey, K. K.; Clegg, W.; Noltemeyer, M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1984**, 719–721.
250. Laurenczy, G.; Helm, L.; Merbach, A. E.; Ludi, A. *Inorg. Chim. Acta* **1991**, *189*, 131–133.
251. Takahashi, T.; Hiratani, K.; Kimura, E. *Chem. Lett.* **1993**, 1329–1332.
252. Sabo-Etienne, S.; Hernandez, M.; Chung, G.; Chaudret, B. *New J. Chem.* **1994**, *18*, 175–177.
253. Albertin, G.; Antoniutti, S.; Baldan, D.; Bordignon, E. *Inorg. Chem.* **1995**, *34*, 6205–6210.
254. Estrin, D. A.; Hamra, O. Y.; Paglieri, L.; Slep, L. D.; Olabe, J. A. *Inorg. Chem.* **1996**, *35*, 6832–6837.
255. Elsegood, M. R. J.; Tocher, D. A. *Acta Crystallogr., Sect. C* **1995**, *51*, 40–42.
256. Desjardins, P.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **1999**, *38*, 5901–5905.
257. Paula, M. M. S.; Meier, M. M.; Szpoganicz, B.; Franco, C. V. *J. Coord. Chem.* **1999**, *46*, 491–504.
258. Seifriz, I.; Konzen, M.; Paula, M. M. S.; Goncalves, N. S.; Spoganickz, B.; CreczynskiPasa, T. B.; Bonetti, V. R.; Beirith, A.; Calixto, J. B.; Franco, C. V. *J. Inorg. Biochem.* **1999**, *76*, 153–163.
259. Coe, B. J.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1995**, *34*, 593–602.
260. Pavanin, L. A.; Darocha, Z. N.; Giesbrecht, E.; Tfouni, E. *Inorg. Chem.* **1991**, *30*, 2185–2190.
261. Silva, D. O.; Saika, J. J.; Toma, H. E. *J. Photochem. Photobiol. A* **1998**, *112*, 209–212.
262. Nagao, H.; Ooyama, D.; Hirano, T.; Naoi, H.; Shimada, M.; Sasaki, S.; Nagao, N.; Mukaida, M.; Oi, T. *Inorg. Chim. Acta* **2001**, *320*, 60–66.
263. Wohnrath, K.; Batista, A. A.; Ferreira, A. G.; Z.-Schpector, J.; de Oliveira, L. A. A.; Castellano, E. E. *Polyhedron* **1998**, *17*, 2013–2020.

264. Mullica, D. F.; Farmer, J. M.; Kautz, J. A.; Gipson, S. L.; Belay, Y. F.; Windmiller, M. S. *Inorg. Chim. Acta* **1999**, *285*, 318–321.
265. Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *Organometallics* **1999**, *18*, 2813–2820.
266. Clark, A. M.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **2000**, *598*, 262–275.
267. Caswell, D. S.; Spiro, T. G. *Inorg. Chem.* **1987**, *26*, 18–22.
268. Bates, W. D.; Chen, P. Y.; Bignozzi, C. A.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 6215–6217.
269. Coe, B. J.; Essex-Lopresti, J. P.; Harris, J. A.; Houbrechts, S.; Persoons, A. *Chem. Commun.* **1997**, 1645–1646.
270. Coe, B. J.; Harris, J. A.; Harrington, L. J.; Jeffery, J. C.; Rees, L. H.; Houbrechts, S.; Persoons, A. *Inorg. Chem.* **1998**, *37*, 3391–3399.
271. Coe, B. J.; Houbrechts, S.; Asselberghs, I.; Persoons, A. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 366–369.
272. Coe, B. J.; Harris, J. A.; Asselberghs, I.; Persoons, A.; Jeffery, J. C.; Rees, L. H.; Gelbrich, T.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1999**, 3617–3625.
273. Coe, B. J.; Harris, J. A.; Brunschwig, B. S. *J. Phys. Chem. A* **2002**, *106*, 897–905.
274. Coe, B. J.; Beyer, T.; Jeffery, J. C.; Coles, S. J.; Gelbrich, T.; Hursthouse, M. B.; Light, M. E. *J. Chem. Soc., Dalton Trans.* **2000**, 797–803.
275. Constable, E. C. *Adv. Inorg. Chem.* **1989**, *34*, 1–64.
276. Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553–3590.
277. Broomhead, J. A.; Young, C. G. *Inorg. Synth.* **1982**, *21*, 127–128.
278. Broomhead, J. A.; Young, C. G. *Inorg. Synth.* **1990**, *28*, 338–340.
279. Kakoti, M.; Deb, A. K.; Goswami, S. *Inorg. Chem.* **1992**, *31*, 1302–1304.
280. Togano, T.; Nagao, N.; Tsuchida, M.; Kumakura, H.; Hisamatsu, K.; Howell, F. S.; Mukaida, M. *Inorg. Chim. Acta* **1992**, *195*, 221–225.
281. Matsumurainoue, T.; Tanabe, M.; Minami, T.; Ohashi, T. *Chem. Lett.* **1994**, 2443–2446.
282. Strouse, G. F.; Anderson, P. A.; Schoonover, J. R.; Meyer, T. J.; Keene, F. R. *Inorg. Chem.* **1992**, *31*, 3004–3006.
283. Jandrasics, E. Z.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1997**, 153–159 and references therein.
284. Richter, M. M.; Scott, B.; Brewer, K. J.; Willett, R. D. *Acta Crystallogr., Sect. C* **1991**, *47*, 2443–2444.
285. Rillema, D. P.; Jones, D. S.; Woods, C.; Levy, H. A. *Inorg. Chem.* **1992**, *31*, 2935–2938.
286. Harrowfield, J. M.; Sobolev, A. N. *Aust. J. Chem.* **1994**, *47*, 763–767.
287. Han, Z. B.; Wang, E. B.; Luan, G. Y.; Li, Y. G.; Hu, C. W.; Wang, P.; Hu, N. H.; Jia, H. Q. *Inorg. Chem. Commun.* **2001**, *4*, 427–429.
288. Pellaux, R.; Decurtins, S.; Schmalle, H. W. *Acta Crystallogr., Sect. C* **1999**, *55*, 1075–1079.
289. Yokoyama, H.; Shinozaki, K.; Hattori, S.; Miyazaki, F. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2357–2367.
290. Breu, J.; Belser, P.; Yersin, H. *Acta Crystallogr., Sect. C* **1996**, *52*, 858–861.
291. Brandt, P.; Norrby, T.; Akermark, E.; Norrby, P. O. *Inorg. Chem.* **1998**, *37*, 4120–4127.
292. Ohsawa, Y.; Dearmond, M. K.; Hanck, K. W.; Moreland, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 5383–5386.
293. Xiao, X. M.; Matsumura-Inoue, T.; Mizutani, S. *Chem. Lett.* **1997**, 241–242.
294. Li, C.; Hoffman, M. Z.; Pizzocaro, C.; Maihot, G.; Bolte, M. *Inorg. Chem.* **1998**, *37*, 3078–3082.
295. Krausz, E.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293–390.
296. Gorelsky, S. I.; Dodsworth, E. S.; Lever, A. B. P.; Vlcek, A. A. *Coord. Chem. Rev.* **1998**, *174*, 469–494.
297. Yersin, H.; Humbs, W.; Strasser, J. *Coord. Chem. Rev.* **1997**, *159*, 325–358.
298. Malone, R. A.; Kelley, D. F. *J. Chem. Phys.* **1991**, *95*, 8970–8976.
299. Kim, P. S.; Sham, T. K.; Zhang, P.; Fung, M. K.; Lee, S. T.; Hu, Y. F.; Yates, B. W. *J. Am. Chem. Soc.* **2001**, *123*, 8870–8871.
300. Lever, A. B. P.; Gorelsky, S. I. *Coord. Chem. Rev.* **2000**, *208*, 153–167.
301. Constable, E. C.; Housecroft, C. E. *Polyhedron* **1990**, *9*, 1939–1947.
302. Mallick, P. K.; Danzer, G. D.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1988**, *92*, 5628–5634.
303. Strommen, D. P.; Mallick, P. K.; Danzer, G. D.; Lumpkin, R. S.; Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 1357–1366.
304. Mallick, P. K.; Strommen, D. P.; Kincaid, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1686–1690.
305. Manuel, D. J.; Strommen, D. P.; Bhuiyan, A.; Sykora, M.; Kincaid, J. R. *J. Raman Spectrosc.* **1997**, *28*, 933–938.
306. Mabrouk, P. A.; Wrighton, M. S. *Inorg. Chem.* **1986**, *25*, 526–531.
307. Carroll, P. J.; Brus, L. E. *J. Am. Chem. Soc.* **1987**, *109*, 7613–7616.
308. Danzer, G. D.; Bajdor, K.; Kincaid, J. R. *J. Raman Spectrosc.* **1993**, *24*, 357–361.
309. Danzer, G. D.; Golus, J. A.; Kincaid, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8643–8648.
310. Danzer, G. D.; Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 3976–3980.
311. Danzer, G. D.; Kincaid, J. R. *J. Raman Spectrosc.* **1992**, *23*, 681–689.
312. Strekas, T. C.; Gafney, H. D.; Tysoe, S. A.; Thummel, R. P.; Lefoulon, F. *Inorg. Chem.* **1989**, *28*, 2964–2967.
313. Braun, D.; Huber, P.; Wudy, J.; Schmidt, J.; Yersin, H. *J. Phys. Chem.* **1994**, *98*, 8044–8049.
314. Huber, P.; Yersin, H. *J. Phys. Chem.* **1993**, *97*, 12705–12709.
315. Tait, C. D.; Vess, T. M.; Dearmond, M. K.; Hanck, K. W.; Wertz, D. W. *J. Chem. Soc., Dalton Trans.* **1987**, 2467–2471.
316. Omberg, K. M.; Schoonover, J. R.; Treadway, J. A.; Leasure, R. M.; Dyer, R. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 7013–7018.
317. Braterman, P. S.; Harriman, A.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1983**, 1801–1803.
318. Braterman, P. S.; Heath, G. A.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1081–1086.
319. Yoshimura, A.; Hoffman, M. Z.; Sun, H. *J. Photochem. Photobiol. A* **1993**, *70*, 29–33.
320. Li, C.; Hoffman, M. Z. *Inorg. Chem.* **1998**, *37*, 830–832.
321. Masuda, A.; Kaizu, Y. *Inorg. Chem.* **1998**, *37*, 3371–3375.
322. Hartmann, P.; Leiner, M. J. P.; Draxler, S.; Lippitsch, M. E. *Chem. Phys.* **1996**, *207*, 137–146.
323. Islam, A.; Ikeda, N.; Yoshimura, A.; Ohno, T. *Inorg. Chem.* **1998**, *37*, 3093–3098.
324. Damrauer, N. H.; Cerullo, G.; Yeh, A.; Boussie, T. R.; Shank, C. V.; McCusker, J. K. *Science* **1997**, *275*, 54–57.
325. Creaser, II; Gahan, L. R.; Geue, R. J.; Launikonis, A.; Lay, P. A.; Lydon, J. D.; McCarthy, M. G.; Mau, A. W. H.; Sargeson, A. M.; Sasse, W. H. F. *Inorg. Chem.* **1985**, *24*, 2671–2680.
326. Turro, N. J.; Khudyakov, I. V.; Gopidas, K. R. *Chem. Phys.* **1992**, *162*, 131–143.

327. Gordon, C. M.; McLean, A. J. *Chem. Commun.* **2000**, 1395–1396.
328. Shen, Y. B.; Walters, K. A.; Abboud, K.; Schanze, K. S. *Inorg. Chim. Acta* **2000**, *300*, 414–426.
329. Clark, C. D.; Debad, J. D.; Yonemoto, E. H.; Mallouk, T. E.; Bard, A. J. *J. Am. Chem. Soc.* **1997**, *119*, 10525–10531.
330. Cooley, L. F.; Headford, C. E. L.; Elliott, C. M.; Kelley, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 6673–6682.
331. Ryu, C. K.; Wang, R. Y.; Schmehl, R. H.; Ferrere, S.; Ludwikow, M.; Merkert, J. W.; Headford, C. E. L.; Elliott, C. M. *J. Am. Chem. Soc.* **1992**, *114*, 430–438.
332. Hiraishi, T.; Kamachi, T.; Okura, I. *J. Photochem. Photobiol. A* **1998**, *116*, 119–125.
333. Hiraishi, T.; Kamachi, T.; Okura, I. *J. Mol. Catal. A* **1999**, *138*, 107–113.
334. Hiraishi, T.; Kamachi, T.; Okura, I. *J. Mol. Catal. A* **2000**, *151*, 7–15.
335. Seiler, M.; Durr, H.; Willner, I.; Joselevich, E.; Doron, A.; Stoddart, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 3399–3404.
336. Kropf, M.; Joselevich, E.; Durr, H.; Willner, I. *J. Am. Chem. Soc.* **1996**, *118*, 655–665.
337. Henbest, K.; Douglas, P.; Garley, M. S.; Mills, A. *J. Photochem. Photobiol. A* **1994**, *80*, 299–305.
338. Lee, E. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 8562–8564.
339. Uddin, M. J.; Yoshimura, A.; Ohno, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 989–996.
340. Otsuka, T.; Takahashi, N.; Fujigasaki, N.; Sekine, A.; Ohashi, Y.; Kaizu, Y. *Inorg. Chem.* **1999**, *38*, 1340–1347.
341. Iguro, T.; Ikeda, N.; Ohno, T. *Inorg. Chim. Acta* **1994**, *226*, 203–211.
342. Iwamura, M.; Otsuka, T.; Kaizu, Y. *Inorg. Chim. Acta* **2002**, *333*, 57–62.
343. Larsen, R. W.; Jasuja, R.; Niu, S. L.; Dwivedi, K. *J. Photochem. Photobiol. A* **1997**, *107*, 71–75.
344. Senz, A.; Gsponer, H. E. *J. Phys. Org. Chem.* **1995**, *8*, 706–712.
345. Clark, C. D.; Hoffman, M. Z. *J. Phys. Chem.* **1996**, *100*, 14688–14693.
346. Sariciftci, N. S.; Wudl, F.; Heeger, A. J.; Maggini, M.; Scorrano, G.; Prato, M.; Bourassa, J.; Ford, P. C. *Chem. Phys. Lett.* **1995**, *247*, 510–514.
347. Cooley, L. F.; Larson, S. L.; Elliott, C. M.; Kelley, D. F. *J. Phys. Chem.* **1991**, *95*, 10694–10700.
348. Larson, S. L.; Elliott, C. M.; Kelley, D. F. *Inorg. Chem.* **1996**, *35*, 2070–2076.
349. Partigianoni, C. M.; Chodorowski-Kimmes, S.; Treadway, J. A.; Striplin, D.; Trammell, S. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 1193–1198.
350. Opperman, K. A.; Mecklenburg, S. L.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 5295–5301.
351. Ford, W. E.; Rodgers, M. A. J. *J. Photochem. Photobiol. A* **1991**, *59*, 73–80.
352. Thompson, D. W.; Wishart, J. F.; Brunschwig, B. S.; Sutin, N. *J. Phys. Chem. A* **2001**, *105*, 8117–8122.
353. Rodriguez, A.; Delarosa, F. F.; Galan, M.; Sanchez, F.; Moya, M. L. *Photochem. Photobiol.* **1992**, *55*, 367–372.
354. Mulazzani, Q. G.; Ciano, M.; D'Angelantonio, M.; Venturi, M.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1988**, *110*, 2451–2457.
355. Mulazzani, Q. G.; D'Angelantonio, M.; Venturi, M.; Rodgers, M. A. J. *J. Phys. Chem.* **1991**, *95*, 9605–9608.
356. Yavin, E.; Weiner, L.; Arad-Yellin, R.; Shanzer, A. *J. Phys. Chem. A* **2001**, *105*, 8018–8024.
357. Thanasekaran, P.; Rajagopal, S.; Srinivasan, C. *J. Photochem. Photobiol. A* **1999**, *120*, 181–184.
358. Shinozaki, K.; Kaizu, Y.; Hirai, H.; Kobayashi, H. *Inorg. Chem.* **1989**, *28*, 3675–3679.
359. Shinozaki, K.; Ohno, O.; Kaizu, Y.; Kobayashi, H.; Sumitani, M.; Yoshihara, K. *Inorg. Chem.* **1989**, *28*, 3680–3683.
360. Rugge, A.; Clark, C. D.; Hoffman, M. Z.; Rillema, D. P. *Inorg. Chim. Acta* **1998**, *279*, 200–205.
361. Kirsch-De Mesmaeker, A.; Jacquet, L.; Nasielski, J. *Inorg. Chem.* **1988**, *27*, 4451–4458.
362. Sun, H.; Hoffman, M. Z. *J. Phys. Chem.* **1993**, *97*, 5014–5018.
363. D'Angelantonio, M.; Mulazzani, Q. G.; Venturi, M.; Ciano, M.; Hoffman, M. Z. *J. Phys. Chem.* **1991**, *95*, 5121–5129.
364. Kunjappu, J. T. *J. Photochem. Photobiol. A* **1994**, *78*, 237–240.
365. Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617–1622.
366. Vlcek, A. A.; Dodsworth, E. S.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chem.* **1995**, *34*, 1906–1913.
367. Mallick, T. K.; Das, P. K.; Sinha, S.; Ghosh, B. K. *Polyhedron* **1994**, *13*, 1817–1823.
368. Posse, M. E. G.; Katz, N. E.; Baraldo, L. M.; Polonuer, D. D.; Colombano, C. G.; Olabe, J. A. *Inorg. Chem.* **1995**, *34*, 1830–1835.
369. Waldhor, E.; Poppe, J.; Kaim, W.; Cutin, E. H.; Posse, M. E. G.; Katz, N. E. *Inorg. Chem.* **1995**, *34*, 3093–3096.
370. Furue, M.; Maruyama, K.; Oguni, T.; Naiki, M.; Kamachi, M. *Inorg. Chem.* **1992**, *31*, 3792–3795.
371. Rillema, D. P.; Blanton, C. B.; Shaver, R. J.; Jackman, D. C.; Boldaji, M.; Bundy, S.; Worl, L. A.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 1600–1606.
372. Sun, H.; Hoffman, M. Z. *J. Phys. Chem.* **1993**, *97*, 11956–11959.
373. Atfah, A.; Tuhl, A. H.; Akasheh, T. S. *Polyhedron* **1991**, *10*, 1485–1490.
374. Juris, A.; Barigelletti, F.; Balzani, V.; Belser, P.; von Zelewsky, A. *Inorg. Chem.* **1985**, *24*, 202–206.
375. Juris, A.; Belser, P.; Barigelletti, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 256–259.
376. Carlson, D. L.; Murphy, W. R. *Inorg. Chim. Acta* **1991**, *181*, 61–64.
377. McClenaghan, N. D.; Barigelletti, F.; Maubert, B.; Campagna, S. *Chem. Commun.* **2002**, 602–603.
378. Tyson, D. S.; Castellano, F. N. *J. Phys. Chem. A* **1999**, *103*, 10955–10960.
379. Cushing, J. P.; Butoi, C.; Kelley, D. F. *J. Phys. Chem. A* **1997**, *101*, 7222–7230.
380. Farina, S. G.; Yuey, W.; Ambrose, C.; Hoggard, P. E. *Inorg. Chim. Acta* **1988**, *148*, 97–100.
381. Ross, H. B.; Boldaji, M.; Rillema, D. P.; Blanton, C. B.; White, R. P. *Inorg. Chem.* **1989**, *28*, 1013–1021.
382. Mills, A.; Meadows, G. *Inorg. Chem.* **1993**, *32*, 3433–3437.
383. Chirayil, S.; Thummel, R. P. *Inorg. Chem.* **1989**, *28*, 812–813.
384. Treadway, J. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 2267–2278.
385. Weathers, N. R.; Sadoski, R. C.; Durham, B.; Cordes, A. W. *Acta Crystallogr., Sect. C* **1997**, *53*, 1047–1049.
386. Cordes, A. W.; Durham, B.; Pennington, W. T.; Kuntz, B.; Allen, L. *J. Crystallogr. Spectrosc. Res.* **1992**, *22*, 699–704.
387. Heeg, M. J.; Kroener, R.; Deutsch, E. *Acta Crystallogr., Sect. C* **1985**, *41*, 684–686.
388. Indelli, M. T.; Bignozzi, C. A.; Marconi, A.; Scandola, F. *J. Am. Chem. Soc.* **1988**, *110*, 7381–7386.
389. Winkler, J. R.; Sutin, N. *Inorg. Chem.* **1987**, *26*, 220–221.
390. Assefa, Z.; Stanbury, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 521–530.
391. Lee, K. W.; Hoggard, P. E. *Inorg. Chem.* **1993**, *32*, 1877–1878.

392. Tong, C. C.; Winkelman, M.; Jain, A.; Jensen, S. P.; Hoggard, P. E. *Inorg. Chim. Acta* **1994**, *226*, 247–250.
393. Lee, L. S.; Wang, C. H. *J. Photochem. Photobiol. A* **1994**, *79*, 163–166.
394. Wang, Y. X.; Jackman, D. C.; Woods, C.; Rillema, D. P. *J. Chem. Crystallogr.* **1995**, *25*, 549–553.
395. Garas, A.; Craig, D. C.; Vagg, R. S.; Baker, A. T. *J. Coord. Chem.* **2000**, *50*, 79–88.
396. Hesek, D.; Inoue, Y.; Everitt, S. R. L. *Chem. Lett.* **1999**, 109–110.
397. Hesek, D.; Hembury, G. A.; Drew, M. G. B.; Taniguchi, S.; Inoue, Y. *Inorg. Chem.* **2001**, *40*, 2478–2479.
398. Hesek, D.; Inoue, Y.; Everitt, S. R. L.; Ishida, H.; Kunieda, M.; Drew, M. G. B. *Chem. Commun.* **1999**, 403–404.
399. Hesek, D.; Inoue, Y.; Everitt, S. R. L.; Ishida, H.; Kunieda, M.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1999**, 3701–3709.
400. Hesek, D.; Inoue, Y.; Everitt, S. R. L.; Ishida, H.; Kunieda, M.; Drew, M. G. B. *Inorg. Chem.* **2000**, *39*, 317–324.
401. Hesek, D.; Inoue, Y.; Ishida, H.; Everitt, S. R. L.; Drew, M. G. B. *Tetrahedron Lett.* **2000**, *41*, 2617–2620.
402. Prasad, R. *Polyhedron* **1995**, *14*, 2151–2158.
403. Blake, A. J.; Marr, A. M.; Rankin, D. W. H.; Schröder, M. *Acta Crystallogr., Sect. C* **1988**, *44*, 935–936.
404. Churchill, M. R.; Krajkowski, L. M.; Huynh, M. H. V.; Takeuchi, K. J. *J. Chem. Crystallogr.* **1996**, *26*, 111–116.
405. Churchill, M. R.; Krajkowski, L. M.; Huynh, M. H. V.; Takeuchi, K. J. *J. Chem. Crystallogr.* **1996**, *26*, 67–73.
406. Churchill, M. R.; See, R. F.; Bessel, C. A.; Takeuchi, K. J. *J. Chem. Crystallogr.* **1996**, *26*, 667–675.
407. Churchill, M. R.; Krajkowski, L. M.; Huynh, M. H. V.; Takeuchi, K. J. *J. Chem. Crystallogr.* **1996**, *26*, 347–354.
408. Churchill, M. R.; Krajkowski, L. M.; Huynh, M. H. V.; Takeuchi, K. J. *J. Chem. Crystallogr.* **1997**, *27*, 589–597.
409. Churchill, M. R.; Lake, C. H.; Bessel, C. A.; Huynh, M. H. V.; McCourt, J.; Takeuchi, K. J. *J. Chem. Crystallogr.* **1996**, *26*, 267–275.
410. Hesek, D.; Hembury, G. A.; Drew, M. G. B.; Borovkov, V. V.; Inoue, Y. *J. Am. Chem. Soc.* **2001**, *123*, 12232–12237.
411. Litke, S. V.; Mezentseva, T. V.; Litke, A. S.; Lyalin, G. N.; Ershov, A. Y. *Opt. Spectrosc.* **2002**, *92*, 167–171.
412. Ershov, A. Y.; Litke, S. V.; Litke, A. S.; Mezentseva, T. V.; Grigor'ev, Y. M.; Lyalin, G. N. *Russ. J. Gen. Chem.* **2001**, *71*, 1329–1332.
413. Haasnoot, J. G.; Hinrichs, W.; Weir, O.; Vos, J. G. *Inorg. Chem.* **1986**, *25*, 4140–4143.
414. Tanaka, H.; Nagao, H.; Tanaka, K. *Inorg. Chem.* **1992**, *31*, 1971–1973.
415. Tanaka, H.; Tzeng, B.-C.; Nagao, H.; Peng, S.-M.; Tanaka, K. *Inorg. Chem.* **1993**, *32*, 1508–1512.
416. Gibson, D. H.; Ding, Y.; Sleadd, B. A.; Franco, J. O.; Richardson, J. F.; Mashuta, M. S. *J. Am. Chem. Soc.* **1996**, *118*, 11984–11985.
417. Ishida, H.; Fujiki, K.; Ohba, T.; Ohkubo, K.; Tanaka, K.; Terada, T.; Tanaka, T. *J. Chem. Soc., Dalton Trans.* **1990**, 2155–2160.
418. Rutherford, T. J.; Reitsma, D. A.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1994**, 3659–3666.
419. Ollino, M. A.; Rest, A. J. *J. Photochem. Photobiol. A* **1992**, *69*, 73–81.
420. Aydin, N.; Schlaepfer, C. W. *Polyhedron* **2001**, *20*, 37–45.
421. Alguindigue, S. S.; Khan, M. A.; Ashby, M. T. *Inorg. Chim. Acta* **2000**, *310*, 156–162.
422. Hitchcock, P. B.; Seddon, K. R.; Turp, J. E.; Yousif, Y. Z.; Zora, J. A.; Constable, E. C.; Wernberg, O. *J. Chem. Soc., Dalton Trans.* **1988**, 1837–1842.
423. Hua, X.; Lappin, A. G. *Inorg. Chem.* **1995**, *34*, 992–994.
424. Binstead, R. A.; Stultz, L. K.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 546–551.
425. Coe, B. J.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1993**, *32*, 4012–4020.
426. Constable, E. C.; Holmes, J. M. *J. Organomet. Chem.* **1986**, *301*, 203–208.
427. Coudret, C.; Fraysse, S.; Launay, J. P. *Chem. Commun.* **1998**, 663–664.
428. Nagao, N.; Mukaida, M.; Tachiyashiki, S.; Mizumachi, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1802–1808.
429. Nagao, N.; Mukaida, M.; Miki, E.; Mizumachi, K.; Ishimori, T. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2447–2453.
430. Sahni, S. K.; Drew, M. G. B.; Bell, T. W.; Brunschwig, B. S. *J. Chem. Soc., Chem. Commun.* **1993**, 123–125.
431. Keene, F. R.; Lay, P. A.; Sneddon, G. E.; Whebell, G. W. *Aust. J. Chem.* **1993**, *46*, 1763–1774.
432. Thompson, A. M. W. C.; Batten, S. R.; Jeffery, J. C.; Rees, L. H.; Ward, M. D. *Aust. J. Chem.* **1997**, *50*, 109–114.
433. Konno, H.; Ishii, Y.; Sakamoto, K.; Ishitani, O. *Polyhedron* **2002**, *21*, 61–68.
434. Choudhury, S.; Deb, A. K.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1994**, 1305–1310.
435. Thompson, D. W.; Schoonover, J. R.; Graff, D. K.; Fleming, C. N.; Meyer, T. J. *J. Photochem. Photobiol. A* **2000**, *137*, 131–134.
436. Giuffrida, G.; Guglielmo, G.; Ricevuto, V.; Campagna, S. *Chem. Phys. Lett.* **1991**, *180*, 28–33.
437. Nakajima, H.; Nagao, H.; Tanaka, K. *J. Chem. Soc., Dalton Trans.* **1996**, 1405–1409.
438. Bell-Loncella, E. T.; Bessel, C. A. *Inorg. Chim. Acta* **2000**, *303*, 199–205.
439. Llanguri, R.; Morris, J. J.; Stanley, W. C.; Bell-Loncella, E. T.; Turner, M.; Boyko, W. J.; Bessel, C. A. *Inorg. Chim. Acta* **2001**, *315*, 53–65.
440. Sinha, S.; Das, P. K.; Ghosh, B. K. *Polyhedron* **1994**, *13*, 2665–2669.
441. Masui, H.; Lever, A. B. P.; Auburn, P. R. *Inorg. Chem.* **1991**, *30*, 2402–2410.
442. Haga, M.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 447–453.
443. Stufkens, D. J.; Snoeck, T. L.; Lever, A. B. P. *Inorg. Chem.* **1988**, *27*, 953–956.
444. Gooden, V. M.; Cai, H. Q.; Dasgupta, T. P.; Gordon, N. R.; Hughes, L. J.; Sadler, G. G. *Inorg. Chim. Acta* **1997**, *255*, 105–110.
445. DelMedico, A.; Auburn, P. R.; Dodsworth, E. S.; Lever, A. B. P.; Pietro, W. J. *Inorg. Chem.* **1994**, *33*, 1583–1584.
446. DelMedico, A.; Pietro, W. J.; Lever, A. B. P. *Inorg. Chim. Acta* **1998**, *281*, 126–133.
447. Gooden, V. M.; Dasgupta, T. P.; Gordon, N. R.; Sadler, G. G. *Inorg. Chim. Acta* **1998**, *268*, 31–36.
448. da Cunha, C. J.; Fielder, S. S.; Stynes, D. V.; Masui, H.; Auburn, P. R.; Lever, A. B. P. *Inorg. Chim. Acta* **1996**, *242*, 293–302.
449. da Cunha, C. J.; Dodsworth, E. S.; Monteiro, M. A.; Lever, A. B. P. *Inorg. Chem.* **1999**, *38*, 5399–5409.
450. Keyes, T. E.; Jayaweera, P. M.; McGarvey, J. J.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1997**, 1627–1632.
451. Metcalfe, R. A.; Dodsworth, E. S.; Fielder, S. S.; Stufkens, D. J.; Lever, A. B. P.; Pietro, W. J. *Inorg. Chem.* **1996**, *35*, 7741–7750.
452. Schwederski, B.; Kaim, W. *Inorg. Chim. Acta* **1992**, *195*, 123–126.
453. El-Hendawy, A. M.; Al-Kubaisi, A. H.; Al-Madfa, H. A. *Polyhedron* **1997**, *16*, 3039–3045.

454. Basuli, F.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **1998**, *17*, 2191–2197.
455. Constantino, V. R. L.; Toma, H. E.; de Oliveira, L. F. C.; Rein, F. N.; Rocha, R. C.; de Oliveira Silva, D. *J. Chem. Soc., Dalton Trans.* **1999**, 1735–1740.
456. Santra, B. K.; Menon, M.; Pal, C. K.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **1997**, 1387–1393.
457. Baitalik, S.; Adhikary, B. *Polyhedron* **1997**, *16*, 4073–4080.
458. Chakraborty, S.; Walawalkar, M. G.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2000**, 2875–2883.
459. Juriga, G.; Sattgast, M.; McGuire, M. E. *Inorg. Chim. Acta* **1991**, *183*, 39–42.
460. Perkovic, M. W. *Inorg. Chem.* **2000**, *39*, 4962–4968.
461. Rogers, C. W.; Zhang, Y.; Patrick, B. O.; Jones, W. E.; Wolf, M. O. *Inorg. Chem.* **2002**, *41*, 1162–1169.
462. Rogers, C. W.; Wolf, M. O. *Chem. Commun.* **1999**, 2297–2298.
463. Lu, Z. L.; Xiao, W.; Kang, B. S.; Su, C. Y.; Liu, J. *J. Mol. Struct.* **2000**, *523*, 133–141.
464. Chabert, N.; Jacquet, L.; Marzin, C.; Tarrago, G. *New J. Chem.* **1995**, *19*, 443–452.
465. Reddy, K. B.; Cho, M. O. P.; Wishart, J. F.; Emge, T. J.; Isied, S. S. *Inorg. Chem.* **1996**, *35*, 7241–7245.
466. Luo, J.; Reddy, K. B.; Salameh, A. S.; Wishart, J. F.; Isied, S. S. *Inorg. Chem.* **2000**, *39*, 2321–2329.
467. Velders, A. H.; Hotze, A. C. G.; van Albada, G. A.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **2000**, *39*, 4073–4080.
468. Velders, A. H.; Massera, C.; Ugozzoli, F.; Biagini-Cingi, M.; Manotti-Lanfredi, A. M.; Haasnoot, J. G.; Reedijk, J. *Eur. J. Inorg. Chem.* **2002**, 193–198.
469. Bond, A. M.; Haga, M. *Inorg. Chem.* **1986**, *25*, 4507–4514.
470. Haga, M. A.; Tsunemitsu, A. *Inorg. Chim. Acta* **1989**, *164*, 137–142.
471. Luo, Y.; Potvin, P. G.; Tse, Y. H.; Lever, A. B. P. *Inorg. Chem.* **1996**, *35*, 5445–5452.
472. Van Vliet, P. M.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1994**, *33*, 1934–1939.
473. Long, C.; Vos, J. G. *Inorg. Chim. Acta* **1984**, *89*, 125–131.
474. Hage, R.; Prins, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1987**, 1389–1395.
475. Hage, R.; Turkenburg, J. P.; Degraaff, R. A. G.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Acta Crystallogr., Sect. C* **1989**, *45*, 381–383.
476. Hage, R.; Haasnoot, J. G.; Reedijk, J.; Wang, R.; Ryan, E. M.; Vos, J. G.; Spek, A. L.; Duisenberg, A. J. M. *Inorg. Chim. Acta* **1990**, *174*, 77–85.
477. Fennema, B.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chim. Acta* **1990**, *171*, 223–228.
478. Hage, R.; Haasnoot, J. G.; Nieuwenhuis, H. A.; Reedijk, J.; Wang, R.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1991**, 3271–3275.
479. Nieuwenhuis, H. A.; Haasnoot, J. G.; Hage, R.; Reedijk, J.; Snoeck, T. L.; Stufkens, D. J.; Vos, J. G. *Inorg. Chem.* **1991**, *30*, 48–54.
480. Hage, R.; Haasnoot, J. G.; Reedijk, J.; Wang, R. Y.; Vos, J. G. *Inorg. Chem.* **1991**, *30*, 3263–3269.
481. Giuffrida, G.; Ricevuto, V.; Guglielmo, G.; Campagna, S.; Ciano, M. *Inorg. Chim. Acta* **1992**, *194*, 23–29.
482. Barigelletti, F.; Decola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* **1991**, *30*, 641–645.
483. Barigelletti, F.; Decola, L.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Inorg. Chem.* **1989**, *28*, 4344–4350.
484. Wang, R.; Vos, J. G.; Schmehl, R. H.; Hage, R. *J. Am. Chem. Soc.* **1992**, *114*, 1964–1970.
485. Hu, Z. S.; Lin, Y. H.; Jin, S. C.; Vos, J. G. *Acta Crystallogr., Sect. C* **1989**, *45*, 1490–1493.
486. Buchanan, B. E.; Wang, R. Y.; Vos, J. G.; Hage, R.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 3263–3265.
487. Buchanan, B. E.; Vos, J. G.; Kaneko, M.; Vanderputten, W. J. M.; Kelly, J. M.; Hage, R.; Degraaff, R. A. G.; Prins, R.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1990**, 2425–2431.
488. Buchanan, B. E.; Hughes, H.; Vandiemen, J. H.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *J. Chem. Soc., Chem. Commun.* **1991**, 300–301.
489. Buchanan, B. E.; Degn, P.; Velasco, J. M. P.; Hughes, H.; Creaven, B. S.; Long, C.; Vos, J. G.; Howie, R. A.; Hage, R.; Vandiemen, J. H.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1992**, 1177–1183.
490. Keyes, T. E.; Weldon, F.; Muller, E.; Pechy, P.; Grätzel, M.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1995**, 2705–2706.
491. Keyes, T. E.; O'Connor, C.; Vos, J. G. *Chem. Commun.* **1998**, 889–890.
492. Keyes, T. E.; O'Connor, C. M.; ODwyer, U.; Coates, C. G.; Callaghan, P.; McGarvey, J. J.; Vos, J. G. *J. Phys. Chem. A* **1999**, *103*, 8915–8920.
493. Keyes, T. E.; Vos, J. G.; Kolnaar, J. A.; Haasnoot, J. G.; Reedijk, J.; Hage, R. *Inorg. Chim. Acta* **1996**, *245*, 237–242.
494. Fanni, S.; Keyes, T. E.; Campagna, S.; Vos, J. G. *Inorg. Chem.* **1998**, *37*, 5933–5935.
495. Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1998**, *84*, 85–277.
496. Downard, A. J.; Steel, P. J.; Steenwijk, J. *Aust. J. Chem.* **1995**, *48*, 1625–1642.
497. Dunne, S. J.; Constable, E. C. *Inorg. Chem. Commun.* **1998**, *1*, 167–169.
498. MacLean, B. J.; Pickup, P. G. *J. Mater. Chem.* **2001**, *11*, 1357–1363.
499. Fennema, B.; Degraaff, R. A. G.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1043–1049.
500. Canty, A. J.; Traill, P. R.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **1997**, *255*, 117–123.
501. Bolger, J. A.; Ferguson, G.; James, J. P.; Long, C.; Mcardle, P.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1993**, 1577–1583.
502. Wang, P. F.; Onozawa-Komatsuzaki, N.; Katoh, R.; Himeda, Y.; Sugihara, H.; Arakawa, H.; Kasuga, K. *Chem. Lett.* **2001**, 940–941.
503. Ferrari, M. B.; Fava, G. G.; Pelosi, G.; Predieri, G.; Vignali, C.; Denti, G.; Serroni, S. *Inorg. Chim. Acta* **1998**, *276*, 320–326.
504. Roffia, S.; Marcaccio, M.; Paradisi, C.; Paolucci, F.; Balzani, V.; Denti, G.; Serroni, S.; Campagna, S. *Inorg. Chem.* **1993**, *32*, 3003–3009.
505. Casalboni, F.; Mulazzani, Q. G.; Clark, C. D.; Hoffman, M. Z.; Orizondo, P. L.; Perkovic, M. W.; Rillema, D. P. *Inorg. Chem.* **1997**, *36*, 2252–2257.
506. Clark, C. D.; Hoffman, M. Z.; Rillema, D. P.; Mulazzani, Q. G. *J. Photochem. Photobiol. A* **1997**, *110*, 285–290.

507. Xue, W. M.; Perez, W. J.; Rillema, D. P. *Inorg. Chim. Acta* **1999**, *296*, 114–126.
508. Ait-Haddou, H.; Bejan, E.; Daran, J. C.; Balavoine, G. G. A.; Berruyer-Penaud, F.; Bonazzola, L.; Smaoui-Chaabouni, H.; Amouyal, E. *J. Chem. Soc., Dalton Trans.* **1999**, 3095–3101.
509. Garoufis, A.; Koutsodimou, A.; Katsaros, N.; Mitsopoulou, C. A.; Hadjiliadis, N. *Polyhedron* **1999**, *18*, 361–369.
510. Richter, M. M.; Brewer, K. J. *Inorg. Chim. Acta* **1991**, *180*, 125–131.
511. Scott, S. M.; Gordon, K. C. *Inorg. Chim. Acta* **1997**, *254*, 267–272.
512. Treadway, J. A.; Strouse, G. F.; Ruminski, R. R.; Meyer, T. J. *Inorg. Chem.* **2001**, *40*, 4508–4509.
513. Taffarel, E.; Chirayil, S.; Kim, W. Y.; Thummel, R. P.; Schmehl, R. H. *Inorg. Chem.* **1996**, *35*, 2127–2131.
514. Campagna, S.; Mamo, A.; Stille, J. K. *J. Chem. Soc., Dalton Trans.* **1991**, 2545–2551.
515. Farah, A. A.; Zobi, F.; Stynes, D. V.; Lough, A. J.; Pietro, W. J. *Acta Crystallogr., Sect. E* **2001**, *57*, 274–276.
516. Wang, Y. X.; Jackman, D. C.; Woods, C.; Rillema, D. P. *J. Chem. Crystallogr.* **1995**, *25*, 549–553.
517. Wang, Y. X.; Perez, W.; Zheng, G. Y.; Rillema, D. P. *Inorg. Chem.* **1998**, *37*, 2051–2059.
518. Thummel, R. P.; Williamson, D.; Hery, C. *Inorg. Chem.* **1993**, *32*, 1587–1596.
519. Ye, B. H.; Ji, L. N.; Xue, F.; Mak, T. C. W. *Transit. Metal Chem.* **1999**, *24*, 8–12.
520. Turro, C.; Bossmann, S. H.; Leroi, G. E.; Barton, J. K.; Turro, N. J. *Inorg. Chem.* **1994**, *33*, 1344–1347.
521. Tzalis, D.; Tor, Y. *Chem. Commun.* **1996**, 1043–1044.
522. Jing, B. W.; Song, A. M.; Zhang, M. H.; Shen, T. *Chem. Lett.* **1999**, 789–790.
523. Chao, H.; Li, R.-H.; Yi, B.-H.; Li, H.; Feng, X.-L.; Cai, J.-W.; Zhou, J.-Y.; Ji, L.-N. *J. Chem. Soc., Dalton Trans.* **1999**, 3711–3717.
524. Amouyal, E.; Homsi, A.; Chambron, J. C.; Sauvage, J.-P. *J. Chem. Soc., Dalton Trans.* **1990**, 1841–1845.
525. Gut, D.; Rudi, A.; Kopilov, J.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2002**, *124*, 5449–5456.
526. Gulyas, P. T.; Smith, T. A.; Paddon-Row, M. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1325–1335.
527. Kelso, L. S.; Smith, T. A.; Schultz, A. C.; Junk, P. C.; Warrener, R. N.; Ghiggino, K. P.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **2000**, 2599–2606.
528. Jacquet, L.; Kirsch-De Mesmaeker, A. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 2471–2480.
529. Golka, A.; Craig, D. C.; Paddon-Row, M. N. *Aust. J. Chem.* **1994**, *47*, 101–110.
530. Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145–6157.
531. Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253–8268.
532. Damrauer, N. H.; McCusker, J. K. *J. Phys. Chem. A* **1999**, *103*, 8440–8446.
533. Tachiyashiki, S.; Nakamaru, K.; Mizumachi, K. *Chem. Lett.* **1992**, 1119–1122.
534. Treffert-Ziemelis, S. M.; Golus, J.; Strommen, D. P.; Kincaid, J. R. *Inorg. Chem.* **1993**, *32*, 3890–3894.
535. Black, S. I.; Skapski, A. C.; Young, G. B. *J. Chem. Soc., Chem. Commun.* **1989**, 911–913.
536. Yousif, Y. Z.; Alrawi, J. M. A. *Polyhedron* **1992**, *11*, 1411–1418.
537. Collins, J. E.; Lamba, J. J. S.; Love, J. C.; McAlvin, J. E.; Ng, C.; Peters, B. P.; Wu, X. F.; Fraser, C. L. *Inorg. Chem.* **1999**, *38*, 2020–2024.
538. Fletcher, N. C.; Nieuwenhuyzen, M.; Rainey, S. *J. Chem. Soc., Dalton Trans.* **2001**, 2641–2648.
539. Holder, E.; Schoetz, G.; Schurig, V.; Lindner, E. *Tetrahedron: Asymmetry* **2001**, *12*, 2289–2293.
540. Constable, E. C.; Henney, R. P. G.; Leese, T. A.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1990**, 443–449.
541. Decola, L.; Barigelletti, F.; Cook, M. J. *Helv. Chim. Acta* **1988**, *71*, 733–741.
542. Wang, Y. S.; Liu, S. X.; Pinto, M. R.; Dattelbaum, D. M.; Schoonover, J. R.; Schanze, K. S. *J. Phys. Chem. A* **2001**, *105*, 11118–11127.
543. Harriman, A.; Hissler, M.; Khatyr, A.; Ziessel, R. *Chem. Commun.* **1999**, 735–736.
544. Sessler, J. L.; Brown, C. T.; Wang, R. Z.; Hirose, T. *Inorg. Chim. Acta* **1996**, *251*, 135–140.
545. Williams, C. E.; Lowry, B. B.; Braven, J.; Belt, S. T. *Inorg. Chim. Acta* **2001**, *315*, 112–119.
546. Bommarito, S. L.; Lowery-Bretz, S. P.; Abruña, H. D. *Inorg. Chem.* **1992**, *31*, 495–502.
547. Bommarito, S. L.; Lowery-Bretz, S. P.; Abruña, H. D. *Inorg. Chem.* **1992**, *31*, 502–507.
548. Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 333–338.
549. Abdel-Shafi, A. A.; Beer, P. D.; Mortimer, R. J.; Wilkinson, F. *J. Phys. Chem. A* **2000**, *104*, 192–202.
550. Aranyos, V.; Hjelm, J.; Hagfeldt, A.; Grennberg, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1319–1325.
551. Beer, P. D.; Kocian, O.; Mortimer, R. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3283–3288.
552. Horwitz, C. P.; Zuo, Q. *Inorg. Chem.* **1992**, *31*, 1607–1613.
553. Lau, C. P.; Chen, Y. Z. *J. Mol. Catal. A-Chem.* **1995**, *101*, 33–36.
554. Araki, K.; Fuse, M.; Kishii, N.; Shiraishi, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1220–1224.
555. Curtright, A. E.; McCusker, J. K. *J. Phys. Chem. A* **1999**, *103*, 7032–7041.
556. Slattery, S. J.; Gokaldas, N.; Mick, T.; Goldsby, K. A. *Inorg. Chem.* **1994**, *33*, 3621–3624.
557. Katoh, A.; Kitamura, Y.; Fujii, H.; Horie, Y.; Satoh, T.; Ohkanda, J.; Yokomori, Y. *Heterocycles* **1998**, *49*, 281–296.
558. Toma, H. E.; Serrasqueiro, R. M.; Rocha, R. C.; Demets, G. J. F.; Winnischofer, H.; Araki, K.; Ribeiro, P. E. A.; Donnici, C. L. *J. Photochem. Photobiol. A* **2000**, *135*, 185–191.
559. Zhu, S. S.; Kingsborough, R. P.; Swager, T. M. *J. Mater. Chem.* **1999**, *9*, 2123–2131.
560. Lepoittevin, J. P.; Mattes, H.; Benezra, C. *Tetrahedron Lett.* **1987**, *28*, 4339–4342.
561. Shukla, A. D.; Whittle, B.; Bajaj, H. C.; Das, A.; Ward, M. D. *Inorg. Chim. Acta* **1999**, *285*, 89–96.
562. Juris, A.; Prodi, L. *New J. Chem.* **2001**, *25*, 1132–1135.
563. Amouyal, E.; Penaud-Berruyer, F.; Azhari, D.; Ait-Haddou, H.; Fontenas, C.; Bejan, E.; Daran, J. C.; Balavoine, G. G. A. *New J. Chem.* **1998**, *22*, 373–380.
564. Bossmann, S.; Durr, H. *New J. Chem.* **1992**, *16*, 769–770.
565. Durr, H.; Bossmann, S.; Schwarz, R.; Kropf, M.; Hayo, R.; Turro, N. J. *J. Photochem. Photobiol. A* **1994**, *80*, 341–350.
566. Hu, Y. Z.; Bossmann, S. H.; van Loyen, D.; Schwarz, O.; Durr, H. *Chem.-Eur. J.* **1999**, *5*, 1267–1277.
567. Chambron, J. C.; Sauvage, J. P. *New J. Chem.* **1990**, *14*, 883–889.
568. Shan, B. Z.; Zhao, Q.; Goswami, N.; Eichhorn, D. M.; Rillema, D. P. *Coord. Chem. Rev.* **2001**, *211*, 117–144.
569. Masui, H.; Murray, R. W. *Inorg. Chem.* **1997**, *36*, 5118–5126.
570. Pichot, F.; Beck, J. H.; Elliott, C. M. *J. Phys. Chem. A* **1999**, *103*, 6263–6267.

571. Yang, X. J.; Janiak, C.; Heinze, J.; Drepper, F.; Mayer, P.; Piotrowski, H.; Klufers, P. *Inorg. Chim. Acta* **2001**, *318*, 103–116.
572. Geisser, B.; Ponce, A.; Alsfasser, R. *Inorg. Chem.* **1999**, *38*, 2030–2037.
573. Bolletta, F.; Costa, I.; Fabbrizzi, L.; Licchelli, M.; Montalti, M.; Pallavicini, P.; Prodi, L.; Zaccheroni, N. *J. Chem. Soc., Dalton Trans.* **1999**, 1381–1385.
574. Hirao, T.; Iida, K. *Chem. Commun.* **2001**, 431–432.
575. Thummel, R. P.; Lefoulon, F.; Korp, J. D. *Inorg. Chem.* **1987**, *26*, 2370–2376.
576. Macatangay, A.; Zheng, G. Y.; Rillema, D. P.; Jackman, D. C.; Merkert, J. W. *Inorg. Chem.* **1996**, *35*, 6823–6831.
577. Beeston, R. F.; Aldridge, W. S.; Treadway, J. A.; Fitzgerald, M. C.; DeGraff, B. A.; Stitzel, S. E. *Inorg. Chem.* **1998**, *37*, 4368–4379.
578. Galland, B.; Limosin, D.; Laguitton-Pasquier, H.; Deronzier, A. *Inorg. Chem. Commun.* **2002**, *5*, 5–8.
579. Maggini, M.; Guldi, D. M.; Mondini, S.; Scorrano, G.; Paolucci, F.; Ceroni, P.; Roffia, S. *Chem.-Eur. J.* **1998**, *4*, 1992–2000.
580. Nazzeeruddin, M.; Grätzel, M. *Comprehensive Coordination Chemistry II*, McCleverty, J. A.; Meyer, T. J., eds. Elsevier: Amsterdam, 2003, Vol. 9, in press.
581. Roberts, J. A.; Kirby, J. P.; Wall, S. T.; Nocera, D. G. *Inorg. Chim. Acta* **1997**, *263*, 395–405.
582. Hammarström, L.; Alsins, J.; Borje, A.; Norrby, T.; Zhang, L. A.; Akermark, B. *J. Photochem. Photobiol. A* **1997**, *102*, 139–150.
583. Ranatunga, A.; Lasey, R. C.; Ogawa, M. Y. *Inorg. Chem. Commun.* **2001**, *4*, 30–32.
584. Fernando, S. R. L.; Maharoof, U. S. M.; Deshayes, K. D.; Kinstle, T. H.; Ogawa, M. Y. *J. Am. Chem. Soc.* **1996**, *118*, 5783–5790.
585. Kalyanasundaram, K.; Nazeeruddin, M. K. *Chem. Phys. Lett.* **1992**, *193*, 292–297.
586. Zheng, G. Y.; Wang, Y.; Rillema, D. P. *Inorg. Chem.* **1996**, *35*, 7118–7123.
587. Xie, P. H.; Hou, Y. J.; Zhang, B. W.; Cao, Y. *J. Photochem. Photobiol. A* **1999**, *122*, 169–174.
588. Zakeeruddin, S. M.; Nazeeruddin, M. K.; Humphry-Baker, R.; Grätzel, M. *Inorg. Chim. Acta* **1999**, *296*, 250–253.
589. Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Gorelsky, S. I.; Lever, A. B. P.; Grätzel, M. *Coord. Chem. Rev.* **2000**, *208*, 213–225.
590. Patterson, B. T.; Keene, F. R. *Aust. J. Chem.* **1998**, *51*, 999–1002.
591. Eskelinen, E.; Luukkanen, S.; Haukka, M.; Ahlgrén, M.; Pakkanen, T. A. *J. Chem. Soc., Dalton Trans.* **2000**, 2745–2752.
592. Falaras, P.; Xagas, A. P.; Hugot-Le Goff, A. *New J. Chem.* **1998**, *22*, 557–558.
593. Park, J. W.; Ahn, J. H.; Lee, C. M. *J. Photochem. Photobiol. A* **1995**, *86*, 89–95.
594. Hou, Y. J.; Xie, P. H.; Zhang, B. W.; Cao, Y.; Xiao, X. R.; Wang, W. B. *Inorg. Chem.* **1999**, *38*, 6320–6322.
595. Zakeeruddin, S. M.; Nazeeruddin, M. K.; Humphry-Baker, R.; Grätzel, M.; Shklover, V. *Inorg. Chem.* **1998**, *37*, 5251–5259.
596. Takahashi, Y.; Arakawa, H.; Sugihara, H.; Hara, K.; Islam, A.; Katoh, R.; Tachibana, Y.; Yanagida, M. *Inorg. Chim. Acta* **2000**, *310*, 169–174.
597. Fletcher, N. C.; Nieuwenhuyzen, M.; Prabarahan, R.; Wilson, A. *Chem. Commun.* **2002**, 1188–1189.
598. Kalyanasundaram, K.; Nazeeruddin, M. K.; Grätzel, M.; Viscardi, G.; Savarino, P.; Barni, E. *Inorg. Chim. Acta* **1992**, *200*, 831–839.
599. Islam, A.; Sugihara, H.; Singh, L. P.; Hara, K.; Katoh, R.; Nagawa, Y.; Yanagida, M.; Takahashi, Y.; Murata, S.; Arakawa, H. *Inorg. Chim. Acta* **2001**, *322*, 7–16.
600. Chen, P. Y.; Omberg, K. M.; Kavaliunas, D. A.; Treadway, J. A.; Palmer, R. A.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 954.
601. Omberg, K. M.; Smith, G. D.; Kavaliunas, D. A.; Chen, P. Y.; Treadway, J. A.; Schoonover, J. R.; Palmer, R. A.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 951–956.
602. Ben Hadda, T.; Sam, N.; Le Bozec, H.; Dixneuf, P. H. *Inorg. Chem. Commun.* **1999**, *2*, 460–462.
603. Anderson, S.; Constable, E. C.; Seddon, K. R.; Turp, J. E.; Baggott, J. E.; Pilling, M. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2247–2261.
604. Montalti, M.; Wadhwa, S.; Kim, W. Y.; Kipp, R. A.; Schmehl, R. H. *Inorg. Chem.* **2000**, *39*, 76–84.
605. Cargill Thompson, A. M. W.; Smailes, M. C. C.; Jeffery, J. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1997**, 737–743.
606. Guardigli, M.; Flamigni, L.; Barigelletti, F.; Richards, C. S. W.; Ward, M. D. *J. Phys. Chem.* **1996**, *100*, 10620–10628.
607. Bierig, K.; Morgan, R. J.; Tysoe, S.; Gafney, H. D.; Strekas, T. C.; Baker, A. D. *Inorg. Chem.* **1991**, *30*, 4898–4903.
608. Hayes, M. A.; Meckel, C.; Schatz, E.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1992**, 703–708.
609. Didier, P.; Jacquet, L.; Kirsch-De Mesmaeker, A.; Hueber, R.; van Dorsselaer, A. *Inorg. Chem.* **1992**, *31*, 4803–4809.
610. Bignozzi, C. A.; Bortolini, O.; Traldi, P. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 600–603.
611. Denti, G.; Serroni, S.; Sindona, G.; Uccella, N. *J. Amer. Soc. Mass Spectrom.* **1993**, *4*, 306–311.
612. Argazzi, R.; Bignozzi, C. A.; Bortolini, O.; Traldi, P. *Inorg. Chem.* **1993**, *32*, 1222–1225.
613. Kelso, L. S.; Reitsma, D. A.; Keene, F. R. *Inorg. Chem.* **1996**, *35*, 5144–5153.
614. Chakraborty, S.; Munshi, P.; Lahiri, G. K. *Polyhedron* **1999**, *18*, 1437–1444.
615. Tolbert, L. M.; Zhao, X. D.; Ding, Y. Z.; Bottomley, L. A. *Inorg. Chim. Acta* **1996**, *251*, 29–33.
616. Chakraborty, S.; Laye, R. H.; Munshi, P.; Paul, R. L.; Ward, M. D.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2002**, 2348–2353.
617. Jeffery, J. C.; Liard, D. J.; Ward, M. D. *Inorg. Chim. Acta* **1996**, *251*, 9–12.
618. Bardwell, D.; Jeffery, J. C.; Joulie, L.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2255–2256.
619. Bardwell, D. A.; Horsburgh, L.; Jeffery, J. C.; Joulie, L. F.; Ward, M. D.; Webster, I.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1996**, 2527–2531.
620. Bignozzi, C. A.; Indelli, M. T.; Scandola, F. *J. Am. Chem. Soc.* **1989**, *111*, 5192–5198.
621. Bignozzi, C. A.; Argazzi, R.; Chiorboli, C.; Scandola, F.; Dyer, R. B.; Schoonover, J. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 1652–1659.
622. Bignozzi, C. A.; Argazzi, R.; Bortolini, O.; Scandola, F.; Harriman, A. *New J. Chem.* **1996**, *20*, 731–738.

623. Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Scandola, F.; Bertolasi, V.; Gilli, G. *J. Chem. Soc., Dalton Trans.* **1994**, 2391–2395.
624. Bignozzi, C. A.; Bortolini, O.; Chiorboli, C.; Indelli, M. T.; Rampi, M. A.; Scandola, F. *Inorg. Chem.* **1992**, *31*, 172–177.
625. Veletsky, N. I.; Dementiev, I. A.; Ershov, A. Y.; Nikolskii, A. B. *J. Photochem. Photobiol. A* **1995**, *89*, 99–103.
626. Wang, P. W.; Fox, M. A. *Inorg. Chem.* **1995**, *34*, 36–41.
627. Haid, R.; Gutmann, R.; Stampfl, T.; Langes, C.; Czermak, G.; Kopacka, H.; Ongania, K. H.; Bruggeller, P. *Inorg. Chem.* **2001**, *40*, 7099–7104.
628. Barigelletti, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1–12.
629. Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, *96*, 759–833.
630. Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85–277.
631. Ward, M. D. *Chem. Soc. Rev.* **1997**, *26*, 365–375.
632. Schoonover, J. R.; Bignozzi, C. A.; Meyer, T. J. *Coord. Chem. Rev.* **1997**, *165*, 239–266.
633. von Zelewsky, A.; Belser, P.; Hayoz, P.; Dux, R.; Hua, X.; Suckling, A.; Stoeckli-Evans, H. *Coord. Chem. Rev.* **1994**, *132*, 75–85.
634. Ward, M. D.; Barigelletti, F. *Coord. Chem. Rev.* **2001**, *216*, 127–154.
635. Beyeler, A.; Belser, P. *Coord. Chem. Rev.* **2002**, *230*, 29–39.
636. Furue, M.; Ishibashi, M.; Satoh, A.; Oguni, T.; Maruyama, K.; Sumi, K.; Kamachi, M. *Coord. Chem. Rev.* **2000**, *208*, 103–113.
637. Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1987**, *26*, 2989–2994.
638. Furue, M.; Kuroda, N.; Nozakura, S. *Chem. Lett.* **1986**, 1209–1212.
639. Furue, M.; Yoshidzumi, T.; Kinoshita, S.; Kushida, T.; Nozakura, S.; Kamachi, M. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1632–1640.
640. Furue, M.; Kinoshita, S.; Kushida, T. *Chem. Lett.* **1987**, 2355–2358.
641. Furue, M.; Maruyama, K.; Kanematsu, Y.; Kushida, T.; Kamachi, M. *Coord. Chem. Rev.* **1994**, *132*, 201–208.
642. Larson, S. L.; Hendrickson, S. M.; Ferrere, S.; Derr, D. L.; Elliott, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 5881–5882.
643. Boyde, S.; Strouse, G. F.; Jones, W. E.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7395–7396.
644. Strouse, G. F.; Schoonover, J. R.; Duesing, R.; Boyde, S.; Jones, W. E.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 473–487.
645. Decola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L.; Belser, P.; von Zelewsky, A.; Frank, M.; Vogtle, F. *Inorg. Chem.* **1993**, *32*, 5228–5238.
646. Frank, M.; Nieger, M.; Vogtle, F.; Belser, P.; von Zelewsky, A.; Decola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L. *Inorg. Chim. Acta* **1996**, *242*, 281–291.
647. De Cola, L.; Balzani, V.; Barigelletti, F.; Flamigni, L.; Belser, P.; Bernhard, S. *Rec. Trav. Chim.* **1995**, *114*, 534–541.
648. El-ghayoury, A.; Harriman, A.; Khatyr, A.; Ziessel, R. *J. Phys. Chem. A* **2000**, *104*, 1512–1523.
649. Warrener, R. N.; Ferreira, A. B. B.; Schultz, A. C.; Butler, D. N.; Keene, F. R.; Kelso, L. S. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2485–2487.
650. Schultz, A. C.; Kelso, L. S.; Johnston, M. R.; Warrener, R. N.; Keene, F. R. *Inorg. Chem.* **1999**, *38*, 4906–4909.
651. Constable, E. C.; Rees, D. G. F. *New J. Chem.* **1997**, *21*, 369–376.
652. Bilakhiya, A. K.; Tyagi, B.; Paul, P. *Polyhedron* **2000**, *19*, 1233–1243.
653. Del Guerzo, A.; Leroy, S.; Fages, F.; Schmehl, R. H. *Inorg. Chem.* **2002**, *41*, 359–366.
654. Pappenfus, T. M.; Mann, K. R. *Inorg. Chem.* **2001**, *40*, 6301–6307.
655. Inoue, M.; Cedeño, R. *Inorg. Chim. Acta* **1988**, *145*, 117–120.
656. Furue, M.; Ishibashi, M.; Satoh, A.; Oguni, T.; Maruyama, K.; Sumi, K.; Kamachi, M. *Coord. Chem. Rev.* **2000**, *208*, 103–113.
657. Belser, P.; Dux, R.; Baak, M.; Decola, L.; Balzani, V. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 595–598.
658. Juris, A.; Balzani, V.; Campagna, S.; Denti, G.; Serroni, S.; Frei, G.; Gudel, H. U. *Inorg. Chem.* **1994**, *33*, 1491–1496.
659. Downard, A. J.; Honey, G. E.; Phillips, L. F.; Steel, P. J. *Inorg. Chem.* **1991**, *30*, 2259–2260.
660. Balzani, V.; Bardwell, D. A.; Barigelletti, F.; Cleary, F. L.; Guardigli, M.; Jeffery, J. C.; Sovrani, T.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 3601–3608.
661. Bardwell, D. A.; Barigelletti, F.; Cleary, R. L.; Flamigni, L.; Guardigli, M.; Jeffery, J. C.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 2438–2446.
662. Schoonover, J. R.; Shreve, A. P.; Dyer, R. B.; Cleary, R. L.; Ward, M. D.; Bignozzi, C. A. *Inorg. Chem.* **1998**, *37*, 2598–2601.
663. Ho, P. K. K.; Cheung, K. K.; Che, C. M. *Chem. Commun.* **1996**, 1197–1198.
664. Haga, M. A.; Bond, A. M. *Inorg. Chem.* **1991**, *30*, 475–480.
665. Rau, S.; Ruben, M.; Buttner, T.; Temme, C.; Dautz, S.; Gorls, H.; Rudolph, M.; Walther, D.; Brodkorb, A.; Duati, M.; O'Connor, C.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **2000**, 3649–3657.
666. Nozaki, K.; Ikeda, N.; Ohno, T. *New J. Chem.* **1996**, *20*, 739–748.
667. Gholamkhass, B.; Nozaki, K.; Ohno, T. *J. Phys. Chem. B* **1997**, *101*, 9010–9021.
668. Haga, M.; Ano, T.; Kano, K.; Yamabe, S. *Inorg. Chem.* **1991**, *30*, 3843–3849.
669. Haga, M.; Ano, T.; Ishizaki, T.; Kano, K.; Nozaki, K.; Ohno, T. *J. Chem. Soc., Dalton Trans.* **1994**, 263–272.
670. Cameron, C. G.; Pickup, P. G. *Chem. Commun.* **1997**, 303–304.
671. Cameron, C. G.; Pittman, T. J.; Pickup, P. G. *J. Phys. Chem. B* **2001**, *105*, 8838–8844.
672. Haga, M. A.; Ali, M. M.; Koseki, S.; Fujimoto, K.; Yoshimura, A.; Nozaki, K.; Ohno, T.; Nakajima, K.; Stufkens, D. J. *Inorg. Chem.* **1996**, *35*, 3335–3347.
673. Baitalik, S.; Florke, U.; Nag, K. *Inorg. Chem.* **1999**, *38*, 3296–3308.
674. Haga, M.; Ale, M. M.; Koseki, S.; Yoshimura, A.; Nozaki, K.; Ohno, T. *Inorg. Chim. Acta* **1994**, *226*, 17–24.
675. Hage, R. *Coord. Chem. Rev.* **1991**, *111*, 161–166.
676. Decola, L.; Barigelletti, F.; Balzani, V.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *Chem. Phys. Lett.* **1991**, *178*, 491–496.
677. Giuffrida, G.; Calogero, G.; Guglielmo, G.; Ricevuto, V.; Ciano, M.; Campagna, S. *Inorg. Chem.* **1993**, *32*, 1179–1183.

678. Giuffrida, G.; Calogero, G.; Ricevuto, V.; Campagna, S. *Inorg. Chem.* **1995**, *34*, 1957–1960.
679. Browne, W. R.; O'Connor, C. M.; Villani, C.; Vos, J. G. *Inorg. Chem.* **2001**, *40*, 5461–5464.
680. Hughes, H. P.; Martin, D.; Bell, S.; McGarvey, J. J.; Vos, J. G. *Inorg. Chem.* **1993**, *32*, 4402–4408.
681. Coates, C. G.; Keyes, T. E.; Hughes, H. P.; Jayaweera, P. M.; McGarvey, J. J.; Vos, J. G. *J. Phys. Chem. A* **1998**, *102*, 5013–5018.
682. Muller, E.; Nazeeruddin, M. K.; Gratzel, M.; Kalyanasundaram, K.; Prome, J. C. *New J. Chem.* **1996**, *20*, 759–772.
683. Weldon, F. M.; Vos, J. G. *Inorg. Chim. Acta* **2000**, *307*, 13–19.
684. Hage, R.; Lempers, H. E. B.; Haasnoot, J. G.; Reedijk, J.; Weldon, F. M.; Vos, J. G. *Inorg. Chem.* **1997**, *36*, 3139–3145.
685. Di Pietro, C.; Serroni, S.; Campagna, S.; Gandolfi, M. T.; Ballardini, R.; Fanni, S.; Browne, W. R.; Vos, J. G. *Inorg. Chem.* **2002**, *41*, 2871–2878.
686. Hughes, H. P.; Vos, J. G. *Inorg. Chem.* **1995**, *34*, 4001–4003.
687. Richter, M. M.; Jensen, G. E.; Brewer, K. J. *Inorg. Chim. Acta* **1995**, *230*, 35–40.
688. Richter, M. M.; Brewer, K. J. *Inorg. Chem.* **1992**, *31*, 1594–1598.
689. Richter, M. M.; Brewer, K. J. *Inorg. Chem.* **1993**, *32*, 2827–2834.
690. Cooper, J. B.; MacQueen, D. B.; Petersen, J. D.; Wertz, D. W. *Inorg. Chem.* **1990**, *29*, 3701–3705.
691. Molnar, S. M.; Neville, K. R.; Jensen, G. E.; Brewer, K. J. *Inorg. Chim. Acta* **1993**, *206*, 69–76.
692. Kalyanasundaram, K.; Grätzel, M.; Nazeeruddin, M. K. *J. Chem. Soc., Dalton Trans.* **1991**, 343–346.
693. Thompson, D. W.; Wallace, A. W.; Swayambunathan, V.; Endicott, J. F.; Petersen, J. D.; Ronco, S. E.; Hsiao, J. S.; Schoonover, J. R. *J. Phys. Chem. A* **1997**, *101*, 8152–8156.
694. D'Alessandro, D. M.; Kelso, L. S.; Keene, F. R. *Inorg. Chem.* **2001**, *40*, 6841–6844.
695. Milkevitch, M.; Brauns, E.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 1737–1739.
696. Johnson, J. E. B.; Ruminski, R. R. *Inorg. Chim. Acta* **1993**, *208*, 231–237.
697. Morgan, O.; Wang, S.; Bae, S. A.; Morgan, R. J.; Baker, A. D.; Strekas, T. C.; Engel, R. *J. Chem. Soc., Dalton Trans.* **1997**, 3773–3776.
698. Knapp, R.; Schott, A.; Rehahn, M. *Macromolecules* **1996**, *29*, 478–480.
699. MacDonnell, F. M.; Bodige, S. *Inorg. Chem.* **1996**, *35*, 5758–5759.
700. Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J. P. *J. Chem. Soc., Chem. Commun.* **1995**, 1799–1800.
701. Bolger, J.; Gourdon, A.; Ishow, E.; Launay, J. P. *Inorg. Chem.* **1996**, *35*, 2937–2944.
702. Chiorboli, C.; Bignozzi, C. A.; Scandola, F.; Ishow, E.; Gourdon, A.; Launay, J. P. *Inorg. Chem.* **1999**, *38*, 2402–2410.
703. Ishow, E.; Gourdon, A.; Launay, J. P.; Chiorboli, C.; Scandola, F. *Inorg. Chem.* **1999**, *38*, 1504–1510.
704. Ishow, E.; Gourdon, A.; Launay, J. P. *Chem. Commun.* **1998**, 1909–1910.
705. Staffilani, M.; Belser, P.; De Cola, L.; Hartl, F. *Eur. J. Inorg. Chem.* **2002**, 335–339.
706. Phillips, I. G.; Steel, P. J. *Aust. J. Chem.* **1998**, *51*, 371–382.
707. Phillips, I. G.; Steel, P. J. *Inorg. Chim. Acta* **1996**, *244*, 3–5.
708. Berger, R. M.; Ellis, D. D. *Inorg. Chim. Acta* **1996**, *241*, 1–4.
709. Berger, R. M.; Holcombe, J. R. *Inorg. Chim. Acta* **1995**, *232*, 217–221.
710. Kaim, W.; Fees, J. *Z. Naturforsch., Teil B* **1995**, *50*, 123–127.
711. Gordon, K. C.; Burrell, A. K.; Simpson, T. J.; Page, S. E.; Kelso, G.; Polson, M. I. J.; Flood, A. *Eur. J. Inorg. Chem.* **2002**, 554–563.
712. Krejčík, M.; Vlček, A. A. *Inorg. Chem.* **1992**, *31*, 2390–2395.
713. Kaes, C.; Hosseini, M. W.; De Cian, A.; Fischer, J. *Chem. Commun.* **1997**, 2229–2230.
714. Kaes, C.; Hosseini, M. W.; Ruppert, R.; Decian, A.; Fischer, J. *J. Chem. Soc., Chem. Commun.* **1995**, 1445–1446.
715. Kaes, C.; Hosseini, M. W.; DeCian, A.; Fischer, J. *Tetrahedron Lett.* **1997**, *38*, 3901–3904.
716. Lagref, J. J.; Hosseini, M. W.; Planeix, J. M.; De Cian, A.; Fischer, J. *Chem. Commun.* **1999**, 2155–2156.
717. Henze, O.; Lentz, D.; Schafer, A.; Franke, P.; Schluter, A. D. *Chem.-Eur. J.* **2002**, *8*, 357–365.
718. Josceanu, A. M.; Moore, P.; Rawle, S. C.; Sheldon, P.; Smith, S. M. *Inorg. Chim. Acta* **1995**, *240*, 159–168.
719. Sessler, J. L.; Capuano, V. L.; Burrell, A. K. *Inorg. Chim. Acta* **1993**, *204*, 93–101.
720. Toyama, M. M.; Franco, M.; Catalani, L. H.; Araki, K.; Toma, H. E. *J. Photochem. Photobiol. A* **1998**, *118*, 11–17.
721. Toyama, M. M.; Demets, G. J. F.; Araki, K.; Toma, H. E. *Electrochem. Commun.* **2000**, *2*, 749–753.
722. Harriman, A.; Romero, F. M.; Ziessel, R.; Benniston, A. C. *J. Phys. Chem. A* **1999**, *103*, 5399–5408.
723. Grosshenny, V.; Harriman, A.; Romero, F. M.; Ziessel, R. *J. Phys. Chem.* **1996**, *100*, 17472–17484.
724. Benniston, A. C.; Grosshenny, V.; Harriman, A.; Ziessel, R. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1884–1885.
725. Barthram, A. M.; Reeves, Z. R.; Jeffery, J. C.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **2000**, 3162–3169.
726. Ward, M. D. *Inorg. Chem.* **1996**, *35*, 1712–1714.
727. Barthram, A. M.; Cleary, R. L.; Jeffery, J. C.; Couchman, S. M.; Ward, M. D. *Inorg. Chim. Acta* **1998**, *267*, 1–5.
728. Sadler, G. G.; Gordon, N. R. *Inorg. Chim. Acta* **1991**, *180*, 271–276.
729. Gooden, V. M.; Dasgupta, T. P.; Gordon, N. R.; Sadler, G. G. *Inorg. Chim. Acta* **1998**, *268*, 31–36.
730. Masui, H.; Freda, A. L.; Zerner, M. C.; Lever, A. B. P. *Inorg. Chem.* **2000**, *39*, 141–152.
731. Keyes, T. E.; Forster, R. J.; Jayaweera, P. M.; Coates, C. G.; McGarvey, J. J.; Vos, J. G. *Inorg. Chem.* **1998**, *37*, 5925–5932.
732. Chakraborty, S.; Laye, R. H.; Paul, R. L.; Gonnade, R. G.; Puranik, V. G.; Ward, M. D.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2002**, 1172–1179.
733. Shukla, A. D.; Das, A. *Polyhedron* **2000**, *19*, 2605–2611.
734. Auburn, P. R.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 2551–2553.
735. Cargill Thompson, A. M. W.; Jeffery, J. C.; Liard, D. J.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1996**, 879–884.
736. Berthon, R. A.; Colbran, S. B.; Moran, G. M. *Inorg. Chim. Acta* **1993**, *204*, 3–7.
737. Panetta, C. A.; Kumpaty, H. J.; Heimer, N. E.; Leavy, M. C.; Hussey, C. L. *J. Org. Chem.* **1999**, *64*, 1015–1021.
738. Constable, E. C. *Comprehensive Coordination Chemistry II*, McCleverty, J. A.; Meyer, T. J., eds. Elsevier, Amsterdam, 2003, in press.
739. Campagna, S.; Denti, G.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 3728–3732.
740. Brauns, E.; Jones, S. W.; Clark, J. A.; Molnar, S. M.; Kawanishi, Y.; Brewer, K. J. *Inorg. Chem.* **1997**, *36*, 2861–2867.

741. Serroni, S.; Denti, G. *Inorg. Chem.* **1992**, *31*, 4251–4255.
742. Denti, G.; Serroni, S.; Campagna, S.; Ricevuto, V.; Juris, A.; Ciano, M.; Balzani, V. *Inorg. Chim. Acta* **1992**, *200*, 507–512.
743. Rutherford, T. J.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 3580–3581.
744. Rutherford, T. J.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1998**, 1155–1162.
745. De Wolf, J. M.; Hage, R.; Haasnoot, J. G.; Reedijk, J.; Vos, J. G. *New J. Chem.* **1991**, *15*, 501–507.
746. De Cola, L.; Belser, P.; Ebmeyer, F.; Barigelletti, F.; Vögtle, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 495–499.
747. Belser, P.; von Zelewsky, A.; Frank, M.; Seel, C.; Vögtle, F.; De Cola, L.; Barigelletti, F.; Balzani, V. *J. Am. Chem. Soc.* **1993**, *115*, 4076–4086.
748. Barthram, A. M.; Cleary, R. L.; Kowallick, R.; Ward, M. D. *Chem. Commun.* **1998**, 2695–2696.
749. Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. *J. Am. Chem. Soc.* **1990**, *112*, 7099–7103.
750. Bridgewater, J. S.; Vogler, L. M.; Molnar, S. M.; Brewer, K. J. *Inorg. Chim. Acta* **1993**, *208*, 179–188.
751. Molnar, S. M.; Nallas, G.; Bridgewater, J. S.; Brewer, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 5206–5210.
752. Nallas, G. N. A.; Brewer, K. J. *Inorg. Chim. Acta* **1996**, *253*, 7–13.
753. Nallas, G. N. A.; Jones, S. W.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 6974–6980.
754. Campagna, S.; Denti, G.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *J. Chem. Soc., Chem. Commun.* **1989**, 1500–1501.
755. Denti, G.; Campagna, S.; Sabatino, L.; Serrni, S.; Ciano, M.; Balzani, V. *Inorg. Chem.* **1990**, *29*, 4750–4758.
756. Serroni, S.; Juris, A.; Campagna, S.; Venturi, M.; Denti, G.; Balzani, V. *J. Am. Chem. Soc.* **1994**, *116*, 9086–9091.
757. Schmehl, R. H.; Auerbach, R. A.; Wacholtz, W. F.; Elliott, C. M.; Freitag, R. A.; Merkert, J. W. *Inorg. Chem.* **1986**, *25*, 2440–2445.
758. Wacholtz, W. F.; Auerbach, R. A.; Schmehl, R. H. *Inorg. Chem.* **1987**, *26*, 2989–2994.
759. Serroni, S.; Campagna, S.; Denti, G.; Keyes, T. E.; Vos, J. G. *Inorg. Chem.* **1996**, *35*, 4513–4518.
760. Ali, M.; Sato, H.; Haga, M. A.; Tanaka, K.; Yoshimura, A.; Ohno, T. *Inorg. Chem.* **1998**, *37*, 6176–6180.
761. Chao, H.; Li, R.-H.; Jiang, C.-W.; Li, H.; Ji, L.-N.; Li, X.-Y. *J. Chem. Soc., Dalton Trans.* **2001**, 1920–1926.
762. Chao, H.; Ye, B.-H.; Li, H.; Li, R.-H.; Zhou, J.-Y.; Ji, L.-N. *Polyhedron* **2000**, *19*, 1975–1983.
763. Chao, H.; Ye, B.-H.; Zhang, Q.-L.; Ji, L.-N. *Inorg Chem Commun* **1999**, *2*, 338–340.
764. Sahai, R.; Rillema, D. P. *J. Chem. Soc., Chem. Commun.* **1986**, 1133–1134.
765. Lempers, H. E. B.; Haasnoot, J. G.; Reedijk, J.; Hage, R.; Weldon, F. M.; Vos, J. G. *Inorg. Chim. Acta* **1994**, *225*, 67–74.
766. Campagna, S.; Serroni, S.; Juris, A.; Venturi, M.; Balzani, V. *New J. Chem.* **1996**, *20*, 773–780.
767. Denti, G.; Campagna, S.; Sabatino, L.; Serroni, S.; Ciano, M.; Balzani, V. *Inorg. Chim. Acta* **1990**, *176*, 175–178.
768. Latterini, L.; Schweitzer, G.; De Schryver, F. C.; Moucheron, C.; Kirsch-De Mesmaeker, A. *Chem. Phys. Lett.* **1997**, *281*, 267–271.
769. Serroni, S.; Denti, G.; Campagna, S.; Ciano, M.; Balzani, V. *J. Chem. Soc., Chem. Commun.* **1991**, 944–945.
770. Denti, G.; Campagna, S.; Serroni, S.; Ciano, M.; Balzani, V. *J. Am. Chem. Soc.* **1992**, *114*, 2944–2950.
771. Forster, R. J.; Vos, J. G. *Macromolecules* **1990**, *23*, 4372–4377.
772. Wang, Q.; Yu, L. P. *J. Am. Chem. Soc.* **2000**, *122*, 11806–11811.
773. Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A. *J. Electroanal. Chem.* **2001**, *506*, 106–114.
774. Walters, K. A.; Trouillet, L.; Guillerez, S.; Schanze, K. S. *Inorg. Chem.* **2000**, *39*, 5496–5509.
775. Belser, P.; Bernhard, S.; Jandrasics, E.; von Zelewsky, A.; De Cola, L.; Balzani, V. *Coord. Chem. Rev.* **1997**, *159*, 1–8.
776. Thomson, A. J.; Skarda, V.; Cook, M. J.; Robbins, D. J. *J. Chem. Soc., Dalton Trans.* **1985**, 1781–1788.
777. Yamagishi, A.; Naing, K.; Goto, Y.; Taniguchi, M.; Takahashi, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2085–2089.
778. Krausz, E.; Riesen, H.; Rae, A. D. *Aust. J. Chem.* **1995**, *48*, 929–954.
779. Tamura, H.; Ikeda, N.; Iguro, T.; Ohno, T.; Matsubayashi, G. *Acta Crystallogr., Sect. C* **1996**, *52*, 1394–1399.
780. Ashby, M. T.; Govindan, G. N.; Grafton, A. K. *Inorg. Chem.* **1993**, *32*, 3803–3804.
781. Noble, B.; Peacock, R. D. *Inorg. Chem.* **1996**, *35*, 1616–1620.
782. Rutherford, T. J.; Van Gijte, O.; Mesmaeker, A. K.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 4465–4474.
783. Murner, H.; Belser, P.; von Zelewsky, A. *J. Am. Chem. Soc.* **1996**, *118*, 7989–7994.
784. Gunde, K. E.; Credi, A.; Jandrasics, E.; von Zelewsky, A.; Richardson, F. S. *Inorg. Chem.* **1997**, *36*, 426–434.
785. Fletcher, N. C.; Keene, F. R.; Viebrock, H.; von Zelewsky, A. *Inorg. Chem.* **1997**, *36*, 1113–1121.
786. Jandrasics, E.; Kolp, B.; Wolny, J. A.; von Zelewsky, A. *Inorg. Chim. Acta* **1998**, *272*, 153–161.
787. Hesek, D.; Inoue, Y.; Ishida, H.; Everitt, S. R. L.; Drew, M. G. B. *Tetrahedron Lett.* **2000**, *41*, 2617–2620.
788. Hesek, D.; Inoue, Y.; Everitt, S. R. L.; Ishida, H.; Kunieda, M.; Drew, M. G. B. *Inorg. Chem.* **2000**, *39*, 308–316.
789. Reitsma, D. A.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1993**, 2859–2860.
790. Browne, W. R.; O'Connor, C. M.; Villani, C.; Vos, J. G. *Inorg. Chem.* **2001**, *40*, 5461–5464.
791. Fletcher, N. C.; Junk, P. C.; Reitsma, D. A.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1998**, 133–138.
792. Fletcher, N. C.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1999**, 683–689.
793. Patterson, B. T.; Keene, F. R. *Inorg. Chem.* **1998**, *37*, 645–650.
794. Rutherford, T. J.; Pellegrini, P. A.; Aldrich-Wright, J.; Junk, P. C.; Keene, F. R. *Eur. J. Inorg. Chem.* **1998**, 1677–1688.
795. Baker, A. D.; Morgan, R. J.; Strekas, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 1411–1412.
796. Shelton, C. M.; Seaver, K. E.; Wheeler, J. F.; Kane-Maguire, N. A. P. *Inorg. Chem.* **1997**, *36*, 1532–1533.
797. Wärnmark, K.; Heyke, O.; Thomas, J. A.; Lehn, J.-M. *Chem. Commun.* **1996**, 2603–2604.
798. Wärnmark, K.; Baxter, P. N. W.; Lehn, J.-M. *Chem. Commun.* **1998**, 993–994.
799. Uppadine, L. H.; Keene, F. R.; Beer, P. D. *J. Chem. Soc., Dalton Trans.* **2001**, 2188–2198.
800. Brissard, M.; Amouri, H.; Gruselle, M.; Thouvenot, R. *Comptes Rend. Chim.* **2002**, *5*, 53–58.
801. Batista, A. A.; Santiago, M. O.; Donnici, C. L.; Moreira, I. S.; Healy, P. C.; Berners-Price, S. J.; Queiroz, S. L. *Polyhedron* **2001**, *20*, 2123–2128.
802. Sarma, U. C.; Sarker, S. C.; Paul, B. C.; Poddar, R. K. *Inorg. Chim. Acta* **1990**, *173*, 195–199.
803. Watson, R. T.; Jackson, J. L.; Harper, J. D.; Kane-Maguire, K. A.; Kane-Maguire, L. A. P.; Kane-Maguire, N. A. P. *Inorg. Chim. Acta* **1996**, *249*, 5–7.

804. Kitamura, N.; Sato, M.; Kim, H. B.; Obata, R.; Tazuke, S. *Inorg. Chem.* **1988**, *27*, 651–658.
805. Kitamura, N.; Obata, R.; Kim, H. B.; Tazuke, S. *J. Phys. Chem.* **1989**, *93*, 5764–5769.
806. Maruyama, M.; Sonoyama, N.; Kaizu, Y. *J. Phys. Chem.* **1994**, *98*, 5332–5337.
807. Sonoyama, N.; Karasawa, O.; Kaizu, Y. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 437–443.
808. Gibson, D. H.; Ding, Y.; Andino, J. G.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1998**, *17*, 5178–5183.
809. Mori, T.; Yamaguchi, M.; Sato, M.; Yamagishi, T. *Inorg. Chim. Acta* **1998**, *267*, 329–333.
810. Breu, J.; Stoll, A. J. *Acta Crystallogr., Sect. C* **1996**, *52*, 1174–1177.
811. Wu, J. Z.; Zhou, Z. Y.; Ji, L. N. *Cryst. Res. Technol.* **2001**, *36*, 101–105.
812. Maloney, D. J.; MacDonell, F. M. *Acta Crystallogr., Sect. C* **1997**, *53*, 705–707.
813. Russell, V.; Scudder, M.; Dance, I. *J. Chem. Soc., Dalton Trans.* **2001**, 789–799.
814. Schoonover, J. R.; Omberg, K. M.; Moss, J. A.; Bernhard, S.; Malueg, V. J.; Woodruff, W. H.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 2585–2587.
815. Karki, L.; Hupp, J. T. *Inorg. Chem.* **1997**, *36*, 3318–3321.
816. Omberg, K. M.; Schoonover, J. R.; Bernhard, S.; Moss, J. A.; Treadway, J. A.; Kober, E. M.; Dyer, R. B.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 3505–3508.
817. Turro, C.; Bossmann, S. H.; Niu, S. F.; Barton, J. K.; Turro, N. J. *Inorg. Chim. Acta* **1996**, *252*, 333–338.
818. Otsuka, T.; Sekine, A.; Fujigasaki, N.; Ohashi, Y.; Kaizu, Y. *Inorg. Chem.* **2001**, *40*, 3406–3412.
819. Draxler, S. *J. Phys. Chem. A* **1999**, *103*, 4719–4722.
820. Tyson, D. S.; Bialecki, J.; Castellano, F. N. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2355–2356.
821. Zheng, K. C.; Wang, J. P.; Liu, X. W.; Shen, Y.; Yun, F. C. *Theochem-J. Mol. Struct.* **2002**, *577*, 95–105.
822. Zheng, K. C.; Wang, J. P.; Shen, Y.; Peng, W. L.; Yun, F. C. *J. Comput. Chem.* **2002**, *23*, 436–443.
823. Zheng, K. C.; Wang, J. P.; Shen, Y.; Peng, W. L.; Yun, F. C. *J. Chem. Soc., Dalton Trans.* **2002**, 111–116.
824. Ryan, E. M.; Wang, R.; Vos, J. G.; Hage, R.; Haasnoot, J. G. *Inorg. Chim. Acta* **1993**, *208*, 49–58.
825. Ichida, H.; Tachiyashiki, S.; Sasaki, Y. *Chem. Lett.* **1989**, 1579–1580.
826. Laemmel, A. C.; Collin, J.-P.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **1999**, 383–386.
827. Baranoff, E.; Collin, J. P.; Furusho, Y.; Laemmel, A. C.; Sauvage, J.-P. *Chem. Commun.* **2000**, 1935–1936.
828. Nagai, T.; Tomizawa, H.; Sugahara, K.; Takeda, Y.; Ishida, K. *J. Mol. Struct.* **1999**, *478*, 211–218.
829. Ruminski, R. R.; Deere, P. T.; Olive, M.; Serveiss, D. *Inorg. Chim. Acta* **1998**, *281*, 1–9.
830. Bergbrennan, C.; Subramanian, P.; Absi, M.; Stern, C.; Hupp, J. T. *Inorg. Chem.* **1996**, *35*, 3719–3722.
831. Juris, A.; Prodi, L.; Harriman, A.; Ziessel, R.; Hissler, M.; El-ghayoury, A.; Wu, F. Y.; Riesgo, E. C.; Thummel, R. P. *Inorg. Chem.* **2000**, *39*, 3590–3598.
832. Riklin, M.; Tran, D.; Bu, X. H.; Laverman, L. E.; Ford, P. C. *J. Chem. Soc., Dalton Trans.* **2001**, 1813–1819.
833. Fees, J.; Ketterle, M.; Klein, A.; Fiedler, J.; Kaim, W. *J. Chem. Soc., Dalton Trans.* **1999**, 2595–2599.
834. Jiang, C. W.; Chao, H.; Li, R. H.; Li, H.; Ji, L. N. *Polyhedron* **2001**, *20*, 2187–2193.
835. Tyson, D. S.; Henbest, K. B.; Bialecki, J.; Castellano, F. N. *J. Phys. Chem. A* **2001**, *105*, 8154–8161.
836. Tyson, D. S.; Luman, C. R.; Zhou, X. L.; Castellano, F. N. *Inorg. Chem.* **2001**, *40*, 4063–4071.
837. Tyson, D. S.; Castellano, F. N. *Inorg. Chem.* **1999**, *38*, 4382–4383.
838. Scott, S. M.; Burrell, A. K.; Cocks, P. A.; Gordon, K. C. *J. Chem. Soc., Dalton Trans.* **1998**, 3679–3684.
839. Wu, F. Y.; Thummel, R. P. *Inorg. Chim. Acta* **2002**, *327*, 26–30.
840. Keuper, R.; Risch, N. *Z. Naturforsch., Teil B* **1995**, *50*, 1115–1120.
841. Yanagida, M.; Singh, L. P.; Sayama, K.; Hara, K.; Katoh, R.; Islam, A.; Sugihara, H.; Arakawa, H.; Nazeeruddin, M. K.; Grätzel, M. *J. Chem. Soc., Dalton Trans.* **2000**, 2817–2822.
842. Wang, P.; Zhu, G. *Luminescence* **2000**, *15*, 261–265.
843. Kapturkiewicz, A. *Chem. Phys. Lett.* **1995**, *236*, 389–394.
844. Fletcher, N. C.; Robinson, T. C.; Behrendt, A.; Jeffery, J. C.; Reeves, Z. R.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1999**, 2999–3006.
845. Tansienhee, L.; Kirsch-De Mesmaeker, A. *J. Chem. Soc., Dalton Trans.* **1994**, 3651–3658.
846. Flamigni, L.; Encinas, S.; Barigelletti, F.; MacDonnell, F. M.; Kim, K. J.; Puntoriero, F.; Campagna, S. *Chem. Commun.* **2000**, 1185–1186.
847. Wu, F. Y.; Riesgo, E.; Pavalova, A.; Kipp, R. A.; Schmehl, R. H.; Thummel, R. P. *Inorg. Chem.* **1999**, *38*, 5620–5628.
848. Griffiths, P. M.; Loiseau, F.; Puntoriero, F.; Serroni, S.; Campagna, S. *Chem. Commun.* **2000**, 2297–2298.
849. Das, A.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **2000**, *19*, 1227–1232.
850. Das, C.; Peng, S. M.; Lee, G. H.; Goswami, S. *New J. Chem.* **2002**, *26*, 222–228.
851. Fees, J.; Hausen, H. D.; Kaim, W. *Z. Naturforsch., Teil B* **1995**, *50*, 15–22.
852. Krejčík, M.; Záliš, S.; Klíma, J.; Sykora, D.; Matheis, W.; Klein, A.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 3362–3368.
853. Maruyama, M.; Kaizu, Y. *J. Phys. Chem.* **1995**, *99*, 6152–6162.
854. Maruyama, M.; Kaizu, Y. *Inorg. Chim. Acta* **1996**, *247*, 155–159.
855. Maruyama, M.; Matsuzawa, H.; Kaizu, Y. *Inorg. Chem.* **1995**, *34*, 3232–3240.
856. Kakoti, M.; Chaudhury, S.; Deb, A. K.; Goswami, S. *Polyhedron* **1993**, *12*, 783–789.
857. Hotze, A. C. G.; Velders, A. H.; Ugozzoli, F.; Biagini-Cingi, M.; Manotti-Lanfredi, A. M.; Haasnoot, J. G.; Reedijk, J. *Inorg. Chem.* **2000**, *39*, 3838–3844.
858. Basuli, F.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **1998**, *18*, 391–402.
859. Mitra, K. N.; Choudhury, S.; Goswami, S.; Peng, S. M. *Polyhedron* **1997**, *16*, 1605–1614.
860. Maji, M.; Hossain, M.; Chatterjee, M.; Chattopadhyay, S. K.; Puranik, V. G.; Chakrabarti, P.; Ghosh, S. *Polyhedron* **1999**, *18*, 3735–3739.
861. Munshi, P.; Samanta, R.; Lahiri, G. K. *Polyhedron* **1998**, *17*, 1913–1922.
862. Misra, T. K.; Das, D.; Sinha, C.; Ghosh, P.; Pal, C. K. *Inorg. Chem.* **1998**, *37*, 1672–1678.
863. Byabartta, P.; Dinda, J.; Santra, P. K.; Sinha, C.; Panneerselvam, K.; Liao, F. L.; Lu, T. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2825–2832.
864. Pal, S.; Misra, T. K.; Sinha, C.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **2000**, *19*, 1925–1933.
865. Santra, P. K.; Misra, T. K.; Das, D.; Sinha, C.; Slawin, A. M. Z.; Woollins, J. D. *Polyhedron* **1999**, *18*, 2869–2878.
866. Shivakumar, M.; Pramanik, K.; Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1998**, *37*, 5968–5969.
867. Shivakumar, M.; Pramanik, K.; Ghosh, P.; Chakravorty, A. *Chem. Commun.* **1998**, 2103–2104.

868. Pramanik, K.; Shivakumar, M.; Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **2000**, *39*, 195–199.
869. Shivakumar, M.; Pramanik, K.; Bhattacharyya, I.; Chakravorty, A. *Inorg. Chem.* **2000**, *39*, 4332–4338.
870. Mallick, T. K.; Das, P. K.; Roy, B. K.; Ghosh, B. K. *J. Chem. Res., S* **1993**, 374–375.
871. Majumdar, P.; Peng, S. M.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1998**, 1569–1574.
872. Majumdar, P.; Goswami, S.; Peng, S. M. *Polyhedron* **1999**, *18*, 2543–2548.
873. Majumdar, P.; Kamar, K. K.; Castiñeiras, A.; Goswami, S. *Chem. Commun.* **2001**, 1292–1293.
874. Bag, N.; Pramanik, A.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1992**, *31*, 40–45.
875. Bhattacharya, S. *Polyhedron* **1993**, *12*, 235–239.
876. Roy, B. K.; Mallick, T. K.; Ghosh, B. K. *Polyhedron* **1992**, *11*, 1829–1835.
877. Choudhury, S.; Kakoti, M.; Deb, A. K.; Goswami, S. *Polyhedron* **1992**, *11*, 3183–3190.
878. Das, P. K.; Ghosh, B. K. *Polyhedron* **1994**, *13*, 77–86.
879. Goswami, S.; Choudhury, S. *Polyhedron* **1996**, *15*, 1191–1196.
880. Niewenhuis, H. A.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1994**, *33*, 3212–3217.
881. Nieuwenhuis, H. A.; Stufkens, D. J.; McNicholl, R. A.; Alobaidi, A. H. R.; Coates, C. G.; Bell, S. E. J.; McGarvey, J. J.; Westwell, J.; George, M. W.; Turner, J. J. *J. Am. Chem. Soc.* **1995**, *117*, 5579–5585.
882. Kleverlaan, C. J.; Stufkens, D. J.; Fraanje, J.; Goubitz, K. *Eur. J. Inorg. Chem.* **1998**, 1243–1251.
883. Rosenberger, V.; Fendesak, G.; Dieck, H. T. *J. Organomet. Chem.* **1991**, *411*, 445–456.
884. Ruben, M.; Rau, S.; Skirl, A.; Krause, K.; Gorls, H.; Walther, D.; Vos, J. G. *Inorg. Chim. Acta* **2000**, *303*, 206–214.
885. van Slageren, J.; Stufkens, D. J. *Inorg. Chem.* **2001**, *40*, 277–285.
886. Clark, T.; Robinson, S. D. *J. Chem. Soc., Dalton Trans.* **1993**, 2827–2834.
887. Robinson, S. D.; Sahajpal, A. *J. Chem. Soc., Dalton Trans.* **1997**, 3349–3351.
888. Menon, M.; Pramanik, A.; Chattopadhyay, S.; Bag, N.; Chakravorty, A. *Inorg. Chem.* **1995**, *34*, 1361–1367.
889. Holman, K. T.; Robinson, S. D.; Sahajpal, A.; Steed, J. W. *J. Chem. Soc., Dalton Trans.* **1999**, 15–18.
890. Danopoulos, A. A.; Hay-Motherwell, R. S.; Wilkinson, G.; Cafferkey, S. M.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1997**, 3177–3184.
891. Manivannan, V.; Dirghangi, B. K.; Pal, C. K.; Chakravorty, A. *Inorg. Chem.* **1997**, *36*, 1526–1528.
892. Khan, M. M. T.; Venkatasubramanian, K.; Abdi, S. H. R.; Bhadbhade, M. M.; Tyagi, B. *Acta Crystallogr., Sect. C* **1992**, *48*, 1402–1405.
893. Anillo, A.; Barrio, C.; Garćia-Granda, S.; Obeso Rosete, R. *J. Chem. Soc., Dalton Trans.* **1993**, 1125–1130.
894. Venegas-Yazigi, D.; Mirza, H.; Lever, A. B. P.; Lough, A. J.; Costamagna, J.; Vega, A.; Latorre, R. *Acta Crystallogr., Sect. C* **2000**, *56*, E245–E246.
895. Metcalfe, R. A.; Lever, A. B. P. *Inorg. Chem.* **1997**, *36*, 4762–4771.
896. Mitra, K. N.; Majumdar, P.; Peng, S. M.; Castiñeiras, A.; Goswami, S. *Chem. Commun.* **1997**, 1267–1268.
897. Mitra, K. N.; Choudhury, S.; Castiñeiras, A.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1998**, 2901–2906.
898. Mitra, K. N.; Goswami, S. *Inorg. Chem.* **1997**, *36*, 1322–1326.
899. Mitra, K. N.; Goswami, S. *Chem. Commun.* **1997**, 49–50.
900. Saha, A.; Das, C.; Mitra, K. N.; Peng, S. M.; Lee, G. H.; Goswami, S. *Polyhedron* **2002**, *21*, 97–104.
901. Bruno, G.; Nicolo, F.; Tresoldi, G.; Lanza, S. *Acta Crystallogr., Sect. C* **2002**, *58*, M56–M58.
902. Rheingold, A. L.; Saisuwan, P.; Thomas, N. C. *Inorg. Chim. Acta* **1993**, *214*, 41–45.
903. Streiff, J. H.; Edwards, W. D.; McHale, J. L. *Chem. Phys. Lett.* **1999**, *312*, 369–375.
904. Streiff, J.; McHale, J. L. *J. Chem. Phys.* **2000**, *112*, 841–850.
905. Mines, G. A.; Roberts, J. A.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 125–128.
906. Kato, M.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1989**, *93*, 3422–3425.
907. Bignozzi, C. A.; Chiorboli, C.; Indelli, M. T.; Rampi Scandola, M. A.; Varani, G.; Scandola, F. *J. Am. Chem. Soc.* **1986**, *108*, 7872–7873.
908. Ulveczky, A.; Horvath, A. *Inorg. Chim. Acta* **1995**, *236*, 173–176.
909. Samuels, A. C.; Dearmond, M. K. *Inorg. Chem.* **1995**, *34*, 5548–5551.
910. Das, A.; Basuli, F.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **1999**, *18*, 2729–2736.
911. Haukka, M.; Ahlgrén, M.; Pakkanen, T. A. *J. Chem. Soc., Dalton Trans.* **1996**, 1927–1933.
912. Haukka, M.; Venäläinen, T.; Ahlgrén, M.; Pakkanen, T. A. *Inorg. Chem.* **1995**, *34*, 2931–2936.
913. Homanen, P.; Haukka, M.; Luukkanen, S.; Ahlgrén, M.; Pakkanen, T. A. *Eur. J. Inorg. Chem.* **1999**, 101–106.
914. Homanen, P.; Haukka, M.; Ahlgrén, M.; Pakkanen, T. A. *Inorg. Chem.* **1997**, *36*, 3794–3797.
915. Ben Hadda, T.; Zidane, I.; Moya, S. A.; Lebozec, H. *Polyhedron* **1996**, *15*, 1571–1573.
916. Eskelinen, E.; Haukka, M.; Venäläinen, T.; Pakkanen, T. A.; Wasberg, M.; Chardon-Noblat, S.; Deronzier, A. *Organometallics* **2000**, *19*, 163–169.
917. Collomb-Dunand-Sauthier, M. N.; Deronzier, A.; Ziessel, R. *J.Organometal. Chem.* **1993**, *444*, 191–198.
918. Chardon-Noblat, S.; Deronzier, A.; Ziessel, R. *Collect. Czech. Chem. Commun.* **2001**, *66*, 207–227.
919. Chardon-Noblat, S.; Da Costa, P.; Deronzier, A.; Haukka, M.; Pakkanen, T. A.; Ziessel, R. *J. Electroanal. Chem.* **2000**, *490*, 62–69.
920. Chardon-Noblat, S.; Cripps, G. H.; Deronzier, A.; Field, J. S.; Gouws, S.; Haines, R. J.; Southway, F. *Organometallics* **2001**, *20*, 1668–1675.
921. Kinnunen, T. J. J.; Haukka, M.; Nousiainen, M.; Patrikka, A.; Pakkanen, T. A. *J. Chem. Soc., Dalton Trans.* **2001**, 2649–2654.
922. Luukkanen, S.; Haukka, M.; Eskelinen, E.; Pakkanen, T. A.; Lehtovuori, V.; Kallioinen, J.; Myllyperkiö, P.; Korppi-Tommola, J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1992–1998.
923. Ferretti, A.; Lami, A.; Villani, G. *Inorg. Chem.* **1998**, *37*, 2799–2805.
924. Ferretti, A.; Lami, A.; Villani, G. *Inorg. Chem.* **1998**, *37*, 4460–4465.
925. Sommovigo, M.; Ferretti, A.; Venturi, M.; Ceroni, P.; Giardi, C.; Denti, G. *Inorg. Chem.* **2002**, *41*, 1263–1271.
926. Tomita, A.; Sano, M. *Inorg. Chem.* **2000**, *39*, 200–205.
927. Pavinato, R. A.; Walk, J. A.; McGuire, M. E. *Inorg. Chem.* **1993**, *32*, 4982–4984.
928. Hatzidimitriou, A.; Gourdon, A.; Devillers, J.; Launay, J. P.; Mena, E.; Amouyal, E. *Inorg. Chem.* **1996**, *35*, 2212–2219.
929. Johnson, J. E. B.; de Groff, C.; Ruminski, R. R. *Inorg. Chim. Acta* **1991**, *187*, 73–80.

930. Ruminski, R. R.; Freiheit, D.; Serveiss, D.; Snyder, B.; Johnson, J. E. B. *Inorg. Chim. Acta* **1994**, *224*, 27–34.
931. Moreira, I. de S.; Franco, D. W. *Inorg. Chem.* **1994**, *33*, 1607–1613.
932. Moreira, I. de S.; de Lima, J. B.; Franco, D. W. *Coord. Chem. Rev.* **2000**, *196*, 197–217.
933. Metcalfe, R. A.; Vasconcellos, L. C. G.; Mirza, H.; Franco, D. W.; Lever, A. B. P. *J. Chem. Soc., Dalton Trans.* **1999**, 2653–2667.
934. Nieuwenhuis, H. A.; Vanloon, A.; Moraal, M. A.; Stufkens, D. J.; Oskam, A.; Goubitz, K. *Inorg. Chim. Acta* **1995**, *232*, 19–25.
935. Greaney, M. A.; Coyle, C. L.; Harmer, M. A.; Jordan, A.; Stiefel, E. I. *Inorg. Chem.* **1989**, *28*, 912–920.
936. Lei, Y. B.; Buranda, T.; Endicott, J. F. *J. Am. Chem. Soc.* **1990**, *112*, 8820–8833.
937. Singh, R.; Dikshit, S. K. *Polyhedron* **1993**, *12*, 1697–1703.
938. Coe, B. J.; McDonald, C. I.; Coles, S. J.; Hursthouse, M. B. *Acta Crystallogr., Sect. C* **2000**, *56*, 963–965.
939. van Wallendael, S.; Rillema, D. P. *Coord. Chem. Rev.* **1991**, *111*, 297–318.
940. van Wallendael, S.; Perkovic, M. W.; Rillema, D. P. *Inorg. Chim. Acta* **1993**, *213*, 253–260.
941. Matheis, W.; Kaim, W. *Inorg. Chim. Acta* **1991**, *181*, 15–21.
942. Scott, S. M.; Gordon, K. C.; Burrell, A. K. *J. Chem. Soc., Dalton Trans.* **1999**, 2669–2673.
943. Yam, V. W. W.; Lee, V. W. M.; Ke, F.; Siu, K. W. M. *Inorg. Chem.* **1997**, *36*, 2124–2129.
944. Kawanishi, Y.; Brewer, K. J. *Mol. Cryst. Liquid Cryst.* **2000**, *342*, 261–266.
945. Hicks, C.; Fan, J. W.; Rutenberg, I.; Gafney, H. D. *Coord. Chem. Rev.* **1998**, *171*, 71–84.
946. Hicks, C.; Ye, G. Z.; Levi, C.; Gonzales, M.; Rutenburg, I.; Fan, J. W.; Helmy, R.; Kassis, A.; Gafney, H. D. *Coord. Chem. Rev.* **2001**, *211*, 207–222.
947. Lam, M. H. W.; Cheung, S. T. C.; Fung, K. M.; Wong, W. T. *Inorg. Chem.* **1997**, *36*, 4618–4619.
948. Fox, G. A.; Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 2895–2899.
949. Hill, P. L.; Lee, L. Y.; Younkin, T. R.; Orth, S. D.; McElwee-White, L. *Inorg. Chem.* **1997**, *36*, 5655–5657.
950. Paw, W.; Connick, W. B.; Eisenberg, R. *Inorg. Chem.* **1998**, *37*, 3919–3926.
951. Harriman, A.; Hissler, M.; Trompette, O.; Ziessel, R. *J Amer Chem Soc* **1999**, *121*, 2516–2525.
952. Toma, H. E.; Chavez-Gil, T. E. *Inorg. Chim. Acta* **1997**, *257*, 197–202.
953. Das, A.; McCleverty, J. A.; Ward, M. D.; Jones, C. J.; Thompson, A. *Polyhedron* **1992**, *11*, 2119–2122.
954. Amoroso, A. J.; Das, A.; McCleverty, J. A.; Ward, M. D.; Barigelletti, F.; Flamigni, L. *Inorg. Chim. Acta* **1994**, *226*, 171–177.
955. Ortega, J. V.; Hong, B.; Ghosal, S.; Hemminger, J. C.; Breedlove, B.; Kubiak, C. P. *Inorg. Chem.* **1999**, *38*, 5102–5112.
956. Ortega, J. V.; Khin, K.; van der Veer, W. E.; Ziller, J.; Hong, B. *Inorg. Chem.* **2000**, *39*, 6038–6050.
957. Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107–129.
958. Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1–73.
959. Ward, M. D. *Chem. Soc. Rev.* **1995**, *24*, 121–134.
960. Launay, J. P. *Chem. Soc. Rev.* **2001**, *30*, 386–397.
961. Demadis, K. D.; Hartshorn, C. M. *Chem. Rev.* **2001**, *101*, 2655–2685.
962. Brunschwig, B. S.; Creutz, C.; Sutin, N. *Chem. Soc. Rev.* **2002**, *31*, 168–184.
963. Kaim, W.; Klein, A.; Glockle, M. *Acc. Chem. Res.* **2000**, *33*, 755–763.
964. Chen, P. Y.; Meyer, T. J. *Chem. Rev.* **1998**, *98*, 1439–1477.
965. Cooper, J. B.; Vess, T. M.; Kalsbeck, W. A.; Wertz, D. W. *Inorg. Chem.* **1991**, *30*, 2286–2290.
966. Forlano, P.; Baraldo, L. M.; Olabe, J. A.; Dellavedova, C. O. *Inorg. Chim. Acta* **1994**, *223*, 37–42.
967. Forlano, P.; Cukiernik, F. D.; Poizat, O.; Olabe, J. A. *J. Chem. Soc., Dalton Trans.* **1997**, 1595–1599.
968. Dong, Y. H.; Hupp, J. T. *Inorg. Chem.* **1992**, *31*, 3170–3172 and references therein.
969. Cutin, E. H.; Katz, N. E. *Polyhedron* **1993**, *12*, 955–960.
970. Bignozzi, C. A.; Argazzi, R.; Strouse, G. F.; Schoonover, J. R. *Inorg. Chim. Acta* **1998**, *276*, 380–384.
971. Bignozzi, C. A.; Argazzi, R.; Bortolini, O.; Scandola, F.; Harriman, A. *New J. Chem.* **1996**, *20*, 731–738.
972. Kunkely, H.; Pawlowski, V.; Vogler, A. *Inorg. Chim. Acta* **1994**, *225*, 327–330.
973. Aquino, M. A. S.; Bostock, A. E.; Crutchley, R. J. *Inorg. Chem.* **1990**, *29*, 3641–3644.
974. Naklicki, M. L.; Crutchley, R. J. *Inorg. Chim. Acta* **1994**, *225*, 123–127.
975. Naklicki, M. L.; Crutchley, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 6045–6046.
976. Naklicki, M. L.; Evans, C. E. B.; Crutchley, R. J. *J. Mol. Struct.* **1997**, *405*, 87–92.
977. Rezvani, A. R.; Bensimon, C.; Cromp, B.; Reber, C.; Greedan, J. E.; Kondratiev, V. V.; Crutchley, R. J. *Inorg. Chem.* **1997**, *36*, 3322–3329.
978. Evans, C. E. B.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **1998**, *37*, 6161–6167.
979. De Rosa, M. C.; White, C. A.; Evans, C. E. B.; Crutchley, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 1396–1402.
980. Mosher, P. J.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **2001**, *40*, 1189–1195.
981. Huang, H.-Y.; Chen, W.-J.; Yang, C.-C.; Yeh, A. *Inorg. Chem.* **1991**, *30*, 1862–1868.
982. Cutin, E. H.; Katz, N. E. *Polyhedron* **1991**, *10*, 653–657.
983. Curtis, J. C.; Roberts, J. A.; Blackbourn, R. L.; Dong, Y. H.; Massum, M.; Johnson, C. S.; Hupp, J. T. *Inorg. Chem.* **1991**, *30*, 3856–3860.
984. Chou, M. H.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1992**, *31*, 2318–2327.
985. Benaltabef, A.; Degallo, S. B. R.; Folquer, M. E.; Katz, N. E. *Inorg. Chim. Acta* **1991**, *188*, 67–70.
986. Petrov, V.; Hupp, J. T.; Mottley, C.; Mann, L. C. *J. Am. Chem. Soc.* **1994**, *116*, 2171–2172.
987. Hupp, J. T.; Dong, Y. H. *Inorg. Chem.* **1994**, *33*, 4421–4424.
988. Zhang, X. L.; Kankel, C. R.; Hupp, J. T. *Inorg. Chem.* **1994**, *33*, 4738–4743.
989. Bencini, A.; Ciofini, I.; Daul, C. A.; Ferretti, A. *J Amer Chem Soc* **1999**, *121*, 11418–11424.
990. Das, A.; Bajaj, H. C. *Polyhedron* **1997**, *16*, 1023–1030.
991. Poppe, J.; Moscherosch, M.; Kaim, W. *Inorg. Chem.* **1993**, *32*, 2640–2643.
992. Parise, A. R.; Baraldo, L. M.; Olabe, J. A. *Inorg. Chem.* **1996**, *35*, 5080–5086.
993. Moreira, I. D.; Lima, E. C.; Franco, D. W. *Inorg. Chim. Acta* **1998**, *267*, 93–99.
994. Reimers, J. R.; Hush, N. S. *Inorg. Chem.* **1990**, *29*, 3686–3697.
995. Hupp, J. T.; Dong, Y. H.; Blackbourn, R. L.; Lu, H. *J. Phys. Chem.* **1993**, *97*, 3278–3282.

996. Nozaki, K.; Ohno, T. *Coord. Chem. Rev*. **1994**, *132*, 215–222.
997. Roche, S.; Yellowlees, L. J.; Thomas, J. A. *Chem. Commun*. **1998**, 1429–1430.
998. Matsumoto, K.; Uemura, H.; Kawano, M. *Chem. Lett*. **1994**, 1215–1218.
999. Beley, M.; Collin, J.-P.; Sauvage, J. P. *Inorg. Chem*. **1993**, *32*, 4539–4543.
1000. Fagalde, F.; Katz, N. E.; Povse, V. G.; Olabe, J. A. *Polyhedron* **1998**, *18*, 25–31.
1001. Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Chem. Commun*. **1991**, 1460–1463.
1002. Beer, P. D.; Kocian, O.; Mortimer, R. J.; Ridgway, C. *J. Chem. Soc., Dalton Trans*. **1993**, 2629–2638.
1003. Durr, H.; Schwarz, R.; Willner, I.; Joselevich, E.; Eichen, Y. *J. Chem. Soc., Chem. Commun*. **1992**, 1338–1339.
1004. Chiba, M.; Ogawa, K.; Tsuge, K.; Abe, M.; Kim, H. B.; Sasaki, Y.; Kitamura, N. *Chem. Lett*. **2001**, 692–693.
1005. Yam, V. W. W.; Lee, V. W. M.; Ke, F.; Siu, K. W. M. *Inorg. Chem*. **1997**, *36*, 2124–2129.
1006. Harriman, A.; Hissler, M.; Jost, P.; Wipff, G.; Ziessel, R. *J. Am. Chem. Soc*. **1999**, *121*, 14–27.
1007. Kimura, E.; Wada, S.; Shionoya, M.; Takahashi, T.; Iitaka, Y. *J. Chem. Soc., Chem. Commun*. **1990**, 397–398.
1008. Rawle, S. C.; Moore, P.; Alcock, N. W. *J. Chem. Soc., Chem. Commun*. **1992**, 684–687.
1009. Lodeiro, C.; Pina, F.; Parola, A. J.; Bencini, A.; Bianchi, A.; Bazzicalupi, C.; Ciattini, S.; Giorgi, C.; Masotti, A.; Valtancoli, B.; de Melo, J. S. *Inorg. Chem*. **2001**, *40*, 6813–6819.
1010. Beer, P. D.; Kocian, O.; Mortimer, R. J.; Spencer, P. *J. Chem. Soc., Chem. Commun*. **1992**, 602–604.
1011. Beer, P. D.; Cadman, J. *Coord. Chem. Rev*. **2000**, *205*, 131–155.
1012. Beer, P. D.; Dent, S. W.; Wear, T. J. *J. Chem. Soc., Dalton Trans*. **1996**, 2341–2346.
1013. Szemes, F.; Hesek, D.; Chen, Z.; Dent, S. W.; Drew, M. G. B.; Goulden, A. J.; Graydon, A. R.; Grieve, A.; Mortimer, R. J.; Wear, T.; Weightman, J. S.; Beer, P. D. *Inorg. Chem*. **1996**, *35*, 5868–5879.
1014. Beer, P. D.; Fletcher, N. C.; Wear, T. *Polyhedron* **1996**, *15*, 1339–1347.
1015. Beer, P. D.; Fletcher, N. C.; Wear, T. *Inorg. Chim. Acta* **1996**, *251*, 335–340.
1016. Beer, P. D.; Dent, S. W. *Chem. Commun*. **1998**, 825–826.
1017. Beer, P. D.; Timoshenko, V.; Maestri, M.; Passaniti, P.; Balzani, V.; Balzani, B. *Chem. Commun*. **1999**, 1755–1756.
1018. Cooper, J. B.; Drew, M. G. B.; Beer, P. D. *J. Chem. Soc., Dalton Trans*. **2001**, 392–401.
1019. Grigg, R.; Holmes, J. M.; Jones, S. K.; Norbert, W. D. J. A. *J. Chem. Soc., Chem. Commun*. **1994**, 185–187.
1020. Beer, P. D.; Chen, Z.; Goulden, A. J.; Grieve, A.; Hesek, D.; Szemes, F.; Wear, T. *J. Chem. Soc., Chem. Commun*. **1994**, 2021.
1021. Dumazet, I.; Beer, P. D. *Tetrahedron Lett*. **1999**, *40*, 785–788.
1022. Hesek, D.; Inoue, Y.; Everitt, S. R. L.; Kunieda, M.; Ishida, H.; Drew, M. G. B. *Tetrahedron Asymmetry* **1998**, *9*, 4089–4097.
1023. Beer, P. D.; Dent, S. W.; Hobbs, G. S.; Wear, T. J. *Chem. Commun*. **1997**, 99–100.
1024. Beer, P. D.; Cadman, J. *New J. Chem*. **1999**, *23*, 347–349.
1025. Laurent, F.; Plantalech, E.; Donnadieu, B.; Jimenez, A.; Hernandez, F.; Martinez-Ripoll, M.; Biner, M.; Llobet, A. *Polyhedron* **1999**, *18*, 3321–3331.
1026. Craig, D. C.; Scudder, M. L.; McHale, W. A.; Goodwin, H. A. *Aust. J. Chem*. **1998**, *51*, 1131–1139.
1027. Lashgari, K.; Kritikos, M.; Norrestam, R.; Norrby, T. *Acta Crystallogr., Sect. C* **1999**, *55*, 64–67.
1028. Hansen, P. W.; Jensen, P. W. *Spectrochim Acta Pt A-Mol Spe* **1994**, *50*, 169–183.
1029. Gibson, D. H.; Sleadd, B. A.; Mashuta, M. S.; Richardson, J. F. *Acta Crystallogr., Sect. C* **1998**, *54*, 1584–1586.
1030. Abel, E. W.; Orrell, K. G.; Osborne, A. G.; Pain, H. M.; Sik, V. *J. Chem. Soc., Dalton Trans*. **1994**, 111–116.
1031. Kintop, J. A.; Machado, W. V. M.; Franco, M.; Toma, H. E. *Chem. Phys. Lett*. **1999**, *309*, 90–94.
1032. Ponce, A.; Bachrach, M.; Farmer, P. J.; Winkler, J. R. *Inorg. Chim. Acta* **1996**, *243*, 135–140.
1033. Sondaz, E.; Gourdon, A.; Launay, J. P.; Bonvoisin, J. *Inorg. Chim. Acta* **2001**, *316*, 79–88.
1034. Pramanik, A.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans*. **1992**, 97–99.
1035. Perez, W. J.; Lake, C. H.; See, R. F.; Toomey, L. M.; Churchill, M. R.; Takeuchi, K. J.; Radano, C. P.; Boyko, W. J.; Bessel, C. A. *J. Chem. Soc., Dalton Trans*. **1999**, 2281–2292.
1036. Seok, W. K.; Yim, S. B.; Klapotke, T. M.; White, P. S. *J. Organometal. Chem*. **1998**, *559*, 165–171.
1037. Leising, R. A.; Kubow, S. A.; Takeuchi, K. J. *Inorg. Chem*. **1990**, *29*, 4569–4574.
1038. Szczepura, L. F.; Kubow, S. A.; Leising, R. A.; Perez, W. J.; Huynh, M. H. V.; Lake, C. H.; Churchill, D. G.; Churchill, M. R.; Takeuchi, K. J. *J. Chem. Soc., Dalton Trans*. **1996**, 1463–1470.
1039. Churchill, M. R.; Krajkowski, L. M.; Szczepura, L. F.; Takeuchi, K. J. *J. Chem. Crystallogr*. **1996**, *26*, 853–859.
1040. Churchill, M. R.; See, R. F.; Bessel, C. A.; Takeuchi, K. J. *J. Chem. Crystallogr*. **1996**, *26*, 543–551.
1041. Bryan, C. D.; Bryan, T. A.; Cordes, A. W.; Durham, B.; Jeter, D. Y.; Yarbrough, J. C. *J. Chem. Crystallogr*. **1997**, *27*, 413–415.
1042. Dovletoglou, A.; Adeyemi, S. A.; Meyer, T. J. *Inorg. Chem*. **1996**, *35*, 4120–4127.
1043. Bessel, C. A.; Margarucci, J. A.; Acquaye, J. H.; Rubino, R. S.; Crandall, J.; Jircitano, A. J.; Takeuchi, K. J. *Inorg. Chem*. **1993**, *32*, 5779–5784.
1044. Degiovani, W. F.; Deronzier, A. *J. Electroanal. Chem*. **1992**, *337*, 285–298.
1045. Fletcher, N. C.; Keene, F. R. *J. Chem. Soc., Dalton Trans*. **1998**, 2293–2301.
1046. Hecker, C. R.; Fanwick, P. E.; McMillin, D. R. *Inorg. Chem*. **1991**, *30*, 659–666.
1047. Rasmussen, S. C.; Ronco, S. E.; Mlsna, D. A.; Billadeau, M. A.; Pennington, W. T.; Kolis, J. W.; Petersen, J. D. *Inorg. Chem*. **1995**, *34*, 821–829.
1048. Fagalde, F.; deKatz, N. D. L.; Katz, N. E. *Polyhedron* **1997**, *16*, 1921–1923.
1049. Konno, H.; Kobayashi, A.; Sakamoto, K.; Fagalde, F.; Katz, N. E.; Saitoh, H.; Ishitani, O. *Inorg. Chim. Acta* **2000**, *299*, 155–163.
1050. Navarro, M.; Galembeck, S. E.; Romero, J. R.; Degiovani, W. F. *Polyhedron* **1996**, *15*, 1531–1537.
1051. Gulyas, P. T.; Hambley, T. W.; Lay, P. A. *Aust. J. Chem*. **1996**, *49*, 527–532.
1052. Silva, M. I.; Burrows, H. D.; Formosinho, S. J.; Miguel, M. D. *J. Mol. Struct*. **2001**, *565*, 79–82.
1053. Constable, E. C.; Dunne, S. J.; Rees, D. G. F.; Schmitt, C. X. *Chem. Commun*. **1996**, 1169–1170.
1054. Constable, E. C.; Cargill Thompson, A. M. W.; Cherryman, J.; Liddiment, T. *Inorg. Chim. Acta* **1995**, *235*, 165–171.
1055. Chotalia, R.; Constable, E. C.; Hannon, M. J.; Tocher, D. A. *J. Chem. Soc., Dalton Trans*. **1995**, 3571–3580.
1056. Yu, W. Y.; Cheng, W. C.; Che, C. M.; Wang, Y. *Polyhedron* **1994**, *13*, 2963–2969.
1057. Catalano, V. J.; Heck, R. A.; Immoos, C. E.; Ohman, A.; Hill, M. G. *Inorg. Chem*. **1998**, *37*, 2150–2157.

1058. Heirtzler, F. R.; Neuburger, M.; Zehnder, M.; Bird, S. J.; Orrell, K. G.; Sik, V. *J. Chem. Soc., Dalton Trans.* **1999**, 565–574.
1059. Vogler, L. M.; Franco, C.; Jones, S. W.; Brewer, K. J. *Inorg. Chim. Acta* **1994**, *221*, 55–59.
1060. Gerli, A.; Reedijk, J.; Lakin, M. T.; Spek, A. L. *Inorg. Chem.* **1995**, *34*, 1836–1843.
1061. Spek, A. L.; Gerli, A.; Reedijk, J. *Acta Crystallogr., Sect. C* **1994**, *50*, 394–397.
1062. Sinha, P. K.; Chakravarty, J.; Bhattacharya, S. *Polyhedron* **1996**, *15*, 2931–2938.
1063. Mondal, B.; Chakraborty, S.; Munshi, P.; Walawalkar, M. G.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **2000**, 2327–2335.
1064. Couchman, S. M.; Dominguez-Vera, J. M.; Jeffery, J. C.; McKee, C. A.; Nevitt, S.; Pohlman, M.; White, C. M.; Ward, M. D. *Polyhedron* **1998**, *17*, 3541–3550.
1065. Tsuge, K.; Kurihara, M.; Tanaka, K. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 607–614.
1066. Constable, E. C.; Cathey, C. J.; Hannon, M. J.; Tocher, D. A.; Walker, J. V.; Ward, M. D. *Polyhedron* **1998**, *18*, 159–173.
1067. Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chim. Acta* **1994**, *223*, 177–179.
1068. Constable, E. C.; Cargill Thompson, A. M. W.; Tocher, D. A.; Daniels, M. A. M. *New J. Chem.* **1992**, *16*, 855–867.
1069. Constable, E. C.; Cargill Thompson, A. M. W.; Armaroli, N.; Balzani, V.; Maestri, M. *Polyhedron* **1992**, *11*, 2707–2709.
1070. Maestri, M.; Armaroli, N.; Balzani, V.; Constable, E. C.; Cargill Thompson, A. M. W. *Inorg. Chem.* **1995**, *34*, 2759–2767.
1071. Amouyal, E.; Mouallem-Bahout, M.; Calzaferri, G. *J. Phys. Chem.* **1991**, *95*, 7641–7649.
1072. Holbrey, J. D.; Tiddy, G. J. T.; Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1995**, 1769–1774.
1073. Ben Hadda, T.; Le Bozec, H. *Inorg. Chim. Acta* **1993**, *204*, 103–107.
1074. Ben Hadda, T.; Le Bozec, H. *Polyhedron* **1988**, *7*, 575–577.
1075. Ben Hadda, T.; Mountassir, C.; Le Bozec, H. *Polyhedron* **1995**, *14*, 953–955.
1076. Rao, K. M.; Rao, C. R. K.; Zacharias, P. S. *Polyhedron* **1997**, *16*, 2369–2374.
1077. Hecker, C. R.; Gushurst, A. K. I.; McMillin, D. R. *Inorg. Chem.* **1991**, *30*, 538–541.
1078. Beley, M.; Collin, J.-P.; Sauvage, J.-P.; Sugihara, H.; Heisel, F.; Miehe, A. *J. Chem. Soc., Dalton Trans.* **1991**, 3157–3159.
1079. Amouyal, E.; Mouallem-Bahout, M. *J. Chem. Soc., Dalton Trans.* **1992**, 509–513.
1080. Laemmel, A. C.; Collin, J.-P.; Sauvage, J.-P. *Comptes Rend. Chim.* **2000**, *3*, 43–49.
1081. Constable, E. C.; Neuburger, M.; Smith, D. R.; Zehnder, M. *Inorg. Chim. Acta* **1998**, *276*, 359–365.
1082. Amouyal, E.; Mouallem-Bahout, M.; Calzaferri, G. *Comptes Rend. Acad. Sci. Ser II Mec Phys* **1991**, *313*, 1129–1133.
1083. Whittle, B.; Everest, N. S.; Howard, C.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 2025–2032.
1084. Constable, E. C.; Housecroft, C. E.; Neuburger, M.; Schneider, A. G.; Zehnder, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2427–2434.
1085. Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Kaden, T. A.; Grätzel, M. *Inorg. Chem.* **2000**, *39*, 4542–4547.
1086. Fallahpour, R. A. *Eur. J. Inorg. Chem.* **1998**, 1205–1207.
1087. Fallahpour, R. A.; Neuburger, M.; Zehnder, M. *New J. Chem.* **1999**, *23*, 53–61.
1088. Storrier, G. D.; Colbran, S. B.; Craig, D. C. *J. Chem. Soc., Dalton Trans.* **1997**, 3011–3028.
1089. Storrier, G. D.; Colbran, S. B. *Inorg. Chim. Acta* **1999**, *284*, 76–84.
1090. Ng, W. Y.; Gong, X.; Chan, W. K. *Chem. Mater.* **1999**, *11*, 1165–1170.
1091. Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1994**, 1409–1418.
1092. Laine, P.; Bedioui, F.; Ochsenbein, P.; Marvaud, V.; Bonin, M.; Amouyal, E. *J. Am. Chem. Soc.* **2002**, *124*, 1364–1377.
1093. Barigelletti, F.; Flamigni, L.; Calogero, G.; Hammarström, L.; Sauvage, J.-P.; Collin, J.-P. *Chem. Commun.* **1998**, 2333–2334.
1094. Chambron, J. C.; Collin, J.-P.; Dalbavie, J. O.; Dietrich-Buchecker, C. O.; Heitz, V.; Odobel, F.; Solladie, N.; Sauvage, J.-P. *Coord. Chem. Rev.* **1998**, *180*, 1299–1312.
1095. Flamigni, L.; Barigelletti, F.; Armaroli, N.; Collin, J.-P.; Sauvage, J.-P.; Williams, J. A. G. *Chem. Eur. J.* **1998**, *4*, 1744–1754.
1096. Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; Flamigni, L.; De Cola, L.; Balzani, V. *Coord. Chem. Rev.* **1991**, *111*, 291–296.
1097. Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1992**, *31*, 4112–4117.
1098. Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; De Cola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230–4238.
1099. Chichak, K.; Branda, N. R. *Chem. Commun.* **1999**, 523–524.
1100. Albano, G.; Balzani, V.; Constable, E. C.; Maestri, M.; Smith, D. R. *Inorg. Chim. Acta* **1998**, *277*, 225–231.
1101. Weidner, S.; Pikramenou, Z. *Chem. Commun.* **1998**, 1473–1474.
1102. Armspach, D.; Matt, D.; Harriman, A. *Eur. J. Inorg. Chem.* **2000**, 1147–1150.
1103. Armspach, D.; Constable, E. C.; Diederich, F.; Housecroft, C. E.; Nierengarten, J. F. *Chem Eur J* **1998**, *4*, 723–733.
1104. Sauvage, J.-P.; Ward, M. *Inorg. Chem.* **1991**, *30*, 3869–3874.
1105. Ziegler, M.; Monney, V.; Stoeckli-Evans, H.; von Zelewsky, A.; Sasaki, I.; Dupic, G.; Daran, J.-C.; Balavoine, G. G. A. *J. Chem. Soc., Dalton Trans.* **1999**, 667–675.
1106. Padilla-Tosta, V. E.; Lloris, J. M.; Martínez-Máñez, R.; Pardo, T.; Soto, J.; Benito, A.; Marcos, M. D. *Inorg. Chem. Commun.* **2000**, *3*, 45–48.
1107. Whittle, B.; Batten, S. R.; Jeffery, J. C.; Rees, L. H.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1996**, 4249–4255.
1108. Yam, V. W. W.; Lee, V. W. M. *J. Chem. Soc., Dalton Trans.* **1997**, 3005–3010.
1109. Sauvage, J.-P.; Collin, J.-P.; Chambron, J.-C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelletti, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993–1019.
1110. Collin, J.-P.; Gavina, P.; Heitz, V.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **1998**, 1–14.

1111. Rezvani, A. R.; Evans, C. E. B.; Crutchley, R. J. *Inorg. Chem.* **1995**, *34*, 4600–4604.
1112. Gibson, D. H.; Sleadd, B. A.; Mashuta, M. S.; Richardson, J. F. *Organometallics* **1997**, *16*, 4421–4427.
1113. Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1997**, *36*, 5678–5679.
1114. Liang, Y. Y.; Baba, A. I.; Kim, W. Y.; Atherton, J.; Schmehl, R. H. *J. Phys. Chem.* **1996**, *100*, 18408–18414.
1115. Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1994**, 3095–3098.
1116. Akasaka, T.; Otsuki, J.; Araki, K. *Chem. Eur. J.* **2002**, *8*, 130–136.
1117. Constable, E. C.; Housecroft, C. E.; Schofield, E. R.; Encinas, S.; Armaroli, N.; Barigelletti, F.; Flamigni, L.; Figgemeier, E.; Vos, J. G. *Chem. Commun.* **1999**, 869–870.
1118. Encinas, S.; Flamigni, L.; Barigelletti, F.; Constable, E. C.; Housecroft, C. E.; Schofield, E. R.; Figgemeier, E.; Fenske, D.; Neuburger, M.; Vos, J. G.; Zehnder, M. *Chem. Eur. J.* **2002**, *8*, 137–150.
1119. Constable, E. C.; Cargill Thompson, A. M. W.; Harveson, P.; Macko, L.; Zehnder, M. *Chem. Eur. J.* **1995**, *1*, 360–367.
1120. Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Dalton Trans.* **1992**, 3467–3475.
1121. Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Cargill Thompson, A. M. W. *J. Chem. Soc., Chem. Commun.* **1993**, 942–944.
1122. Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E. C.; Cargill Thompson, A. M. W. *J. Am. Chem. Soc.* **1994**, *116*, 7692–7699.
1123. Barigelletti, F.; Flamigni, L.; Guardigli, M.; Sauvage, J.-P.; Collin, J.-P.; Sour, A. *Chem. Commun.* **1996**, 1329–1330.
1124. Barigelletti, F.; Flamigni, L.; Guardigli, M.; Juris, A.; Beley, M.; Chodorows-Kikimmes, S.; Collin, J.-P.; Sauvage, J.-P. *Inorg. Chem.* **1996**, *35*, 136–142.
1125. Hammarstrom, L.; Barigelletti, F.; Flamigni, L.; Indelli, M. T.; Armaroli, N.; Calogero, G.; Guardigli, M.; Sour, A.; Collin, J.-P.; Sauvage, J.-P. *J. Phys. Chem. A* **1997**, *101*, 9061–9069.
1126. Indelli, M. T.; Scandola, F.; Flamigni, L.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *Inorg. Chem.* **1997**, *36*, 4247–4250.
1127. Indelli, M. T.; Scandola, F.; Collin, J.-P.; Sauvage, J.-P.; Sour, A. *Inorg. Chem.* **1996**, *35*, 303–312.
1128. Barigelletti, F.; Flamigni, L.; Collin, J.-P.; Sauvage, J.-P. *Chem. Commun.* **1997**, 333–338.
1129. Hammarstrom, L.; Barigelletti, F.; Flamigni, L.; Armaroli, N.; Sour, A.; Collin, J.-P.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 11972–11973.
1130. Kelch, S.; Rehahn, M. *Chem. Commun.* **1999**, 1123–1124.
1131. Hasenknopf, B.; Hall, J.; Lehn, J.-M.; Balzani, V.; Credi, A.; Campagna, S. *New J. Chem.* **1996**, *20*, 725–730.
1132. Vogler, L. M.; Brewer, K. J. *Inorg. Chem.* **1996**, *35*, 818–824.
1133. Vogler, L. M.; Jones, S. W.; Jensen, G. E.; Brewer, R. G.; Brewer, K. J. *Inorg. Chim. Acta* **1996**, *250*, 155–162.
1134. Jones, S. W.; Vrana, L. M.; Brewer, K. J. *J. Organometal. Chem.* **1998**, *554*, 29–40.
1135. Lee, J. D.; Vrana, L. M.; Bullock, E. R.; Brewer, K. J. *Inorg. Chem.* **1998**, *37*, 3575–3580.
1136. Bonhôte, P.; Lecas, A.; Amouyal, E. *Chem. Commun.* **1998**, 885–886.
1137. Hossain, M. D.; Ueno, R.; Haga, M. *Inorg. Chem. Commun.* **2000**, *3*, 35–38.
1138. Chamchoumis, C. M.; Potvin, P. G. *J. Chem. Soc., Dalton Trans.* **1999**, 1373–1374.
1139. Hissler, M.; El-ghayoury, A.; Harriman, A.; Ziessel, R. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1717–1720.
1140. Grosshenny, V.; Harriman, A.; Hissler, M.; Ziessel, R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 2223–2238.
1141. Harriman, A.; Ziessel, R. *Chem. Commun.* **1996**, 1707–1716.
1142. Harriman, A.; Ziessel, R. *Coord. Chem. Rev.* **1998**, *171*, 331–339.
1143. Hanan, G. S.; Arana, C. R.; Lehn, J.-M.; Fenske, D. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1122–1124.
1144. Hanan, G. S.; Arana, C. R.; Lehn, J.-M.; Baum, G.; Fenske, D. *Chem. Eur. J.* **1996**, *2*, 1292–1302.
1145. Ceroni, P.; Credi, A.; Balzani, V.; Campagna, S.; Hanan, G. S.; Arana, C. R.; Lehn, J.-M. *Eur. J. Inorg. Chem.* **1999**, 1409–1414.
1146. Steenwinkel, P.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 5647–5655.
1147. Collin, J. P.; Beley, M.; Sauvage, J.-P.; Barigelletti, F. *Inorg. Chim. Acta* **1991**, *186*, 91–93.
1148. Constable, E. C.; Hannon, M. J. *Inorg. Chim. Acta* **1993**, *211*, 101–110.
1149. Constable, E. C.; Cargill Thompson, A. M. W. *New J. Chem.* **1996**, *20*, 65–82.
1150. Constable, E. C.; Rees, D. G. F. *Polyhedron* **1998**, *17*, 3281–3289.
1151. Beley, M.; Chodorowski, S.; Collin, J.-P.; Sauvage, J.-P.; Flamigni, L.; Barigelletti, F. *Inorg. Chem.* **1994**, *33*, 2543–2547.
1152. Chavarot, M.; Pikramenou, Z. *Tetrahedron Lett.* **1999**, *40*, 6865–6868.
1153. Jouaiti, A.; Geoffroy, M.; Collin, J.-P. *Inorg. Chim. Acta* **1996**, *245*, 69–73.
1154. Collin, J.-P.; Kayhanian, R.; Sauvage, J.-P.; Calogero, G.; Barigelletti, F.; De Cian, A.; Fischer, J. *Chem. Commun.* **1997**, 775–776.
1155. Barigelletti, F.; Ventura, B.; Collin, J.-P.; Kayhanian, R.; Gavina, P.; Sauvage, J.-P. *Eur. J. Inorg. Chem.* **2000**, 113–119.
1156. Bonnefous, C.; Chouai, A.; Thummel, R. P. *Inorg. Chem.* **2001**, *40*, 5851–5859.
1157. Abbenhuis, R. A. T. M.; del Rio, I.; Bergshoef, M. M.; Boersma, J.; Veldman, N.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1998**, *37*, 1749–1758.
1158. Bardwell, D. A.; Cargill Thompson, A. M. W.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1996**, 873–878.
1159. Redmore, S. M.; Rickard, C. E. F.; Webb, S. J.; Wright, L. J. *Inorg. Chem.* **1997**, *36*, 4743–4748.
1160. Liegghio, R.; Potvin, P. G.; Lever, A. B. P. *Inorg. Chem.* **2001**, *40*, 5485–5486.
1161. Hung, C. Y.; Wang, T. L.; Jang, Y. C.; Kim, W. Y.; Schmehl, R. H.; Thummel, R. P. *Inorg. Ch.* **1996**, *35*, 5953–5956.
1162. Chirayil, S.; Hegde, V.; Jahng, Y.; Thummel, R. P. *Inorg. Chem.* **1991**, *30*, 2821–2823.
1163. Mahapatra, S.; Mukherjee, R. *J. Chem. Soc., Dalton Trans.* **1992**, 2337–2341.
1164. Bessel, C. A.; See, R. F.; Jameson, D. L.; Churchill, M. R.; Takeuchi, K. J. *J. Chem. Soc., Dalton Trans.* **1993**, 1563–1576.
1165. Bessel, C. A.; See, R. F.; Jameson, D. L.; Churchill, M. R.; Takeuchi, K. J. *J. Chem. Soc., Dalton Trans.* **1991**, 2801–2805.
1166. Slattery, S. J.; Bare, W. D.; Jameson, D. L.; Goldsby, K. A. *J. Chem. Soc., Dalton Trans.* **1999**, 1347–1352.

1167. Catalano, V. J.; Kurtaran, R.; Heck, R. A.; Ohman, A.; Hill, M. G. *Inorg. Chim. Acta* **1999**, *286*, 181–188.
1168. Downard, A. J.; Honey, G. E.; Steel, P. J. *Inorg. Chem.* **1991**, *30*, 3733–3737.
1169. Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Iglesias, L.; Garćia-Granda, S. *Inorg. Chem.* **1999**, *38*, 2874–2879.
1170. Xiao, X. M.; Haga, M. A.; Matsumurainoue, T.; Ru, Y.; Addison, A. W.; Kano, K. *J. Chem. Soc., Dalton Trans.* **1993**, 2477–2484.
1171. Lim, J.-W.; Yeo, H.-J.; Jeong, J.-H. *Acta Crystallogr., Sect. C* **1997**, *53*, 1405–1407.
1172. Ayers, T.; Caylor, N.; Ayers, G.; Godwin, C.; Hathcock, D. J.; Stuman, V.; Slattery, S. J. *Inorg. Chim. Acta* **2002**, *328*, 33–38.
1173. Zadykowicz, J.; Potvin, P. G. *Inorg. Chem.* **1999**, *38*, 2434–2441.
1174. Jahng, Y.; Thummel, R. P.; Bott, S. G. *Inorg. Chem.* **1997**, *36*, 3133–3138.
1175. Chao, H.; Yang, G.; Xue, G.-Q.; Li, H.; Zang, H.; Williams, I. D.; Ji, L.-N.; Chen, X.-M.; Li, X.-Y. *J. Chem. Soc., Dalton Trans.* **2001**, 1326–1331.
1176. Mamo, A.; Stefio, I.; Poggi, A.; Tringali, C.; Di Pietro, C.; Campagna, S. *New J. Chem.* **1997**, *21*, 1173–1185.
1177. Tondreau, V.; Leiva, A. M.; Loeb, B.; Stultz, L. K.; Meyer, T. J. *Polyhedron* **1996**, *15*, 2035–2040.
1178. Brewer, R. G.; Jensen, G. E.; Brewer, K. J. *Inorg. Chem.* **1994**, *33*, 124–129.
1179. Vrana, L. M.; Brewer, K. J. *J. Photochem. Photobiol. A* **1997**, *109*, 201–211.
1180. Hartshorn, C. M.; Daire, N.; Tondreau, V.; Loeb, B.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1999**, *38*, 3200–3206.
1181. Constable, E. C.; Walker, J. V. *Polyhedron* **1998**, *17*, 3089–3100.
1182. Ruba, E.; Simanko, W.; Mereiter, K.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **2000**, *39*, 382–384.
1183. Mizobe, Y.; Hosomizu, M.; Hidai, M. *Inorg. Chim. Acta* **1998**, *273*, 238–243.
1184. Gemel, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1996**, 4071–4076.
1185. Trimmel, G.; Slugovc, C.; Wiede, P.; Mereiter, K.; Sapunov, V. N.; Schmid, R.; Kirchner, K. *Inorg. Chem.* **1997**, *36*, 1076–1083.
1186. Chen, Y.-Z.; Chan, W.-C.; Lau, C.-P.; Chu, H.-S.; Lee, H.-L.; Jia, G.-C. *Organometallics* **1997**, *16*, 1241–1246.
1187. Sun, N. Y.; Simpson, S. J. *J. Organometal. Chem.* **1992**, *434*, 341–349.
1188. Buriez, B.; Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1999**, *18*, 1504–1516.
1189. Tenorio, M. J.; Tenorio, M. A. J.; Puerta, M. C.; Valerga, P. *Inorg. Chim. Acta* **1997**, *259*, 77–84.
1190. Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G.-C. *Organometallics* **1997**, *16*, 34–44.
1191. Burns, I. D.; Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 1552–1557.
1192. Halcrow, M. A.; Chaudret, B.; Trofimenko, S. *J. Chem. Soc., Chem. Commun.* **1993**, 465–467.
1193. Huh, S.; Kim, Y.; Youm, K. T.; Jun, M. J. *Polyhedron* **1999**, *18*, 2625–2631.
1194. Takahashi, Y.; Akita, M.; Hikichi, S.; Morooka, Y. *Inorg. Chem.* **1998**, *37*, 3186–3194.
1195. Hill, A. F.; White, A. J. P.; Williams, D. J.; Wilton-Ely, J. D. E. T. *Organometallics* **1998**, *17*, 4249–4258.
1196. Bellachioma, G.; Cardaci, G.; Gramlich, V.; Macchioni, A.; Pieroni, F.; Venanzi, L. M. *J. Chem. Soc., Dalton Trans.* **1998**, 947–951.
1197. Huh, S.; Kim, Y.; Park, S.; Park, T. J.; Jun, M. J. *Acta Crystallogr., Sect. C* **1999**, *55*, 850–852.
1198. Cartwright, J.; Hill, A. F. *J. Organometal. Chem.* **1992**, *429*, 229–238.
1199. Onishi, M.; Ikemoto, K.; Hiraki, K. *Inorg. Chim. Acta* **1991**, *190*, 157–159.
1200. Onishi, M.; Ikemoto, K.; Hiraki, K. *Inorg. Chim. Acta* **1994**, *219*, 3–5.
1201. Llobet, A.; Hodgson, D. J.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 3760–3766.
1202. Llobet, A. *Inorg. Chim. Acta* **1994**, *221*, 125–131.
1203. Jones, W. E.; Bignozzi, C. A.; Chen, P.-Y.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 1167–1178.
1204. Huang, L.; Seward, K. J.; Sullivan, B. P.; Jones, W. E.; Mecholsky, J. J.; Dressick, W. J. *Inorg. Chim. Acta* **2000**, *310*, 227–236.
1205. Renouard, T.; Fallahpour, R.-A.; Nazeeruddin, M. K.; Humphry-Baker, R.; Gorelsky, S. I.; Lever, A. B. P.; Grätzel, M. *Inorg. Chem.* **2002**, *41*, 367–378.
1206. Mizushima, K.; Nakaura, M.; Park, S. B.; Nishiyama, H.; Monjushiro, H.; Harada, K.; Haga, M. *Inorg. Chim. Acta* **1997**, *261*, 175–180.
1207. Masood, M. A.; Sullivan, B. P.; Hodgson, D. J. *Inorg. Chem.* **1994**, *33*, 4611–4612.
1208. Kojima, T.; Amano, T.; Ishii, Y.; Ohba, M.; Okaue, Y.; Matsuda, Y. *Inorg. Chem.* **1998**, *37*, 4076–4085.
1209. Kojima, T. *Chem. Lett.* **1996**, 121–122.
1210. Xu, L.; Sasaki, Y. *Inorg. Chem. Commun.* **1999**, *2*, 121–123.
1211. Kojima, T.; Hayashi, K.; Matsuda, Y. *Chem. Lett.* **2000**, 1008–1009.
1212. Cheng, R. J.; Lin, S. H.; Mo, H. M. *Organometallics* **1997**, *16*, 2121–2126.
1213. Vitols, S. E.; Roman, J. S.; Ryan, D. E.; Blackwood, M. E.; Spiro, T. G. *Inorg. Chem.* **1997**, *36*, 764–769.
1214. Birnbaum, E. R.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 1751–1755.
1215. Groves, J. T.; Bonchio, M.; Carofiglio, T.; Shalyaev, K. *J. Am. Chem. Soc.* **1996**, *118*, 8961–8962.
1216. Gentemann, S.; Albaneze, J.; Garcia-Ferrer, R.; Knapp, S.; Potenza, J. A.; Schugar, H. J.; Holten, D. *J. Am. Chem. Soc.* **1994**, *116*, 281–289.
1217. Kadish, K. M.; Tagliatesta, P.; Hu, Y.; Deng, Y.-J.; Mu, X.-H.; Bao, L.-Y. *Inorg. Chem.* **1991**, *30*, 3737–3743.
1218. Bartczak, T. J.; Rachlewicz, K.; LatosGrazynski, L. *Acta Crystallogr., Sect B* **1997**, *53*, 767–772.
1219. Galardon, E.; Le Maux, P.; Toupet, L.; Simonneaux, G. *Organometallics* **1998**, *17*, 565–569.
1220. Rachlewicz, K.; Grzeszczuk, M.; Latosgrazynski, L. *Polyhedron* **1993**, *12*, 821–829.
1221. Kadish, K. M.; Hu, Y.; Tagliatesta, P.; Boschi, T. *J. Chem. Soc., Dalton Trans.* **1993**, 1167–1172.
1222. Wyllie, G. R. A.; Scheidt, W. R. *Chem. Rev.* **2002**, *102*, 1067–1089.
1223. Yi, G. B.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1996**, *35*, 3453–3454.
1224. Chen, L.; Yi, G. B.; Wang, L. S.; Dharmawardana, U. R.; Dart, A. C.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1998**, *37*, 4677–4688.
1225. Kadish, K. M.; Adamian, V. A.; van Caemelbecke, E.; Tan, Z.; Tagliatesta, P.; Bianco, P.; Boschi, T.; Yi, G. B.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1996**, *35*, 1343–1348.

1226. Miranda, K. M.; Bu, X. H.; Lorkovic, I.; Ford, P. C. *Inorg. Chem.* **1997**, *36*, 4838–4848.
1227. Lorkovic, I. M.; Ford, P. C. *Inorg. Chem.* **1999**, *38*, 1467–1473.
1228. Hodge, S. J.; Wang, L. S.; Khan, M. A.; Young, V. G.; Richter-Addo, G. B. *Chem. Commun.* **1996**, 2283–2284.
1229. Cheng, L.; Chen, L.; Chung, H. S.; Khan, M. A.; Richter-Addo, G. B. *Organometallics* **1998**, *17*, 3853–3864.
1230. Bohle, D. S.; Goodson, P. A.; Smith, B. D. *Polyhedron* **1996**, *15*, 3147–3150.
1231. Yi, G. B.; Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1997**, *36*, 3876–3885.
1232. Chen, L.; Khan, M. A.; Richter-Addo, G. B. *Inorg. Chem.* **1998**, *37*, 533–540.
1233. Yi, G. B.; Khan, M. A.; Powell, D. R.; Richter-Addo, G. B. *Inorg. Chem.* **1998**, *37*, 208–214.
1234. Fomitchev, D. V.; Coppens, P.; Li, T. S.; Bagley, K. A.; Chen, L.; Richter-Addo, G. B. *Chem. Commun.* **1999**, 2013–2014.
1235. Leung, W. H.; Chim, J. L. C.; Lai, W.; Lam, L.; Wong, W. T.; Chan, W. H.; Yeung, C. H. *Inorg. Chim. Acta* **1999**, *290*, 28–35.
1236. Bohle, D. S.; Hung, C. H.; Powell, A. K.; Smith, B. D.; Wocadlo, S. *Inorg. Chem.* **1997**, *36*, 1992–1993.
1237. Groves, J. T.; Roman, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5594–5595.
1238. Bailey, A. J.; James, B. R. *Chem. Commun.* **1996**, 2343–2344.
1239. Huang, J. S.; Leung, S. K. Y.; Cheung, K. K.; Che, C. M. *Chem. Eur. J.* **2000**, *6*, 2971–2981.
1240. Gèze, C.; Legrand, N.; Bondon, A.; Simonneaux, G. *Inorg. Chim. Acta* **1992**, *195*, 73–76.
1241. Ikonen, M.; Guez, D.; Marvaud, V.; Markovitsi, D. *Chem. Phys. Lett.* **1994**, *231*, 93–97.
1242. Jeoung, S. C.; Kim, D. H.; Cho, D. W.; Yoon, M. J.; Ahn, K. H. *J. Phys. Chem.* **1996**, *100*, 8867–8874.
1243. Vitols, S. E.; Kumble, R.; Blackwood, M. E.; Roman, J. S.; Spiro, T. G. *J. Phys. Chem.* **1996**, *100*, 4180–4187.
1244. Pacheco, A.; James, B. R.; Rettig, S. J. *Inorg. Chem.* **1995**, *34*, 3477–3484.
1245. Pacheco, A.; James, B. R.; Rettig, S. J. *Inorg. Chem.* **1999**, *38*, 5579–5587.
1246. Yee, G. T.; Noll, B. C.; Williams, D. K. C.; Sellers, S. P. *Inorg. Chem.* **1997**, *36*, 2904–2907.
1247. Mazzanti, M.; Veyrat, M.; Ramasseul, R.; Marchon, J. C.; Turowskatyrk, I.; Shang, M.; Scheidt, W. R. *Inorg. Chem.* **1996**, *35*, 3733–3734.
1248. Morice, C.; Le Maux, P.; Simonneaux, G.; Toupet, L. *J. Chem. Soc., Dalton Trans.* **1998**, 4165–4171.
1249. Galardon, E.; Le Maux, P.; Bondon, A.; Simonneaux, G. *Tetrahedron Asymmetry* **1999**, *10*, 4203–4210.
1250. Le Maux, P.; Bahri, H.; Simonneaux, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1350–1352.
1251. Slebodnick, C.; Seok, W. K.; Kim, K. M.; Ibers, J. A. *Inorg. Chim. Acta* **1996**, *243*, 57–65.
1252. Slebodnick, C.; Kim, K.; Ibers, J. A. *Inorg. Chem.* **1993**, *32*, 5338–5342.
1253. Marvaud, V.; Launay, J.-P. *Inorg. Chem.* **1993**, *32*, 1376–1382.
1254. Saito, M.; Endo, A.; Shimizu, K.; Sato, G. P. *Electrochim. Acta* **2000**, *45*, 3021–3028.
1255. Endo, A.; Okamoto, Y.; Suzuki, K.; Shimamura, J.; Shimizu, K.; Sato, G. P. *Chem. Lett.* **1994**, 1317–1320.
1256. Endo, A.; Tagami, U.; Wada, Y.; Saito, M.; Shimizu, K.; Sato, G. P. *Chem. Lett.* **1996**, 243–244.
1257. Stuzhin, P. A.; Vagin, S. I.; Hanack, M. *Inorg. Chem.* **1998**, *37*, 2655–2662.
1258. Alessio, E.; Macchi, M.; Heath, S.; Marzilli, L. G. *Chem. Commun.* **1996**, 1411–1412.
1259. Alessio, E.; Macchi, M.; Heath, S. L.; Marzilli, L. G. *Inorg. Chem.* **1997**, *36*, 5614–5623.
1260. Kariya, N.; Imamura, T.; Sasaki, Y. *Inorg. Chem.* **1997**, *36*, 833–839.
1261. Funatsu, K.; Kimura, A.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.* **1997**, *36*, 1625–1635.
1262. Funatsu, K.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.* **1998**, *37*, 1798–1804.
1263. Funatsu, K.; Imamura, T.; Ichimura, A.; Sasaki, Y. *Inorg. Chem.* **1998**, *37*, 4986–4995.
1264. Okumura, A.; Funatsu, K.; Sasaki, Y.; Imamura, T. *Chem. Lett.* **1999**, 779–780.
1265. Mak, C. C.; Bampos, N.; Sanders, J. K. M. *Chem. Commun.* **1999**, 1085–1086.
1266. Collman, J. P.; Arnold, H. J.; Fitzgerald, J. P.; Weissman, K. J. *J. Am. Chem. Soc.* **1993**, *115*, 9309–9310.
1267. Godwin, H. A.; Collman, J. P.; Marchon, J. C.; Maldivi, P.; Yee, G. T.; Conklin, B. J. *Inorg. Chem.* **1997**, *36*, 3499–3502.
1268. Collman, J. P.; Arnold, H. J.; Weissman, K. J.; Burton, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 9761–9762.
1269. Collman, J. P.; Harford, S. T.; Franzen, S.; Shreve, A. P.; Woodruff, W. H. *Inorg. Chem.* **1999**, *38*, 2093–2097.
1270. Collman, J. P.; Harford, S. T.; Franzen, S.; Marchon, J. C.; Maldivi, P.; Shreve, A. P.; Woodruff, W. H. *Inorg. Chem.* **1999**, *38*, 2085–2092.
1271. Collman, J. P.; Harford, S. T.; Maldivi, P.; Marchon, J. C. *J. Am. Chem. Soc.* **1998**, *120*, 7999–8000.
1272. Collman, J. P.; Harford, S. T. *Inorg. Chem.* **1998**, *37*, 4152–4153.
1273. Collman, J. P.; Fish, H. T. *Inorg. Chem.* **1996**, *35*, 7922–7923.
1274. Gal, M.; Lobo-Recio, M. A.; Marzin, C.; Seghrouchni, S.; Tarrago, G. *Inorg. Chem.* **1994**, *33*, 4054–4061.
1275. Marzin, C.; Naji, M.; Coquelet, C.; Tarrago, G. *Inorg. Chim. Acta* **1996**, *246*, 217–227.
1276. Chabert-Couchouron, N.; Marzin, C.; Reibel, C.; Tarrago, G. *New J. Chem.* **1997**, *21*, 993–999.
1277. Keppeler, U.; Kobel, W.; Siehl, H.-U.; Hanack, M. *Chem. Ber.-Recl.* **1985**, *118*, 2095–2104.
1278. Hanack, M.; Kang, Y. G. *Chem. Ber.* **1991**, *124*, 1607–1612.
1279. Bulatov, A.; Knecht, S.; Subramanian, L. R.; Hanack, M. *Chem. Ber.* **1993**, *126*, 2565–2566.
1280. Czekalla, M.; Sievertsen, S.; Homborg, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1205–1210.
1281. Sievertsen, S.; Weidemann, M.; Tsantzikrause, O.; Homborg, H. *Z. Anorg. Allg. Chem.* **1995**, *621*, 1567–1572.
1282. Weidemann, M.; Homborg, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1705–1710.
1283. Weidemann, M.; Homborg, H. *Z. Anorg. Allg. Chem.* **1996**, *622*, 1182–1186.
1284. Weidemann, M.; Huckstadt, H.; Homborg, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 846–852.
1285. Weidemann, M.; Sievertsen, S.; Homborg, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 909–918.
1286. Sekota, M.; Nyokong, T. *Polyhedron* **1996**, *15*, 2901–2908.
1287. Hanack, M.; Vermehren, P. *Chem. Ber.* **1991**, *124*, 1733–1738.
1288. Guez, D.; Markovitsi, D.; Sommerauer, M.; Hanack, M. *Chem. Phys. Lett.* **1996**, *249*, 309–313.
1289. Hanack, M.; Knecht, S.; Polley, R. *Chem. Ber.* **1995**, *128*, 929–933.
1290. Durr, K.; Hanack, M. *J. Porphyr. Phthalocya.* **1999**, *3*, 224–229.
1291. Hanack, M.; Polley, R. *Inorg. Chem.* **1994**, *33*, 3201–3204.
1292. Bertagnolli, H.; Weber, A.; Horner, W.; Ertel, T. S.; Reinohl, U.; Hanack, M.; Hees, M.; Polley, R. *Inorg. Chem.* **1997**, *36*, 6397–6400.

1293. Caminiti, R.; Donzello, M. P.; Ercolani, C.; Sadun, C. *Inorg. Chem.* **1999**, *38*, 3027–3029.
1294. Caminiti, R.; Donzello, M. P.; Ercolani, C.; Sadun, C. *Inorg. Chem.* **1998**, *37*, 4210–4213.
1295. Hanack, M.; Hees, M.; Witke, E. *New J. Chem.* **1998**, *22*, 169–172.
1296. Pohmer, J.; Hanack, M.; Barcina, J. O. *J. Mater. Chem.* **1996**, *6*, 957–962.
1297. Robinson, P. D.; Ali, I. A.; Hinckley, C. C. *Acta Crystallogr., Sect. C* **1991**, *47*, 651–654.
1298. Clucas, W. A.; Armstrong, R. S.; Buys, I. E.; Hambley, T. W.; Nugent, K. W. *Inorg. Chem.* **1996**, *35*, 6789–6794.
1299. Schneider, R.; Justel, T.; Wieghardt, K.; Nuber, B. *Z. Naturforsch., Teil B* **1994**, *49*, 330–336.
1300. Cheng, W.-C.; Yu, W.-Y.; Cheung, K.-K.; Che, C.-M. *J. Chem. Soc., Dalton Trans.* **1994**, 57–62.
1301. Ware, D. C.; Olmstead, M. M.; Wang, R. Y.; Taube, H. *Inorg. Chem.* **1996**, *35*, 2576–2582.
1302. Justel, T.; Bendix, J.; Metzler-Nolte, N.; Weyhermuller, T.; Nuber, B.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 35–43.
1303. Ng, S. M.; Fang, Y. Q.; Lau, C. P.; Wong, W. T.; Jia, G. C. *Organometallics* **1998**, *17*, 2052–2059.
1304. da Silva, R. S.; Tfouni, E. *Inorg. Chem.* **1992**, *31*, 3313–3316.
1305. Chiu, W. H.; Che, C. M.; Mak, T. C. W. *Polyhedron* **1996**, *15*, 4421–4423.
1306. Luo, L. B.; Stevens, E. D.; Nolan, S. P. *Inorg. Chem.* **1996**, *35*, 252–254.
1307. Tarrago, G.; Elkadiri, S.; Marzin, C.; Coquelet, C. *New J. Chem.* **1991**, *15*, 677–684.
1308. Tresoldi, G.; Loschiavo, S.; Piraino, P.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1996**, 885–892.
1309. Ribou, A. C.; Wada, T.; Sasabe, H. *Inorg. Chim. Acta* **1999**, *288*, 134–141.
1310. Posse, M. E. G.; Fagalde, F.; Vergara, M. M.; Katz, N. E. *Polyhedron* **1998**, *17*, 2733–2738.
1311. Hamra, O. Y.; Slep, L. D.; Olabe, J. A.; Estrin, D. A. *Inorg. Chem.* **1998**, *37*, 2033–2038.
1312. Toma, H. E.; De Oliveira, D. *Polyhedron* **1991**, *10*, 1699–1704.
1313. Khan, M. M. T.; Khan, N. H.; Kureshy, R. I.; Venkatasubramanian, K. *Polyhedron* **1992**, *11*, 431–441.
1314. Olby, B. G.; Robinson, S. D.; Hursthouse, M. B.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1990**, 621–627.
1315. Olby, B. G.; Robinson, S. D.; Hursthouse, M. B.; Short, R. L. *Polyhedron* **1988**, *7*, 1781–1783.
1316. Baird, I. R.; Rettig, S. J.; James, B. R.; Skov, K. A. *Can. J. Chem.* **1998**, *76*, 1379–1388.
1317. Pifferi, C.; Cini, R. *J. Chem. Soc., Dalton Trans.* **1998**, 2679–2688.
1318. Sammes, P. G.; Yahioglu, G. *Chem. Soc. Rev.* **1994**, *23*, 327–334.
1319. Coury, J. E.; Anderson, J. R.; McFail-Isom, L.; Williams, L. D.; Bottomley, L. A. *J. Am. Chem. Soc.* **1997**, *119*, 3792–3796.
1320. Hurley, D. J.; Tor, Y. *J. Am. Chem. Soc.* **1998**, *120*, 2194–2195.
1321. Hurley, D. J.; Tor, Y. *J. Am. Chem. Soc.* **2002**, *124*, 3749–3762.
1322. Haworth, I. S.; Elcock, A. H.; Freeman, J.; Rodger, A.; Richards, W. G. *J. Biomol. Struct. Dyn.* **1991**, *9*, 23–44.
1323. Haworth, I. S.; Elcock, A. H.; Rodger, A.; Richards, W. G. *J. Biomol. Struct. Dyn.* **1991**, *9*, 553–569.
1324. Broo, A.; Lincoln, P. *Inorg. Chem.* **1997**, *36*, 2544–2553.
1325. Goldstein, B. M.; Barton, J. K.; Berman, H. M. *Inorg. Chem.* **1986**, *25*, 842–847.
1326. Satyanarayana, S.; Dabrowiak, J. C.; Chaires, J. B. *Biochemistry* **1992**, *31*, 9319–9324.
1327. Satyanarayana, S.; Dabrowiak, J. C.; Chaires, J. B. *Biochemistry* **1993**, *32*, 2573–2584.
1328. Kim, H. K.; Lincoln, P.; Norden, B.; Tuite, E. *Chem. Commun.* **1997**, 2375–2376.
1329. Eriksson, M.; Leijon, M.; Hiort, C.; Nordén, B.; Gräslund, A. *J. Am. Chem. Soc.* **1992**, *114*, 4933–4934.
1330. Eriksson, M.; Leijon, M.; Hiort, C.; Nordén, B.; Gräslund, A. *Biochemistry* **1994**, *33*, 5031–5040.
1331. Coggan, D. Z. M.; Haworth, I. S.; Bates, P. J.; Robinson, A.; Rodger, A. *Inorg. Chem.* **1999**, *38*, 4486–4497.
1332. Naing, K.; Takahashi, M.; Taniguchi, M.; Yamagishi, A. *Inorg. Chem.* **1995**, *34*, 350–356.
1333. Liu, J.-G.; Ye, B.-H.; Li, H.; Zhen, Q.-X.; Ji, L.-N.; Fu, Y.-H. *J. Inorg. Biochem.* **1999**, *76*, 265–271.
1334. Liu, J.-G.; Ye, B.-H.; Zhang, Q.-L.; Zou, X.-H.; Zhen, Q.-X.; Tian, X.; Ji, L.-N. *J. Biol. Inorg. Chem.* **2000**, *5*, 119–128.
1335. O'Reilly, F. M.; Kelly, J. M. *New J. Chem.* **1998**, *22*, 215–217.
1336. O'Reilly, F.; Kelly, J.; Kirsch-De Mesmaeker, A. *Chem. Commun.* **1996**, 1013–1014.
1337. O'Reilly, F. M.; Kelly, J. M. *J. Phys. Chem. B* **2000**, *104*, 7206–7213.
1338. Mishra, L.; Yadaw, A. K.; Srivastava, S.; Patel, A. B. *New J. Chem.* **2000**, *24*, 505–510.
1339. Del Guerzo, A.; Kirsch-De Mesmaeker, A.; Demeunynck, M.; Lhomme, J. *J. Chem. Soc., Dalton Trans.* **2000**, *7*, 1173–1179.
1340. Pierard, F.; Del Guerzo, A.; Kirsch-De Mesmaeker, A.; Demeunynck, M.; Lhomme, J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 2911–2920.
1341. Del Guerzo, A.; Kirsch-De Mesmaeker, A. *Inorg. Chem.* **2002**, *41*, 938–945.
1342. Wu, J. Z.; Yang, G.; Chen, S.; Ji, L. N.; Zhou, J. Y.; Xu, Y. *Inorg. Chim. Acta* **1998**, *283*, 17–23.
1343. Wu, J. Z.; Ye, B. H.; Wang, L.; Ji, L. N.; Zhou, J. Y.; Li, R. H.; Zhou, Z. Y. *J. Chem. Soc., Dalton Trans.* **1997**, 1395–1401.
1344. Wu, J. Z.; Li, L.; Zeng, T. X.; Ji, L. N.; Zhou, J. Y.; Luo, T.; Li, R. H. *Polyhedron* **1997**, *16*, 103–107.
1345. Xiong, Y.; He, X. F.; Zou, X. H.; Wu, J. Z.; Chen, X. M.; Ji, L. N.; Li, R. H.; Zhou, J. Y.; Yu, K. B. *J. Chem. Soc., Dalton Trans.* **1999**, 19–23.
1346. Zou, X. H.; Ye, B. H.; Li, H.; Lin, J. G.; Xiong, Y.; Ji, L. N. *J. Chem. Soc., Dalton Trans.* **1999**, 1423–1428.
1347. Vickery, K.; Vagg, R.; Lincoln, P.; Norden, B.; Eriksson, M. *J. Biomol. Struct. Dyn.* **1999**, *17*, 519–525.
1348. Proudfoot, E. M.; Mackay, J. P.; Karuso, P. *Biochemistry* **2001**, *40*, 4867–4878.
1349. Grover, N.; Gupta, N.; Thorp, H. H. *J. Am. Chem. Soc.* **1992**, *114*, 3390–3393.
1350. Vicendo, P.; Mouysset, S.; Paillous, N. *Photochem. Photobiol.* **1997**, *65*, 647–655.
1351. Yang, G.; Wu, J. Z.; Wang, L.; Ji, L. N.; Tian, X. *J. Inorg. Biochem.* **1997**, *66*, 141–144.
1352. Foley, F. M.; Keene, F. R.; Collins, J. G. *J. Chem. Soc., Dalton Trans.* **2001**, 2968–2974.
1353. Dixon, D. W.; Thornton, N. B.; Steullet, V.; Netzel, T. *Inorg. Chem.* **1999**, *38*, 5526–5534.
1354. Armaroli, N.; Barigelletti, F.; Calogero, G.; Flamigni, L.; White, C. M.; Ward, M. D. *Chem. Commun.* **1997**, 2181–2182.
1355. Ward, M. D.; White, C. M.; Barigelletti, F.; Armaroli, N.; Calogero, G.; Flamigni, L. *Coord. Chem. Rev.* **1998**, *171*, 481–488.
1356. White, C. M.; Gonzalez, M. F.; Bardwell, D. A.; Rees, L. H.; Jeffery, J. C.; Ward, M. D.; Armaroli, N.; Calogero, G.; Barigelletti, F. *J. Chem. Soc., Dalton Trans.* **1997**, 727–735.

1357. Constable, E. C.; Fallahpour, R. A. *J. Chem. Soc., Dalton Trans.* **1996**, 2389–2390.
1358. Hotze, A. C. G.; Broekhuisen, M. E. T.; Velders, A. H.; van der Schilden, K.; Haasnoot, J. G.; Reedijk, J. *Eur. J. Inorg. Chem.* **2002**, 369–376.
1359. Lewis, F. D.; Helvoigt, S. A.; Letsinger, R. L. *Chem. Commun.* **1999**, 327–328.
1360. Krider, E. S.; Rack, J. J.; Frank, N. L.; Meade, T. J. *Inorg. Chem.* **2001**, *40*, 4002–4009.
1361. Khan, S. I.; Beilstein, A. E.; Smith, G. D.; Sykora, M.; Grinstaff, M. W. *Inorg. Chem.* **1999**, *38*, 2411–2415.
1362. Grover, N.; Gupta, N.; Singh, P.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 2014–2020.
1363. Smith, S. R.; Neyhart, G. A.; Kalsbeck, W. A.; Thorp, H. H. *New J. Chem.* **1994**, *18*, 397–406.
1364. van Vliet, P. M.; Toekimin, S. M. S.; Haasnoot, J. G.; Reedijk, J.; Novakova, O.; Vrana, O.; Brabec, V. *Inorg. Chim. Acta* **1995**, *231*, 57–64.
1365. Orellana, G.; Kirsch-De Mesmaeker, A.; Barton, J. K.; Turro, N. J. *Photochem. Photobiol.* **1991**, *54*, 499–509.
1366. Lecomte, J. P.; Kirsch-De Mesmaeker, A.; Kelly, J. M.; Tossi, A. B.; Gorner, H. *Photochem. Photobiol.* **1992**, *55*, 681–689.
1367. Lecomte, J. P.; Kirsch-De Mesmaeker, A.; Feeney, M. M.; Kelly, J. M. *Inorg. Chem.* **1995**, *34*, 6481–6491.
1368. Jacquet, L.; Kelly, J. M.; Kirsch-De Mesmaeker, A. *J. Chem. Soc., Chem. Commun.* **1995**, 913–914.
1369. Jacquet, L.; Davies, R. J. H.; Kirsch-De Mesmaeker, A.; Kelly, J. M. *J. Am. Chem. Soc.* **1997**, *119*, 11763–11768.
1370. Jacquet, L.; Kelly, J. M.; Kirsch-De Mesmaeker, A. *Inorg Chem Commun* **1999**, *2*, 135–138.
1371. Content, S.; Kirsch-De Mesmaeker, A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1089–1094.
1372. Moucheron, C.; Kirsch-De Mesmaeker, A.; Choua, S. *Inorg. Chem.* **1997**, *36*, 584–592.
1373. Zhen, Q. X.; Ye, B. H.; Zhang, Q. L.; Liu, J. G.; Li, H.; Ji, L. N.; Wang, L. *J. Inorg. Biochem.* **1999**, *76*, 47–53.
1374. Zhen, Q. X.; Zhang, Q. L.; Liu, J. G.; Ye, B. H.; Ji, L. N.; Wang, L. *J. Inorg. Biochem.* **2000**, *78*, 293–298.
1375. Brodkorb, A.; Kirsch-De Mesmaeker, A.; Rutherford, T. J.; Keene, F. R. *Eur. J. Inorg. Chem.* **2001**, 2151–2160.
1376. van Gijte, O.; Kirsch-De Mesmaeker, A. *J. Chem. Soc., Dalton Trans.* **1999**, 951–956.
1377. Ortmans, I.; Content, S.; Boutonnet, N.; Kirsch-De Mesmaeker, A.; Bannwarth, W.; Constant, J. F.; Defrancq, E.; Lhomme, J. *Chem. Eur. J.* **1999**, *5*, 2712–2721.
1378. Schumm, S.; Prevost, M.; Garcia-Fresnadillo, D.; Lentzen, O.; Moucheron, C.; Kirsch-De Mesmaeker, A. *J. Phys. Chem. B* **2002**, *106*, 2763–2768.
1379. Morgan, R. J.; Chatterjee, S.; Baker, A. D.; Strekas, T. C. *Inorg. Chem.* **1991**, *30*, 2687–2692.
1380. Tysoe, S. A.; Morgan, R. J.; Baker, A. D.; Strekas, T. C. *J. Phys. Chem.* **1993**, *97*, 1707–1711.
1381. Coates, C. G.; Jacquet, L.; McGarvey, J. J.; Bell, S. E. J.; Alobaidi, A. H. R.; Kelly, J. M. *Chem. Commun.* **1996**, 35–36.
1382. Coates, C. G.; Callaghan, P. L.; McGarvey, J. J.; Kelly, J. M.; Kruger, P. E.; Higgins, M. E. *J. Raman Spectrosc.* **2000**, *31*, 283–288.
1383. Coates, C. G.; Olofsson, J.; Coletti, M.; McGarvey, J. J.; Onfelt, B.; Lincoln, P.; Norden, B.; Tuite, E.; Matousek, P.; Parker, A. W. *J. Phys. Chem. B* **2001**, *105*, 12653–12664.
1384. Coates, C. G.; Callaghan, P.; McGarvey, J. J.; Kelly, J. M.; Jacquet, L.; Kirsch-De Mesmaeker, A. *J. Mol. Struct.* **2001**, *598*, 15–25.
1385. Friedman, A. E.; Chambron, J. C.; Sauvage, J.-P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 4960–4962.
1386. Hartshorn, R. M.; Barton, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 5919–5925.
1387. Holmlin, R. E.; Barton, J. K. *Inorg. Chem.* **1995**, *34*, 7–8.
1388. Holmlin, R. E.; Yao, J. A.; Barton, J. K. *Inorg. Chem.* **1999**, *38*, 174–189.
1389. Haq, I.; Lincoln, P.; Suh, D. C.; Norden, B.; Chowdhry, B. Z.; Chaires, J. B. *J. Am. Chem. Soc.* **1995**, *117*, 4788–4796.
1390. Dupureur, C. M.; Barton, J. K. *J. Am. Chem. Soc.* **1994**, *116*, 10286–10287.
1391. Greguric, A.; Greguric, I. D.; Hambley, T. W.; Aldrich-Wright, J. R.; Collins, J. G. *J. Chem. Soc., Dalton Trans.* **2002**, 849–855.
1392. Collins, J. G.; Sleeman, A. D.; Aldrich-Wright, J. R.; Greguric, I.; Hambley, T. W. *Inorg. Chem.* **1998**, *37*, 3133–3141.
1393. Marincola, F. C.; Casu, M.; Saba, G.; Lai, A.; Lincoln, P.; Norden, B. *Chem. Phys.* **1998**, *236*, 301–308.
1394. Hiort, C.; Lincoln, P.; Norden, B. *J. Am. Chem. Soc.* **1993**, *115*, 3448–3454.
1395. Lincoln, P.; Broo, A.; Norden, B. *J. Am. Chem. Soc.* **1996**, *118*, 2644–2653.
1396. Tuite, E.; Lincoln, P.; Norden, B. *J. Am. Chem. Soc.* **1997**, *119*, 239–240.
1397. Olson, E. J. C.; Hu, D.; Hormann, A.; Jonkman, A. M.; Arkin, M. R.; Stemp, E. D. A.; Barton, J. K.; Barbara, P. F. *J. Am. Chem. Soc.* **1997**, *119*, 11458–11467.
1398. Nair, R. B.; Cullum, B. M.; Murphy, C. J. *Inorg. Chem.* **1997**, *36*, 962–965.
1399. Nair, R. B.; Murphy, C. J. *J. Inorg. Biochem.* **1998**, *69*, 129–133.
1400. Nair, R. B.; Teng, E. S.; Kirkland, S. L.; Murphy, C. J. *Inorg. Chem.* **1998**, *37*, 139–141.
1401. Ling, L. S.; He, Z. K.; Song, G. W.; Zeng, Y. E. *Spectrosc Lett* **1999**, *32*, 931–939.
1402. Liu, J.-G.; Ye, B.-H.; Li, H.; Ji, L.-N.; Li, R.-H.; Zhou, J-Y. *J. Inorg. Biochem.* **1999**, *73*, 117–122.
1403. Albano, G.; Belser, P.; De Cola, L.; Gandolfi, M. T. *Chem. Commun.* **1999**, 1171–1172.
1404. Lincoln, P.; Norden, B. *Chem. Commun.* **1996**, 2145–2146.
1405. Milkevitch, M.; Shirley, B. W.; Brewer, K. J. *Inorg. Chim. Acta* **1997**, *264*, 249–256.
1406. Milkevitch, M.; Storrie, H.; Brauns, E.; Brewer, K. J.; Shirley, B. W. *Inorg. Chem.* **1997**, *36*, 4534–4538.
1407. Ambroise, A.; Maiya, B. G. *Inorg. Chem.* **2000**, *39*, 4264–4272.
1408. Turro, C.; Bossmann, S. H.; Jenkins, Y.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 9026–9032.
1409. Tysoe, S. A.; Kopelman, R.; Schelzig, D. *Inorg. Chem.* **1999**, *38*, 5196–5197.
1410. Önfelt, B.; Lincoln, P.; Nordén, B. *J Amer Chem Soc* **1999**, *121*, 10846–10847.
1411. Jenkins, Y.; Barton, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 8736–8738.
1412. Ossipov, D.; Zamaratski, E.; Chattopadhyaya, J. *Helv. Chim. Acta* **1999**, *82*, 2186–2200.
1413. Ossipov, D.; Pradeepkumar, P. I.; Holmer, M.; Chattopadhyaya, J. *J. Am. Chem. Soc.* **2001**, *123*, 3551–3562.
1414. Meggers, E.; Kusch, D.; Giese, B. *Helv Chim Acta* **1997**, *80*, 640–652.
1415. Holmlin, R. E.; Stemp, E. D. A.; Barton, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 5236–5244.
1416. Stemp, E. D. A.; Holmlin, R. E.; Barton, J. K. *Inorg. Chim. Acta* **2000**, *297*, 88–97.

1417. Madureira, J.; Santos, T. M.; Goodfellow, B. J.; Lucena, M.; de Jesus, J. L. P.; Santana-Marques, M. G.; Drew, M. G. B.; Felix, V. *J. Chem. Soc., Dalton Trans.* **2000**, 4422–4431.
1418. Sun, L. C.; Hammarström, L.; Akermark, B.; Styring, S. *Chem. Soc. Rev.* **2001**, *30*, 36–49.
1419. Durr, H.; Bossmann, S. *Acc. Chem. Res.* **2001**, *34*, 905–917.
1420. Sun, L. C.; Hammarström, L.; Norrby, T.; Berglund, H.; Davydov, R.; Andersson, M.; Börje, A.; Korall, P.; Philouze, C.; Almgren, M.; Styring, S.; Åkermark, B. *Chem. Commun.* **1997**, 607–608.
1421. Sun, L. C.; Berglund, H.; Davydov, R.; Norrby, T.; Hammarström, L.; Korall, P.; Börje, A.; Philouze, C.; Berg, K.; Tran, A.; Andersson, M.; Stenhagen, G.; Martensson, J.; Almgren, M.; Styring, S.; Åkermark, B. *J. Am. Chem. Soc.* **1997**, *119*, 6996–7004.
1422. Hammarström, L.; Sun, L.; Magnusson, A.; Frapart, Y.; Berglund-Baudin, H.; Åkermark, B.; Styring, S. *Z Phys Chem* **1999**, *213*, 157–163.
1423. Sjodin, M.; Styring, S.; Åkermark, B.; Sun, L. C.; Hammarström, L. *J. Am. Chem. Soc.* **2000**, *122*, 3932–3936.
1424. Burdinski, D.; Bothe, E.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 105–116.
1425. Dahlenburg, L.; Frosin, K. M. *Polyhedron* **1993**, *12*, 427–434.
1426. Rappert, T.; Yamamoto, A. *Organometallics* **1994**, *13*, 4984–4993.
1427. Holmes, N. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4223–4229.
1428. Ikuo, A.; Otani, K.; Chijimatsu, T.; Uzawa, J.; Yasufuku, K.; Teratani, S. *Chem. Lett.* **1999**, 185–186.
1429. Holmes, N. J.; Genge, A. R. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1997**, 2331–2334.
1430. Rosales, M.; Gonzalez, A.; Navarro, J.; Soscun, H.; Zarraga, J. *Inorg. Chim. Acta* **1997**, *257*, 131–135.
1431. Batista, A. A.; Z.-Schpector, J.; Porcu, O. M.; Queiroz, S. L.; Araujo, M. P.; Oliva, G.; Souza, D. H. F. *Polyhedron* **1994**, *13*, 689–693.
1432. Robinson, P. D.; Hinckley, C. C.; Ikuo, A. *Acta Crystallogr., Sect. C* **1988**, *44*, 1491–1492.
1433. Robinson, P. D.; Ali, I. A.; Hinckley, C. C. *Acta Crystallogr., Sect. C* **1991**, *47*, 1397–1401.
1434. Clark, H. C. S.; Coleman, K. S.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Redding, J.; Russell, D. R. *Polyhedron* **1999**, *18*, 1207–1210.
1435. Evans, E. W.; Howlader, M. B. H.; Atlay, M. T. *Inorg. Chim. Acta* **1995**, *230*, 193–197.
1436. Notheis, J. U.; Heyn, R. H.; Caulton, K. G. *Inorg. Chim. Acta* **1995**, *229*, 187–193.
1437. Arguello, E.; Bolanos, A.; Cuenu, F.; Navarro, M.; Herrera, V.; Fuentes, A.; Sanchez-Delgado, R. A. *Polyhedron* **1996**, *15*, 909–915.
1438. Bustelo, E.; Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1999**, 2399–2404.
1439. Rickard, C. E. F.; Roper, W. R.; Woodgate, S. D.; Wright, L. J. *J. Organomet. Chem.* **2002**, *643*, 168–173.
1440. Baratta, W.; Herdtweck, E.; Rigo, P. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 1629–1631.
1441. Higham, L.; Powell, A. K.; Whittlesey, M. K.; Wocadlo, S.; Wood, P. T. *Chem. Commun.* **1998**, 1107–1108.
1442. Ziessel, R.; Matt, D.; Toupet, L. *J. Chem. Soc., Chem. Commun.* **1995**, 2033–2035.
1443. Champness, N. R.; Levason, W.; Webster, M. *Inorg. Chim. Acta* **1993**, *208*, 189–194.
1444. Bellucci, C.; Cini, R. *J. Inorg. Biochem.* **1999**, *76*, 243–250.
1445. Kim, J. Y.; Jun, M. J.; Lee, W. Y. *Polyhedron* **1996**, *15*, 3787–3793.
1446. Paul, B. C.; Das, H. K. *Polyhedron* **1996**, *15*, 2433–2437.
1447. Paul, B. C.; Sarma, K. P.; Poddar, R. K. *Polyhedron* **1993**, *12*, 285–289.
1448. Huh, S.; Kim, Y.; Park, S.; Park, T. J.; Jun, M. J. *Acta Crystallogr., Sect. C* **1999**, *55*, 850–852.
1449. Ruiz, J.; Mosquera, M. E. G.; Riera, V. *J. Organometal. Chem.* **1997**, *527*, 35–41.
1450. Batista, A. A.; Pereira, C.; Wohnrath, K.; Queiroz, S. L.; Santos, R. H. D.; Gambardella, M. T. D. *Polyhedron* **1999**, *18*, 2079–2083.
1451. Barral, M. C.; Jimenez-Aparicio, R.; Royer, E. C.; Saucedo, M. J.; Urbanos, F. A.; Gutierrez-Puebla, E.; Ruiz-Valero, C. *Inorg. Chim. Acta* **1993**, *209*, 105–109.
1452. Ballester, L.; Barral, M. C.; Jimenez-Aparicio, R.; Olombrada, B. *Polyhedron* **1996**, *15*, 211–217.
1453. Polam, J. R.; Porter, L. C. *J. Coord. Chem.* **1993**, *29*, 109–119.
1454. Szczepura, L. F.; Giambra, J.; See, R. F.; Lawson, H.; Janik, T. S.; Jircitano, A. J.; Churchill, M. R.; Takeuchi, K. J. *Inorg. Chim. Acta* **1995**, *239*, 77–85.
1455. Na, K. I.; Huh, S.; Sung, K. M.; Jun, M. J. *Polyhedron* **1996**, *15*, 1841–1846.
1456. Umezawa-Vizzini, K.; Lee, T. R. *Organometallics* **1997**, *16*, 5613–5615.
1457. Hall, C.; Jones, W. D.; Mawby, R. J.; Osman, R.; Perutz, R. N.; Whittlesey, M. K. *J. Am. Chem. Soc.* **1992**, *114*, 7425–7435.
1458. Kirkham, M. S.; Mahon, M. F.; Whittlesey, M. K. *Chem. Commun.* **2001**, 813–814.
1459. Fontes, M. R. M.; Oliva, G.; Cordeiro, L. A. C.; Batista, A. A. *J. Coord. Chem.* **1993**, *30*, 125–129.
1460. Batista, A. A.; Cordeiro, L. A. C.; Oliva, G. *Inorg. Chim. Acta* **1993**, *203*, 185–191.
1461. Barthazy, P.; Hintermann, L.; Stoop, R. M.; Worle, M.; Mezzetti, A.; Togni, A. *Helv. Chim. Acta* **1999**, *82*, 2448–2453.
1462. Saburi, M.; Fujii, T.; Shibusawa, T.; Masui, D.; Ishii, Y. *Chem. Lett.* **1999**, 1343–1344.
1463. Fogg, D. E.; James, B. R. *Inorg. Chem.* **1995**, *34*, 2557–2561.
1464. MacFarlane, K. S.; Joshi, A. M.; Rettig, S. J.; James, B. R. *Inorg. Chem.* **1996**, *35*, 7304–7310.
1465. Queiroz, S. L.; Batista, A. A.; Oliva, G.; Gambardella, M.; Santos, R. H. A.; MacFarlane, K. S.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1998**, *267*, 209–221.
1466. Jimenez-Tenorio, M.; Puerta, M. C.; Valerga, P. *Inorg. Chem.* **1994**, *33*, 3515–3520.
1467. Barthazy, P.; Worle, M.; Ruegger, H.; Mezzetti, A. *Inorg. Chem.* **2000**, *39*, 4903–4912.
1468. de los Rios, I.; Jimenez-Tenorio, M.; Puerta, M. C.; Salcedo, I.; Valerga, P. *J. Chem. Soc., Dalton Trans.* **1997**, 4619–4624.
1469. Han, S. H.; Sung, K. M.; Huh, S.; Jun, M. J.; Whang, D. M.; Kim, K. M. *Polyhedron* **1996**, *15*, 3811–3820.
1470. Huh, S.; Cho, Y. G.; Jun, M. J.; Whang, D. M.; Kim, K. M. *Polyhedron* **1994**, *13*, 1887–1894.
1471. Kawano, H.; Tanaka, R.; Fujikawa, T.; Hiraki, K.; Onishi, M. *Chem. Lett.* **1999**, 401–402.
1472. Winter, R. F.; Hornung, F. M. *Inorg. Chem.* **1997**, *36*, 6197–6204.
1473. Batista, A. A.; Pereira, C.; Queiroz, S. L.; de Oliveira, L. A. A.; Santos, R. H. D.; Gambardella, M. T. D. *Polyhedron* **1997**, *16*, 927–931.

1474. Barkley, J.; Higgins, S. J.; McCart, M. K. *J. Chem. Soc., Dalton Trans.* **1998**, 1787–1792.
1475. Barkley, J. V.; Higgins, S. J.; McCart, M. K.; Pounds, T. J. *Inorg. Chem.* **1997**, *36*, 6188–6196.
1476. Hong, B.; Woodcock, S. R.; Saito, S. K.; Ortega, J. V. *J. Chem. Soc., Dalton Trans.* **1998**, 2615–2623.
1477. Shen, J. Y.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1998**, *17*, 3875–3882.
1478. Balakrishna, M. S.; Abhyankar, R. M.; Mague, J. T. *J. Chem. Soc., Dalton Trans.* **1999**, 1407–1412.
1479. Gray, G. M.; Varshney, A.; Duffey, C. H. *Organometallics* **1995**, *14*, 238–244.
1480. Loeber, C.; Matt, D.; Decian, A.; Fischer, J. *J. Organometal. Chem.* **1994**, *475*, 297–305.
1481. Jia, G.-C.; Lee, H.-M.; Williams, I. D.; Lau, C.-P.; Chen, Y.-Z. *Organometallics* **1997**, *16*, 3941–3949.
1482. Jia, G. C.; Lee, H. M.; Williams, L. D. *J. Organometal. Chem.* **1997**, *534*, 173–180.
1483. Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317–11318.
1484. Hockless, D. C. R.; Wild, S. B.; McDonagh, A. M.; Whittall, I. R.; Humphrey, M. G. *Acta Crystallogr., Sect. C* **1996**, *52*, 1639–1641.
1485. McDonagh, A. M.; Humphrey, M. G.; Hockless, D. C. R. *Tetrahedron Asymmetry* **1997**, *8*, 3579–3583.
1486. Champness, N. R.; Levason, W.; Preece, S. R.; Webster, M.; Frampton, C. S. *Inorg. Chim. Acta* **1996**, *244*, 65–72.
1487. La Pensee, A. A.; Higgins, S. J.; Stuart, C. A.; Bickley, J. F. *Inorg. Chem. Commun.* **1999**, *2*, 524–526.
1488. Coe, B. J.; Chery, M.; Beddoes, R. L.; Hope, H.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1996**, 3917–3924.
1489. Coe, B. J.; Hayat, S.; Beddoes, R. L.; Helliwell, M.; Jeffery, J. C.; Batten, S. R.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1997**, 591–599.
1490. Coe, B. J.; McDonald, C. I.; Coles, S. J.; Hursthouse, M. B. *Acta Crystallogr., Sect. C* **2000**, *56*, 963–965.
1491. Coe, B. J.; McDonald, C. I.; Beddoes, R. L. *Polyhedron* **1998**, *17*, 1997–2007.
1492. Coe, B. J.; McDonald, C. I.; Couchman, S. M.; Jeffery, J. C.; Rees, L. H.; Coles, S. J.; Gelbrich, T.; Hursthouse, M. B. *Polyhedron* **2000**, *19*, 1193–1203.
1493. Carmichael, D.; Le Floch, P.; Ricard, L.; Mathey, F. *Inorg. Chim. Acta* **1992**, *198–200*, 437–441.
1494. Li, R. X.; Tin, K. C.; Wong, N. B.; Mak, T. C. W.; Zhang, Z. Y.; Li, X. J. *J. Organometal. Chem.* **1998**, *557*, 207–212.
1495. Mezzetti, A.; Consiglio, G. *J. Chem. Soc., Chem. Commun.* **1991**, 1675–1677.
1496. Mezzetti, A.; Tschumper, A.; Consiglio, G. *J. Chem. Soc., Dalton Trans.* **1995**, 49–56.
1497. Kawano, H.; Ikariya, T.; Ishii, Y.; Kodama, T.; Saburi, M.; Yoshikawa, S.; Uchida, Y.; Akutagawa, S. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1595–1602.
1498. Fogg, D. E.; James, B. R.; Kilner, M. *Inorg. Chim. Acta* **1994**, *222*, 85–90.
1499. Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 1703–1707.
1500. Stoop, R. M.; Bauer, C.; Setz, P.; Worle, M.; Wong, T. Y. H.; Mezzetti, A. *Organometallics* **1999**, *18*, 5691–5700.
1501. Kawano, H.; Ishii, Y.; Kodama, T.; Saburi, M.; Uchida, Y. *Chem. Lett.* **1987**, 1311–1314.
1502. Tsukahara, T.; Kawano, H.; Ishii, Y.; Takahashi, T.; Saburi, M.; Uchida, Y.; Akutagawa, S. *Chem. Lett.* **1988**, 2055–2058.
1503. Mashima, K.; Hino, T.; Takaya, H. *J. Chem. Soc., Dalton Trans.* **1992**, 2099–2107.
1504. Joshi, A. M.; Thorburn, I. S.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1992**, *198–200*, 283–296.
1505. Chan, A. S. C.; Laneman, S. *Inorg. Chim. Acta* **1994**, *223*, 165–167.
1506. Chan, A. S.; Laneman, S. A.; Day, C. X. *Inorg. Chim. Acta* **1995**, *228*, 159–163.
1507. Chen, C. C.; Huang, T. T.; Lin, C. W.; Cao, R.; Chan, A. S. C.; Wong, W. T. *Inorg. Chim. Acta* **1998**, *270*, 247–251.
1508. Uemura, T.; Zhang, X. Y.; Matsumura, K.; Sayo, N.; Kumobayashi, H.; Ohta, T.; Nozaki, K.; Takaya, H. *J. Org. Chem.* **1996**, *61*, 5510–5516.
1509. Doucet, H.; Legendre, P.; Bruneau, C.; Dixneuf, P. H.; Souvie, J. C. *Tetrahedron: Asymmetry* **1996**, *7*, 525–528.
1510. Wiles, J. A.; Lee, C. E.; McDonald, R.; Bergens, S. H. *Organometallics* **1996**, *15*, 3782–3784.
1511. Wiles, J. A.; Bergens, S. H.; Young, V. G. *J. Am. Chem. Soc.* **1997**, *119*, 2940–2941.
1512. Cyr, P. W.; Patrick, B. O.; James, B. R. *Chem. Commun.* **2001**, 1570–1571.
1513. Murahashi, S.; Watanabe, S.; Shiota, T. *J. Chem. Soc., Chem. Commun.* **1994**, 725–726.
1514. Gelpke, A. E. S.; Kooijman, H.; Spek, A. L.; Hiemstra, H. *Chem.-Eur. J.* **1999**, *5*, 2472–2482.
1515. Fehr, M. J.; Consiglio, G.; Scalone, M.; Schmid, R. *New J. Chem.* **1998**, *22*, 1499–1504.
1516. Fehr, M. J.; Consiglio, G.; Scalone, M.; Schmid, R. *J. Org. Chem.* **1999**, *64*, 5768–5776.
1517. Albinati, A.; Jiang, Q. Z.; Ruegger, H.; Venanzi, L. M. *Inorg. Chem.* **1993**, *32*, 4940–4950.
1518. Jia, G. C.; Meek, D. W. *Inorg. Chim. Acta* **1990**, *178*, 195–201.
1519. Jia, G. C.; Rheingold, A. L.; Haggerty, B. S.; Meek, D. W. *Inorg. Chem.* **1992**, *31*, 900–904.
1520. Jia, G. C.; Meek, D. W.; Gallucci, J. C. *Inorg. Chem.* **1991**, *30*, 403–410.
1521. Jia, G. C.; Meek, D. W. *Organometallics* **1991**, *10*, 1444–1450.
1522. Jia, G. C.; Lee, I. M.; Meek, D. W.; Gallucci, J. C. *Inorg. Chim. Acta* **1990**, *177*, 81–88.
1523. Jia, G. C.; Lee, H. M.; Williams, I. D. *Organometallics* **1996**, *15*, 4235–4239.
1524. Sheldrick, W. S.; Brandt, K. *Inorg. Chim. Acta* **1994**, *217*, 51–59.
1525. Jiang, Q. Z.; Ruegger, H.; Venanzi, L. M. *Inorg. Chim. Acta* **1999**, *290*, 64–79.
1526. Sung, K. M.; Huh, S.; Jun, M. J. *Polyhedron* **1998**, *18*, 469–479.
1527. Delgado, G.; Rivera, A. V.; Suarez, T.; Fontal, B. *Inorg. Chim. Acta* **1995**, *233*, 145–149.
1528. Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Vizza, F.; Zanobini, F. *Organometallics* **1998**, *17*, 2495–2502.
1529. Bianchini, C.; Meli, A.; Moneti, S.; Vizza, F. *Organometallics* **1998**, *17*, 2636–2645.
1530. Bakhmutov, V. I.; Bakhmutova, E. V.; Belkova, N. V.; Bianchini, C.; Epstein, L. M.; Masi, D.; Peruzzini, M.; Shubina, E. S.; Vorontsov, E. V.; Zanobini, F. *Can. J. Chem.* **2001**, *79*, 479–489.
1531. Landgrafe, C.; Sheldrick, W. S.; Südfeld, H. *Eur. J. Inorg. Chem.* **1998**, 407–414.
1532. Sulu, M.; Venanzi, L. M. *Inorg. Chim. Acta* **1999**, *293*, 70–79.
1533. Jia, G. C.; Drouin, S. D.; Jessop, P. G.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 906–916.
1534. Herold, S.; Mezzetti, A.; Venanzi, L. M.; Albinati, A.; Lianza, F.; Gerfin, T.; Gramlich, V. *Inorg. Chim. Acta* **1995**, *235*, 215–231.
1535. Becker, C.; Dahlenburg, L.; Kerstan, S. *Z. Naturforsch., Teil B* **1993**, *48*, 577–582.

1536. Butler, I. R.; Griesbach, U.; Zanello, P.; Fontani, M.; Hibbs, D.; Hursthouse, M. B.; Malik, K. L. M. A. *J. Organometal. Chem.* **1998**, *565*, 243–258.
1537. Osman, J. R.; Crayston, J. A.; Richens, D. T. *Inorg. Chem.* **1998**, *37*, 1665.
1538. Bianchini, C.; Laschi, F.; Peruzzini, M.; Zanello, P. *Gazz. Chim. Ital.* **1994**, *124*, 271–274.
1539. Bianchini, C.; Peruzzini, M.; Ceccanti, A.; Laschi, F.; Zanello, P. *Inorg. Chim. Acta* **1997**, *259*, 61–70.
1540. Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *Can. J. Chem.* **1994**, *72*, 547–560.
1541. Steenwinkel, P.; Kolmschot, S.; Gossage, R. A.; Dani, P.; Veldman, N.; Spek, A. L.; van Koten, G. *Eur. J. Inorg. Chem.* **1998**, 477–483.
1542. Hong, B.; Woodcock, S. R.; Saito, S. K.; Ortega, J. V. *J. Chem. Soc., Dalton Trans.* **1998**, 2615–2623.
1543. Dinelli, L. R.; Batista, A. A.; Wohnrath, K.; de Araujo, M. P.; Queiroz, S. L.; Bonfadini, M. R.; Oliva, G.; Nascimento, O. R.; Cyr, P. W.; MacFarlane, K. S.; James, B. R. *Inorg. Chem.* **1999**, *38*, 5341–5345.
1544. Yeomans, B. D.; Humphrey, D. G.; Heath, G. A. *J. Chem. Soc., Dalton Trans.* **1997**, 4153–4166.
1545. Cornils, B; Herman, W. A, (eds) *Aqueous-phase Organometallic Catalysis; Concepts and Applications*, Wiley-VCH, Weinheim, 1998.
1546. Kalck, P.; Monteil, F. *Adv. Organometal. Chem.* **1992**, *34*, 219–284.
1547. Roundhill, D. M. *Adv. Organometal. Chem.* **1995**, *38*, 155–188.
1548. Fache, E.; Santini, C.; Senocq, F.; Basset, J. M. *J. Mol. Catal.* **1992**, *72*, 331–336.
1549. Fache, E.; Santini, C.; Senocq, F.; Basset, J. M. *J. Mol. Catal.* **1992**, *72*, 337–350.
1550. Andriollo, A.; Bolivar, A.; Lopez, F. A.; Paez, D. E. *Inorg. Chim. Acta* **1995**, *238*, 187–192.
1551. Bényei, A. Cs.; Lehel, S.; Joó, F. *J. Mol. Catal. A* **1997**, *116*, 349–354.
1552. Hernandez, M.; Kalck, P. *J. Mol. Catal. A* **1997**, *116*, 117–130.
1553. Hernandez, M.; Kalck, P. *J. Mol. Catal. A* **1997**, *116*, 131–146.
1554. Andriollo, A.; Carrasquel, J.; Marino, J.; Lopez, F. A.; Paez, D. E.; Rojas, I.; Valencia, N. *J. Mol. Catal. A* **1997**, *116*, 157–165.
1555. Sanchez-Delgado, R. A.; Medina, M.; Lopez-Linares, F.; Fuentes, A. *J. Mol. Catal. A* **1997**, *116*, 167–177.
1556. Joó, F.; Kovács, J.; Bényei, A. Cs.; Kathó, Á. *Catalysis Today* **1998**, *42*, 441–448.
1557. Wan, K.; Davis, M. E. *Tetrahedron: Asymmetry* **1993**, *4*, 2461–2468.
1558. Herrmann, W. A.; Kohlpaintner, C. W.; Bahrmann, H.; Konkol, W. *J. Mol. Catal.* **1992**, *73*, 191–201.
1559. Kayaki, Y.; Suzuki, T.; Ikariya, T. *Chem. Lett.* **2001**, 1016–1017.
1560. Drießen-Hölscher, B.; Heinen, J. *J.Organometal. Chem.* **1998**, *570*, 141–146.
1561. Darensbourg, D. J.; Joó, F.; Kannisto, M.; Kathó, Á.; Reibenspies, J. H.; Daigle, D. J. *Inorg. Chem.* **1994**, *33*, 200–208.
1562. Laurenczy, G.; Joó, F.; Nádasdi, L. *Inorg. Chem.* **2000**, *39*, 5083–5088.
1563. Gao, J.; Xu, P.; Yi, X.; Wan, H.; Tsai, K. *J. Mol. Catal. A* **1999**, *147*, 99–104.
1564. Aebischer, N.; Laurenczy, G.; Ludi, A.; Merbach, A. E. *Inorg. Chem.* **1993**, *32*, 2810–2814.
1565. Patel, A.; Leitch, P.; Richens, D. T. *J. Chem. Soc., Dalton Trans.* **1991**, 1029–1036.
1566. Kolle, U.; Flunkert, G.; Gorissen, R.; Schmidt, M. U.; Englert, U. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 440–442.
1567. Harding, P. A.; Robinson, S. D.; Henrick, K. *J. Chem. Soc., Dalton Trans.* **1988**, 415–420.
1568. Sun, Y.; Taylor, N. J.; Carty, A. J. *Inorg. Chem.* **1993**, *32*, 4457–4459.
1569. Remita, H.; Brik, M. E.; Daran, J. C.; Delcourt, M. O. *J. Organometal. Chem.* **1995**, *486*, 283–285.
1570. Hinckley, C. C.; Ikuo, A.; Robinson, P. D. *Acta Crystallogr., Sect. C* **1988**, *44*, 1827–1829.
1571. Zanetti, N. C.; Spindler, F.; Spencer, J.; Togni, A.; Rihs, G. *Organometallics* **1996**, *15*, 860–866.
1572. Frediani, P.; Faggi, C.; Salvini, A.; Bianchi, M.; Piacenti, F. *Inorg. Chim. Acta* **1998**, *272*, 141–149.
1573. Lindner, E.; Fawzi, R.; Hiller, W.; Carvill, A.; McCann, M. *Chem. Ber.* **1991**, *124*, 2691–2695.
1574. Frediani, P.; Bianchi, M.; Salvini, A.; Guarducci, R.; Carluccio, L. C.; Piacenti, F. *J. Organometal. Chem.* **1994**, *476*, 7–11.
1575. Gibson, D. H.; Ding, Y.; Miller, R. L.; Sleadd, B. A.; Mashuta, M. S.; Richardson, J. F. *Polyhedron* **1999**, *18*, 1189–1200.
1576. Severin, K.; Koch, D.; Polborn, K.; Beck, W. *Z. Anorg. Allg. Chem.* **1996**, *622*, 562–570.
1577. Renkema, K. B.; Huffman, J. C.; Caulton, K. G. *Polyhedron* **1999**, *18*, 2575–2578.
1578. Burn, M. J.; Fickes, M. G.; Hartwig, J. F.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 5875–5876.
1579. Flood, T. C.; Lim, J. K.; Deming, M. A.; Keung, W. *Organometallics* **2000**, *19*, 1166–1174.
1580. Bag, N.; Choudhury, S. B.; Pramanik, A.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1990**, *29*, 5013–5014.
1581. Aneetha, H.; Rao, C. R. K.; Rao, K. M.; Zacharias, P. S.; Feng, X.; Mak, T. C. W.; Srinivas, B.; Chiang, M. Y. *J. Chem. Soc., Dalton Trans.* **1997**, 1697–1703.
1582. Silva, A. M. S.; Cavaleiro, J. A. S.; Tarrago, G.; Marzin, C. *New J. Chem.* **1999**, *23*, 329–335.
1583. Haga, M.; Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1986**, *25*, 447–453.
1584. Boone, S. R.; Pierpont, C. G. *Inorg. Chem.* **1987**, *26*, 1769–1773.
1585. Lever, A. B. P.; Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Wei, L.; Melnik, M.; Nevin, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 8076–8084.
1586. Auburn, P. R.; Dodsworth, E. S.; Haga, M.; Liu, W.; Nevin, W. A.; Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 3502–3512.
1587. Lever, A. B. P.; Masui, H.; Metcalfe, R. A.; Stufkens, D. J.; Dodsworth, E. S.; Auburn, P. R. *Coord. Chem. Rev.* **1993**, *125*, 317–331.
1588. Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 2906–2911.
1589. Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 6038–6042.
1590. Bhattacharya, S. *Polyhedron* **1994**, *13*, 451–456.
1591. Bag, N.; Lahiri, G. K.; Basu, P.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1992**, 113–117.
1592. Tanke, R. S.; Holt, E. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 1714–1719.
1593. Day, V. W.; Eberspacher, T. A.; Klemperer, W. G.; Planalp, R. P.; Schiller, P. W.; Yagasaki, A.; Zhong, B. *Inorg. Chem.* **1993**, *32*, 1629–1637.
1594. Klemperer, W. G.; Zhong, B. X. *Inorg. Chem.* **1993**, *32*, 5821–5826.

1595. Geremia, S.; Calligaris, M. *J. Chem. Soc., Dalton Trans.* **1997**, 1541–1547.
1596. Sarma, U. C.; Poddar, R. K. *Polyhedron* **1988**, *7*, 1737–1743.
1597. Alessio, E.; Milani, B.; Calligaris, M.; Brescianipahor, N. *Inorg. Chim. Acta* **1992**, *194*, 85–91.
1598. Paul, B. C.; Sarma, U. C.; Poddar, R. K. *Inorg. Chim. Acta* **1991**, *179*, 17–23.
1599. Geremia, S.; Calligaris, M.; Kukushkin, Y. N.; Zinchenko, A. V.; Kukushkin, V. Y. *J. Mol. Struct.* **2000**, *516*, 49–56.
1600. McDonagh, A. M.; Humphrey, M. G.; Hockless, D. C. R. *Aust. J. Chem.* **1998**, *51*, 807–811.
1601. Tian, Y. N.; Yang, P.; Li, Q. S.; Guo, M. L.; Zhao, M. G. *Polyhedron* **1997**, *16*, 1993–1998.
1602. Davey, J. M.; Moerman, K. L.; Ralph, S. F.; Kanitz, R.; Sheil, M. M. *Inorg. Chim. Acta* **1998**, *281*, 10–17.
1603. Tomita, A.; Sano, M. *Inorg. Chem.* **1994**, *33*, 5825–5830.
1604. Alessio, E.; Milani, B.; Bolle, M.; Mestroni, G.; Faleschini, P.; Todone, F.; Geremia, S.; Calligaris, M. *Inorg. Chem.* **1995**, *34*, 4722–4734.
1605. Smith, M. K.; Gibson, J. A.; Young, C. G.; Broomhead, J. A.; Junk, P. C.; Keene, F. R. *Eur. J. Inorg. Chem.* **2000**, 1365–1370.
1606. Henn, M.; Alessio, E.; Mestroni, G.; Calligaris, M.; Attia, W. M. *Inorg. Chim. Acta* **1991**, *187*, 39–50.
1607. Jaswal, J. S.; Yapp, D. T. T.; Rettig, S. J.; James, B. R.; Skov, K. A. *Inorg. Chim. Acta* **1993**, *207*, 97–103.
1608. Breitinger, D. K.; Breiter, R. *J. Mol. Struct.* **1995**, *349*, 45–48.
1609. Breitinger, D. K.; Breiter, R. *Z. Naturforsch., Teil B* **1996**, *51*, 517–524.
1610. Müller, A.; Khan, M. I.; Krickemeyer, E.; Bögge, H. *Inorg. Chem.* **1991**, *30*, 2040–2043.
1611. Treichel, P. M.; Rublein, E. K. *J. Organometal. Chem.* **1992**, *424*, 71–77.
1612. Jessop, P. G.; Rettig, S. J.; Lee, C. L.; James, B. R. *Inorg. Chem.* **1991**, *30*, 4617–4627.
1613. Jessop, P. G.; Lee, C. L.; Rastar, G.; James, B. R.; Lock, C. J. L.; Faggiani, R. *Inorg. Chem.* **1992**, *31*, 4601–4605.
1614. Bartucz, T. Y.; Golombek, A.; Lough, A. J.; Maltby, P. A.; Morris, R. H.; Ramachandran, R.; Schlaf, M. *Inorg. Chem.* **1998**, *37*, 1555–1562.
1615. Walsh, J. L.; McCracken, R.; McPhail, A. T. *Polyhedron* **1998**, *17*, 3221–3226.
1616. Krogh-Jespersen, K.; Zhang, X.; Ding, Y.; Westbrook, J. D.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1992**, *114*, 4345–4353.
1617. Bell, M. N.; Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3841–3847.
1618. Bell, M. N.; Blake, A. J.; Christie, R. M.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2977–2986.
1619. Goodfellow, B. J.; Felix, V.; Pacheco, S. M. D.; Dejesus, J. P.; Drew, M. G. B. *Polyhedron* **1997**, *16*, 393–401.
1620. Landgrafe, C.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1994**, 1885–1893.
1621. Landgrafe, C.; Sheldrick, W. S. *J. Chem. Soc., Dalton Trans.* **1996**, 989–998.
1622. Grant, G. J.; McCosar, B. M.; Setzer, W. N.; Zubkowski, J. D.; Valente, E. J.; Mehne, L. F. *Inorg. Chim. Acta* **1996**, *244*, 73–77.
1623. Degroot, B.; Jenkins, H. A.; Loeb, S. J.; Murphy, S. L. *Can. J. Chem.* **1995**, *73*, 1102–1110.
1624. Goodfellow, B. J.; Pacheco, S. M. D.; de Jesus, J. P.; Felix, V.; Drew, M. G. B. *Polyhedron* **1997**, *16*, 3293–3304.
1625. Yoshida, T.; Adachi, T.; Ueda, T.; Goto, F.; Baba, K.; Tanaka, T. *J. Organometal. Chem.* **1994**, *473*, 225–241.
1626. Yoshida, T.; Adachi, T.; Ueda, T.; Akao, H.; Tanaka, T.; Goto, F. *Inorg. Chim. Acta* **1995**, *231*, 95–101.
1627. Blake, A. J.; Reid, G.; Schröder, M. *Polyhedron* **1992**, *11*, 2501–2506.
1628. Blake, A. J.; Radek, C.; Schröder, M. *Acta Crystallogr., Sect. C* **1996**, *52*, 1401–1403.
1629. Sellmann, D.; Neuner, H.-P.; Eberlein, R.; Moll, M.; Knoch, F. *Inorg. Chim. Acta* **1990**, *175*, 231–239.
1630. Arbuckle, B. W.; Bharadwaj, P. K.; Musker, W. K. *Inorg. Chem.* **1991**, *30*, 440–445.
1631. Sellmann, D.; Käppler, J.; Moll, M.; Knoch, F. *Inorg. Chem.* **1993**, *32*, 960–964.
1632. Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W.; Knoch, F. *Chem. Ber.* **1997**, *130*, 571–579.
1633. Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W. *Inorg. Chem.* **1998**, *37*, 3982–3988.
1634. Sellmann, D.; Engl, K.; Gottschalk-Gaudig, T.; Heinemann, F. W. *Eur. J. Inorg. Chem.* **1999**, 333–339.
1635. Sellmann, D.; Geck, M.; Moll, M. *Z. Naturforsch., Teil B* **1992**, *47*, 74–78.
1636. Sellmann, D.; Rohm, C.; Moll, M.; Knoch, F. *Z. Naturforsch., Teil B* **1995**, *50*, 1229–1244.
1637. Yapp, D. T. T.; Rettig, S. J.; James, B. R.; Skov, K. A. *Inorg. Chem.* **1997**, *36*, 5635–5641.
1638. Tokunoh, R.; Sodeoka, M.; Aoe, K.; Shibasaki, M. *Tetrahedron Lett.* **1995**, *36*, 8035–8038.
1639. Geremia, S.; Vicentini, L.; Calligaris, M. *Inorg. Chem.* **1998**, *37*, 4094–4103.
1640. Nonoyama, M.; Nakajima, K.; Mizuno, H.; Hayashi, S. *Inorg. Chim. Acta* **1994**, *215*, 91–101.
1641. Leung, W. H.; Wu, M. C.; Chim, J. L. C.; Wong, W. T. *Inorg. Chem.* **1996**, *35*, 4801–4803.
1642. Leung, W. H.; Chim, J. L. C.; Hou, H. W.; Hun, T. S. M.; Williams, I. D.; Wong, W. T. *Inorg. Chem.* **1997**, *36*, 4432–4437.
1643. Baitalik, S.; Mohanta, S.; Adhikary, B. *Polyhedron* **1997**, *16*, 983–988.
1644. Ballester, L.; Esteban, O.; Gutierrez, A.; Perpinan, M. F.; Ruiz-Valero, C.; Gutierrez-Puebla, E.; Gonzalez, M. J. *Polyhedron* **1992**, *11*, 3173–3182.
1645. Gutierrez-Alonso, A.; Ballester-Reventos, L. *Polyhedron* **1991**, *10*, 1019–1023.
1646. Pramanik, A.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1993**, 237–244.
1647. Pramanik, A.; Bag, N.; Lahiri, G. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1992**, 101–105.
1648. Pramanik, A.; Bag, N.; Lahiri, G. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1990**, 3823–3828.
1649. Pramanik, A.; Bag, N.; Ray, D.; Lahiri, G. K.; Chakravorty, A. *Inorg. Chem.* **1991**, *30*, 410–417.
1650. Blake, A. J.; Ewan, A.; McQueen, D.; Schroder, M.; Stephenson, T. A.; Yellowlees, L. J. *Acta Crystallogr., Sect. C* **1993**, *49*, 135–137.
1651. Leung, W. H.; Zheng, H. G.; Chim, J. L. C.; Chan, J.; Wong, W. T.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **2000**, 423–430.
1652. Natsuaki, K.; Nakano, M.; Matsubayashi, G. E.; Arakawa, R. *Inorg. Chim. Acta* **2000**, *299*, 112–117.
1653. Matsumoto, K.; Koyama, T.; Koide, Y. *J. Amer. Chem. Soc.* **1999**, *121*, 10913–10923.
1654. Matsumoto, T.; Matsumoto, K. *Chem. Lett.* **1992**, 559–562.
1655. Matsumoto, K.; Matsumoto, T.; Kawano, M.; Ohnuki, H.; Shichi, Y.; Nishide, T.; Sato, T. *J. Am. Chem. Soc.* **1996**, *118*, 3597–3609.

1656. Koyama, T.; Koide, Y.; Matsumoto, K. *Inorg. Chem.* **1999**, *38*, 3241–3243.
1657. Schmidt, C.; Sheldrick, W. S. *Z. Krist.* **1998**, *213*, 251–253.
1658. Uemura, H.; Kawano, M.; Watanabe, T.; Matsumoto, T.; Matsumoto, K. *Inorg. Chem.* **1992**, *31*, 5137–5139.
1659. Furuhashi, T.; Kawano, M.; Koide, Y.; Somazawa, R.; Matsumoto, K. *Inorg. Chem.* **1999**, *38*, 109–114.
1660. Kawano, M.; Uemura, H.; Watanabe, T.; Matsumoto, K. *J. Am. Chem. Soc.* **1993**, *115*, 2068–2070.
1661. Soler, J.; Ros, J.; Carrasco, M. R.; Ruiz, A.; Alvarez-Larena, A.; Piniella, J. F. *Inorg. Chem.* **1995**, *34*, 6211–6214.
1662. Treichel, P. M.; Crane, R. A.; Haller, K. J. *Polyhedron* **1990**, *9*, 1893–1899.
1663. Wagner, C.; Herzog, F.; Knaudt, J.; Thiele, G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 279–284.
1664. Paulus, M.; Thiele, G. *Z. Naturforsch. Teil B* **1992**, *47*, 253–257.
1665. Lessing, S. F.; Lotz, S.; Roos, H. M.; van Rooyen, P. H. *J. Chem. Soc., Dalton Trans.* **1999**, 1499–1502.
1666. Mizutani, J.; Matsumoto, K. *Chem. Lett.* **2000**, 72–73.
1667. Champness, N. R.; Levason, W.; Preece, S. R.; Webster, M. *Polyhedron* **1994**, *13*, 881–886.
1668. Levason, W.; Orchard, S. D.; Reid, G. *Chem. Commun.* **1999**, 1071–1072.
1669. Barton, A. J.; Levason, W.; Reid, G.; Tolhurst, V. A. *Polyhedron* **2000**, *19*, 235–240.
1670. Levason, W.; Quirk, J. J.; Reid, G.; Smith, S. M. *J. Chem. Soc., Dalton Trans.* **1997**, 3719–3724.
1671. Menon, M.; Pramanik, A.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1417–1422.
1672. Miki, E.; Masano, H.; Iwasaki, H.; Tomizawa, H.; Mizumachi, K.; Ishimori, T.; Tanaka, M.; Nagai, T.; Nagao, N. *Inorg. Chim. Acta* **1993**, *205*, 129–136.
1673. Nagata-Tanba, S.; Tomizawa, H.; Miki, E.; Tanaka, M.; Nagai, T. *Inorg. Chim. Acta* **1998**, *267*, 147–149.
1674. Ikezawa, H.; Ikezawa, Y.; Miki, E.; Mizumachi, K.; Ishimori, T. *Inorg. Chim. Acta* **1995**, *238*, 89–97.
1675. Barral, M. C.; Jimenez-Aparicio, R.; Royer, E. C.; Saucedo, M. J.; Urbanos, F. A.; Gutierrez-Puebla, E.; Ruiz-Valero, C. *J. Chem. Soc., Dalton Trans.* **1991**, 1609–1613.
1676. Ghatak, N.; Bhattacharya, S. *Polyhedron* **1994**, *13*, 2999–3004.
1677. Sengupta, P.; Dinda, R.; Ghosh, S.; Sheldrick, W. S. *Polyhedron* **2001**, *20*, 3349–3354.
1678. Norrby, T.; Borje, A.; Akermark, A.; Hammarström, L.; Alsins, J.; Lashgari, K.; Norrestam, R.; Martensson, J.; Stenhagen, G. *Inorg. Chem.* **1997**, *36*, 5850–5858.
1679. Severin, K.; Sunkel, K.; Beck, W. *Chem Ber* **1994**, *127*, 615–620.
1680. Sheldrick, W. S.; Exner, R. *Inorg. Chim. Acta* **1991**, *184*, 119–125.
1681. Dutta, S.; Pal, S.; Bhattacharya, P. K. *Polyhedron* **1999**, *18*, 2157–2162.
1682. Pramanik, N. C.; Bhattacharya, S. *Polyhedron* **1997**, *16*, 3047–3053.
1683. Sui, K.; Peng, S. M.; Bhattacharya, S. *Polyhedron* **1999**, *18*, 631–640.
1684. Chichak, K.; Jacquemard, U.; Branda, N. R. *Eur. J. Inorg. Chem.* **2002**, 357–368.
1685. Mitra, K. N.; Peng, S. M.; Goswami, S. *Chem. Commun.* **1998**, 1685–1686.
1686. Shepherd, R. E.; Zhang, S.; Lin, F. T.; Kortes, R. A. *Inorg. Chem.* **1992**, *31*, 1457–1462.
1687. Shepherd, R. E.; Zhang, S. S. *Inorg. Chim. Acta* **1992**, *191*, 271–278.
1688. Chen, Y.; Lin, F. T.; Shepherd, R. E. *Inorg. Chem.* **1997**, *36*, 818–826.
1689. Chen, Y.; Lin, F. T.; Shepherd, R. E. *Inorg. Chim. Acta* **1998**, *268*, 287–295.
1690. Chen, Y.; Shepherd, R. E. *Inorg. Chim. Acta* **1998**, *279*, 85–94.
1691. Chen, Y.; Shepherd, R. E. *Inorg. Chem.* **1998**, *37*, 1249–1256.
1692. Chen, Y.; Shepherd, R. E. *Inorg. Chim. Acta* **1998**, *268*, 279–285.
1693. Shepherd, R. E.; Chen, Y.; Kortes, R. A.; Ward, M. S. *Inorg. Chim. Acta* **2000**, *303*, 30–39.
1694. Chen, Y.; Lin, F. T.; Shepherd, R. E. *Inorg. Chem.* **1999**, *38*, 973–983.
1695. Chen, Y.; Shepherd, R. E. *J. Inorg. Biochem.* **1997**, *68*, 183–193.
1696. Toma, H. E.; Santos, P. S.; Camera, S. G.; Sernaglia, R. L. *Spectrosc. Lett.* **1997**, *30*, 507–516.
1697. Cotton, F. A.; Kim, Y. M.; Yokochi, A. *Inorg. Chim. Acta* **1995**, *236*, 55–61.
1698. Sahajpal, A.; Robinson, S. D.; Hursthouse, M. B.; Mazid, M. A. *J. Chem. Soc., Dalton Trans.* **1993**, 393–396.
1699. Shiu, K.-B.; Yang, L.-T.; Jean, S.-W.; Li, C.-H.; Wu, R.-R.; Wang, J.-C.; Liou, L.-S.; Chiang, M. Y. *Inorg. Chem.* **1996**, *35*, 7845–7849.
1700. Shen, J. Y.; Slugovc, C.; Wiede, P.; Mereiter, K.; Schmid, R.; Kirchner, K. *Inorg. Chim. Acta* **1998**, *268*, 69–76.
1701. Guo, Z. J.; Habtemariam, A.; Sadler, P. J.; James, B. R. *Inorg. Chim. Acta* **1998**, *273*, 1–7.
1702. Mudalige, D. C.; Rettig, S. J.; James, B. R.; Cullen, W. R. *J. Chem. Soc., Chem. Commun.* **1993**, 830–832.
1703. Drommi, D.; Nicolo, F.; Arena, C. G.; Bruno, G.; Faraone, F.; Gobetto, R. *Inorg. Chim. Acta* **1994**, *221*, 109–116.
1704. Costella, L.; Delzotto, A.; Mezzetti, A.; Zangrando, E.; Rigo, P. *J. Chem. Soc., Dalton Trans.* **1993**, 3001–3008.
1705. Delzotto, A.; Mezzetti, A.; Rigo, P. *J. Chem. Soc., Dalton Trans.* **1994**, 2257–2264.
1706. Barloy, L.; Ku, S. Y.; Osborn, J. A.; DeCian, A.; Fischer, J. *Polyhedron* **1997**, *16*, 291–295.
1707. Rahmouni, N.; Osborn, J. A.; DeCian, A.; Fischer, J.; Ezzamarty, A. *Organometallics* **1998**, *17*, 2470–2476.
1708. Bianchini, C.; Masi, D.; Peruzzini, M.; Romerosa, A.; Zanobini, F. *Acta Crystallogr., Sect. C* **1995**, *51*, 2514–2517.
1709. Schutte, R. P.; Rettig, S. J.; James, B. R. *Can. J. Chem.* **1996**, *74*, 2064–2072.
1710. Schutte, R. P.; Rettig, S. J.; Joshi, A. M.; James, B. R. *Inorg. Chem.* **1997**, *36*, 5809–5817.
1711. Gao, J. X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087–1089.
1712. Wong, W. K.; Chik, T. W.; Feng, X.; Mak, T. C. W. *Polyhedron* **1996**, *15*, 3905–3907.
1713. Wong, W. K.; Gao, J. X.; Zhou, Z. Y.; Mak, T. C. W. *Polyhedron* **1993**, *12*, 1415–1417.
1714. Gao, J. X.; Wan, H. L.; Wong, W. K.; Tse, M. C.; Wong, W. T. *Polyhedron* **1996**, *15*, 1241–1251.
1715. Fryzuk, M. D.; Montgomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467–473.
1716. Braunstein, P.; Fryzuk, M. D.; Naud, F.; Rettig, S. J. *J. Chem. Soc., Dalton Trans.* **1999**, 589–594.
1717. Braunstein, P.; Naud, F.; Graiff, C.; Tiripicchio, A. *Chem. Commun.* **2000**, 897–898.
1718. Perera, S. D.; Shaw, B. L. *Inorg. Chim. Acta* **1995**, *228*, 127–131.
1719. Shaw, B. L.; Ike, U. U.; Perera, S. D.; Thornton-Pett, M. *Inorg. Chim. Acta* **1998**, *279*, 95–103.
1720. Robinson, S. D.; Sahajpal, A.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1997**, 757–762.
1721. Maji, M.; Chatterjee, M.; Chattopadhyay, S. K.; Ghosh, S. *Acta Chem. Scand.* **1999**, *53*, 253–257.
1722. Andreu, P. L.; Cabeza, J. A.; Fernandez-Colinas, J. M.; Riera, V. *J. Chem. Soc., Dalton Trans.* **1990**, 2927–2930.
1723. Deeming, A. J.; Karim, M. *Polyhedron* **1991**, *10*, 837–840.
1724. Lobana, T. S.; Singh, R. *Polyhedron* **1995**, *14*, 907–912.

1725. Horn, E.; Lobana, T. S.; Singh, R.; Tiekink, E. R. T. *Z. Kristallogr.* **1993**, *205*, 291–294.
1726. Constable, E. C.; Raithby, P. R. *Inorg. Chim. Acta* **1991**, *183*, 21–23.
1727. Tresoldi, G.; Lo Schiavo, S.; Lanza, S.; Cardiano, P. *Eur. J. Inorg. Chem.* **2002**, 181–191.
1728. Scopelliti, R.; Bruno, G.; Donato, C.; Tresoldi, G. *Inorg. Chim. Acta* **2001**, *313*, 43–55.
1729. Constable, E. C.; Henney, R. P. G.; Tocher, D. A. *J. Chem. Soc., Dalton Trans.* **1991**, 2335–2347.
1730. Viñas, C.; Anglès, P.; Sánchez, G.; Lucena, N.; Teixidor, F.; Escriche, L.; Casabó, J.; Piniella, J. F.; Alvarez-Larena, A.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1998**, *37*, 701–707.
1731. Yamanari, K.; Nozaki, T.; Fuyuhiro, A.; Kushi, Y.; Kaizaki, S. *J. Chem. Soc., Dalton Trans.* **1996**, 2851–2856.
1732. Cini, R.; Bozzi, R.; Karaulov, A.; Hursthouse, M. B.; Calafat, A. M.; Marzilli, L. G. *J. Chem. Soc., Chem. Commun.* **1993**, 899–901.
1733. Hossain, M.; Chattopadhyay, S. K.; Ghosh, S. *Polyhedron* **1997**, *16*, 1793–1802.
1734. Hossain, M.; Maji, M.; Chattopadhyay, S. K.; Ghosh, S.; Blake, A. J. *Polyhedron* **1998**, *17*, 1897–1906.
1735. Santra, B. K.; Lahiri, G. K. *J. Chem. Soc., Dalton Trans.* **1998**, 1613–1618.
1736. Santra, B. K.; Munshi, P.; Das, G.; Bharadwaj, P.; Lahiri, G. K. *Polyhedron* **1999**, *18*, 617–630.
1737. Hossain, M.; Chattopadhyay, S. K.; Ghosh, S. *Polyhedron* **1997**, *16*, 4313–4321.
1738. Basuli, F.; Peng, S. M.; Bhattacharya, S. *Inorg. Chem.* **2000**, *39*, 1120–1127.
1739. Sellmann, D.; Ruf, R. *Z. Naturforsch. Teil B* **1993**, *48*, 723–729.
1740. Sellmann, D.; Ruf, R.; Knoch, F.; Moll, M. *Z. Naturforsch. Teil B* **1995**, *50*, 791–801.
1741. Sellmann, D.; Ruf, R.; Knoch, F.; Moll, M. *Inorg. Chem.* **1995**, *34*, 4745–4755.
1742. Sellmann, D.; Utz, J.; Heinemann, F. W. *Inorg. Chem.* **1999**, *38*, 459–466.
1743. Sellmann, D.; Utz, J.; Heinemann, F. W. *Eur. J. Inorg. Chem.* **1999**, 341–348.
1744. Sellmann, D.; Gottschalk-Gaudig, T.; Haussinger, D.; Heinemann, F. W.; Hess, B. A. *Chem.-Eur. J.* **2001**, *7*, 2099–2103.
1745. Bernhard, P.; Bull, D. J.; Robinson, W. T.; Sargeson, A. M. *Aust. J. Chem.* **1992**, *45*, 1241–1254.
1746. Hung, C.-H.; Ou, C.-K.; Lee, G.-H.; Peng, S.-M. *Inorg. Chem.* **2001**, *40*, 6845–6847.
1747. McCann, G. M.; Carvill, A.; Lindner, E.; Karle, B.; Mayer, H. A. *J. Chem. Soc., Dalton Trans.* **1990**, 3107–3115.
1748. Lindner, E.; Geprags, M.; Gierling, K.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1995**, *34*, 6106–6117.
1749. Lindner, E.; Mockel, A. *Z. Naturforsch. Teil B* **1992**, *47*, 693–696.
1750. Lindner, E.; Mockel, A.; Mayer, H. A.; Kühbauch, H.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1993**, *32*, 1266–1271.
1751. Lindner, E.; Pautz, S.; Haustein, M. *Coord. Chem. Rev.* **1996**, *155*, 145–162.
1752. Werner, H.; Bank, J.; Steinert, P.; Wolfsberger, W. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2178–2185.
1753. Yamamoto, Y.; Sugawara, K.; Aiko, T.; Ma, J. F. *J. Chem. Soc., Dalton Trans.* **1999**, 4003–4008.
1754. Rogers, C. W.; Patrick, B. O.; Rettig, S. J.; Wolf, M. O. *J. Chem. Soc., Dalton Trans.* **2001**, 1278–1283.
1755. Valls, E.; Suades, J.; Donadieu, B.; Mathieu, R. *Chem. Commun.* **1996**, 771–772.
1756. Valls, E.; Suades, J.; Mathieu, R. *Organometallics* **1999**, *18*, 5475–5483.
1757. Bank, J.; Steinert, P.; Windmuller, B.; Wolfsberger, W.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1996**, 1153–1159.
1758. Henig, G.; Werner, H. *Z. Naturforsch. Teil B* **1998**, *53*, 540–544.
1759. Demerseman, B.; Toupet, L. *Eur. J. Inorg. Chem.* **2002**, 249–257.
1760. Braunstein, P.; Chauvin, Y.; Nahring, J.; Dusausoy, Y.; Bayeul, D.; Tiripicchio, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1995**, 851–862.
1761. Del Zotto, A.; Della Ricca, B.; Zangrando, E.; Rigo, P. *Inorg. Chim. Acta* **1997**, *261*, 147–159.
1762. Dilworth, J. R.; Zheng, Y. F.; Miller, J. R. *J. Chem. Soc., Dalton Trans.* **1992**, 1757–1758.
1763. Khan, M. M. T.; Kureshy, R. I.; Khan, N. H. *Polyhedron* **1992**, *11*, 1053–1057.
1764. Maji, M.; Ghosh, S.; Chattopadhyay, S. K.; Mak, T. C. W. *Inorg. Chem.* **1997**, *36*, 2938–2943.
1765. Arca, M.; Blake, A. J.; Casabo, J.; Demartin, F.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Kivekas, R.; Muns, V.; Schröder, M.; Verani, G. *J. Chem. Soc., Dalton Trans.* **2001**, 1180–1188.
1766. Mullica, D. F.; Hayward, P. K.; Sappenfield, E. L. *Inorg. Chim. Acta* **1996**, *253*, 97–101.
1767. Gentil, L. A.; Navaza, A.; Olabe, J. A.; Rigotti, G. E. *Inorg. Chim. Acta* **1991**, *179*, 89–96.
1768. Slep, L. D.; Albores, P.; Baraldo, L. M.; Olabe, J. A. *Inorg. Chem.* **2002**, *41*, 114–120.
1769. Slep, L. D.; Baraldo, L. M.; Olabe, J. A. *Inorg. Chem.* **1996**, *35*, 6327–6333.
1770. Coleman, K. S.; Holloway, J. H.; Hope, E. G. *J. Chem. Soc., Dalton Trans.* **1997**, 1713–1717.
1771. Brewer, S. A.; Holloway, J. H.; Hope, E. G. *J. Chem. Soc., Dalton Trans.* **1994**, 1067–1071.
1772. Coleman, K. S.; Fawcett, J.; Holloway, J. H.; Hope, E.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1997**, 3557–3562.
1773. Brewer, S. A.; Coleman, K. S.; Fawcett, J.; Holloway, J. H.; Hope, E. G.; Russell, D. R.; Watson, P. G. *J. Chem. Soc., Dalton Trans.* **1995**, 1073–1076.
1774. Coleman, K. S.; Holloway, J. H.; Hope, E. G.; Langer, J. *J. Chem. Soc., Dalton Trans.* **1997**, 4555–4559.
1775. Huang, D. J.; Folting, K.; Caulton, K. G. *Inorg. Chem.* **1996**, *35*, 7035–7040.
1776. Chau, D. E. K. Y.; James, B. R. *Inorg. Chim. Acta* **1995**, *240*, 419–425.
1777. MacFarlane, K. S.; Thorburn, I. S.; Cyr, P. W.; Chau, D. E. K. Y.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1998**, *270*, 130–144.
1778. Fogg, D. E.; James, B. R. *Inorg. Chem.* **1997**, *36*, 1961–1966.
1779. Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 2196–2207.
1780. Batista, A. A.; Porcu, O. M.; Nascimento, O. R.; Barbosa, V. M.; Oliva, G. *J. Coord. Chem.* **1993**, *30*, 345–355.
1781. Sanchez-Delgado, R. A.; Oramas, B. A. *J. Mol. Catal.* **1986**, *36*, 283–291.
1782. Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 3293–3304.
1783. Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 4386–4391.
1784. Kennedy, B. J.; Heath, G. A.; Khoo, T. J. *Inorg. Chim. Acta* **1991**, *190*, 265–269.
1785. Cotton, F. A.; Torralba, R. C. *Inorg. Chem.* **1991**, *30*, 4392–4393.
1786. Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *Aust. J. Chem.* **1999**, *52*, 621–623.
1787. Panneerselvam, K.; Lu, T. H.; Huang, C. H.; Tung, S. F.; Shiu, K. B. *Acta Crystallogr., Sect. C* **1997**, *53*, 1782–1784.
1788. Shiu, K. B.; Peng, S. M.; Cheng, M. C. *J. Organometal. Chem.* **1993**, *452*, 143–149.

1789. Matteoli, U.; Menchi, G.; Bianchi, M.; Piacenti, F.; Ianelli, S.; Nardelli, M. *J. Organometal. Chem.* **1995**, *498*, 177–186.
1790. Soler, J.; Moldes, I.; de la Encarnacion, E.; Ros, J. *J. Organometal. Chem.* **1999**, *580*, 108–109.
1791. Field, J. S.; Haines, R. J.; Parry, C. J. *J. Chem. Soc., Dalton Trans.* **1997**, 2843–2848.
1792. Hilts, R. W.; Sherlock, S. J.; Cowie, M.; Singleton, E.; Steyn, M. M. D. *Inorg. Chem.* **1990**, *29*, 3161–3167.
1793. Andreu, P. L.; Cabeza, J. A.; Carriedo, G. A.; Riera, V.; Garcia-Granda, S.; van der Maelen, J. F.; Mori, G. *J. Organometal. Chem.* **1991**, *421*, 305–314.
1794. Carriedo, C.; Connelly, N. G. *J. Organomet. Chem.* **1991**, *403*, 359–363.
1795. Grunwald, C.; Laubender, M.; Wolf, J.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1998**, 833–839.
1796. Tissot, O.; Gouygou, M.; Daran, J. C.; Balavoine, G. G. A. *Organometallics* **1998**, *17*, 5927–5930.
1797. Arliguie, T.; Chaudret, B.; Chung, G.; Dahan, F. *Organometallics* **1991**, *10*, 2973–2977.
1798. Wesemann, J. L.; Chisholm, M. H. *Inorg. Chem.* **1997**, *36*, 3258–3267.
1799. Cukiernik, F. D.; Giroud-Godquin, A.-M.; Maldivi, P.; Marchon, J.-C. *Inorg. Chim. Acta* **1994**, *215*, 203–207.
1800. Beck, E. J.; Drysdale, K. D.; Thompson, L. K.; Li, L. C.; Murphy, C. A.; Aquino, M. A. S. *Inorg. Chim. Acta* **1998**, *279*, 121–125.
1801. Cukiernik, F. D.; Luneau, D.; Marchon, J. C.; Maldivi, P. *Inorg. Chem.* **1998**, *37*, 3698–3704.
1802. Caplan, J. F.; Murphy, C. A.; Swansburg, S.; Lemieux, R. P.; Cameron, T. S.; Aquino, M. A. S. *Can. J. Chem.* **1998**, *76*, 1520–1523.
1803. Barral, M. C.; Jimenez-Aparicio, R.; Priego, J. L.; Royer, E. C.; Gutierrez-Puebla, E.; Ruiz-Valero, C. *Polyhedron* **1992**, *11*, 2209–2215.
1804. Barral, M. C.; Jimenez-Aparicio, R.; Priego, J. L.; Royer, E. C.; Saucedo, M. J.; Urbanos, F. A.; Amador, U. *J. Chem. Soc., Dalton Trans.* **1995**, 2183–2187.
1805. Barral, M. C.; Jimenez-Aparicio, R.; Royer, E. C.; Saucedo, M. J.; Urbanos, F. A.; Gutierrez-Puebla, E.; Ruiz-Valero, C. *J. Chem. Soc., Dalton Trans.* **1991**, 1609–1613.
1806. Barral, M. C.; Jimenez-Aparicio, R.; Priego, J. L.; Royer, E. C.; Saucedo, M. J.; Urbanos, F. A.; Amador, U. *Polyhedron* **1995**, *14*, 2419–2427.
1807. Barral, M. C.; Jimenez-Aparicio, R.; Priego, J. L.; Royer, E. C.; Urbanos, F. A.; Amador, U. *J. Chem. Soc., Dalton Trans.* **1997**, 863–868.
1808. Barral, M. C.; Jimenez-Aparicio, R.; Priego, J. L.; Royer, E. C.; Urbanos, F. A.; Amador, U. *Inorg. Chim. Acta* **1998**, *279*, 30–36.
1809. Barral, M. C.; Jimenez-Aparicio, R.; Perez-Quintanilla, D.; Pinilla, E.; Priego, J. L.; Royer, E. C.; Urbanos, F. A. *Polyhedron* **1998**, *18*, 371–376.
1810. Drysdale, K. D.; Beck, E. J.; Cameron, T. S.; Robertson, K. N.; Aquino, M. A. S. *Inorg. Chim. Acta* **1997**, *256*, 243–252.
1811. Handa, M.; Yoshioka, D.; Sayama, Y.; Shiomi, K.; Mikuriya, M.; Hiromitsu, I.; Kasuga, K. *Chem. Lett.* **1999**, 1033–1034.
1812. Handa, M.; Sayama, Y.; Mikuriya, M.; Nukada, R.; Hiromitsu, I.; Kasuga, K. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1647–1653.
1813. Handa, M.; Sayama, Y.; Mikuriya, M.; Nukada, R.; Hiromitsu, I.; Kasuga, K. *Chem. Lett.* **1996**, 201–202.
1814. Handa, M.; Sayama, Y.; Mikuriya, M.; Nukada, R.; Hiromitsu, I.; Kasuga, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 119–125.
1815. Sayama, Y.; Handa, M.; Mikuriya, M.; Hiromitsu, I.; Kasuga, K. *Chem. Lett.* **1998**, 777–778.
1816. Cotton, F. A.; Labella, L.; Shang, M. Y. *Inorg. Chim. Acta* **1992**, *197*, 149–158.
1817. Das, B. K.; Chakravarty, A. R. *Inorg. Chem.* **1991**, *30*, 4978–4986.
1818. Barral, M. C.; Jimenez-Aparicio, R.; Royer, E. C.; Urbanos, F. A.; Monge, A.; Ruiz-Valero, C. *Polyhedron* **1991**, *10*, 113–120.
1819. Cotton, F. A.; Yokochi, A. *Polyhedron* **1998**, *17*, 959–963.
1820. Cotton, F. A.; Yokochi, A. *Inorg. Chim. Acta* **1998**, *276*, 557–561.
1821. Cotton, F. A.; Lu, J.; Yokochi, A. *Inorg. Chim. Acta* **1998**, *276*, 447–452.
1822. Mintert, M.; Sheldrick, W. S. *Inorg. Chim. Acta* **1995**, *236*, 13–20.
1823. Sasaki, Y.; Suzuki, M.; Nagasawa, A.; Tokiwa, A.; Ebihara, M.; Yamaguchi, T.; Kabuto, C.; Ochi, T.; Ito, T. *Inorg. Chem.* **1991**, *30*, 4903–4908.
1824. Cipriano, C.; Clark, R. J. H.; Oprescu, D.; Withnall, R. *J. Chem. Soc., Dalton Trans.* **1995**, 2417–2419.
1825. Kikuchi, A.; Fukumoto, T.; Umakoshi, K.; Sasaki, Y.; Ichimura, A. *J. Chem. Soc., Chem. Commun.* **1995**, 2125–2126.
1826. Fukumoto, T.; Kikuchi, A.; Umakoshi, K.; Sasaki, Y. *Inorg. Chim. Acta* **1998**, *283*, 151–159.
1827. Santos, J. M.; Cipriano, C.; Faria, R. B.; Figueroa-Villar, J. D. *Can. J. Chem.* **1997**, *75*, 890–898.
1828. Syamala, A.; Das, B. K.; Chakravarty, A. R. *Polyhedron* **1992**, *11*, 335–339.
1829. Syamala, A.; Nethaji, M.; Chakravarty, A. R. *Inorg. Chim. Acta* **1995**, *229*, 33–38.
1830. Gupta, N.; Mukerjee, S.; Mahapatra, S.; Ray, M.; Mukherjee, R. *Inorg. Chem.* **1992**, *31*, 139–141.
1831. Koshi, C.; Umakoshi, K.; Sasaki, Y. *Chem. Lett.* **1997**, 1155–1156.
1832. Schneider, R.; Weyhermuller, T.; Wieghardt, K.; Nuber, B. *Inorg. Chem.* **1993**, *32*, 4925–4934.
1833. Geilenkirchen, A.; Neubold, P.; Schneider, R.; Wieghardt, K.; Flörke, U.; Haupt, H. J.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1994**, 457–464.
1834. Hotzelmann, R.; Wieghardt, K.; Ensling, J.; Romstedt, H.; Gütlich, P.; Bill, E.; Flörke, U.; Haupt, H.-J. *J. Am. Chem. Soc.* **1992**, *114*, 9470–9483.
1835. Almog, O.; Bino, A.; Garfinkelshweky, D. *Inorg. Chim. Acta* **1993**, *213*, 99–102.
1836. Powell, G.; Richens, D. T.; Bino, A. *Inorg. Chim. Acta* **1995**, *232*, 167–170.
1837. Velayutham, M.; Gopinath, C. S.; Subramanian, S. *Chem. Phys. Lett.* **1996**, *249*, 71–76.
1838. Ohto, A.; Sasaki, Y.; Ito, T. *Inorg. Chem.* **1994**, *33*, 1245–1246.
1839. Sabo-Etienne, S.; Chaudret, B. *Coord. Chem. Rev.* **1998**, *180*, 381–407.
1840. Borowski, A. F.; Donnadieu, B.; Daran, J. C.; Sabo-Etienne, S.; Chaudret, B. *Chem. Commun.* **2000**, 543–544.
1841. Chaudret, B.; Dagnac, P.; Labroue, D.; Sabo-Etienne, S. *New J. Chem.* **1996**, *20*, 1137–1141.
1842. Delpech, F.; Sabo-Etienne, S.; Daran, J. C.; Chaudret, B.; Hussein, K.; Marsden, C. J.; Barthelat, J. C. *J. Amer. Chem. Soc.* **1999**, *121*, 6668–6682.
1843. Carr, S. W.; Fowles, E. H.; Fontaine, X. L. R.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1990**, 573–579.

1844. Esteruelas, M. A.; Lledos, A.; Martin, M.; Maseras, F.; Oses, R.; Ruiz, N.; Tomas, J. *Organometallics* **2001**, *20*, 5297–5309.
1845. Castillo, A.; Barea, G.; Esteruelas, M. A.; Lahoz, F. J.; Lledos, A.; Maseras, F.; Modrego, J.; Onate, E.; Oro, L. A.; Ruiz, N.; Sola, E. *Inorg. Chem.* **1999**, *38*, 1814–1824.
1846. Esteruelas, M. A.; Lahoz, F. J.; Lopez, A. M.; Onate, E.; Oro, L. A.; Ruiz, N.; Sola, E.; Tolosa, J. I. *Inorg. Chem.* **1996**, *35*, 7811–7817.
1847. Gusev, D. G.; Kuhlman, R.; Sini, G.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1994**, *116*, 2685–2686.
1848. Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133.
1849. Desrosiers, P. J.; Cai, L. H.; Lin, Z. R.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173–4184.
1850. Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chim. Acta* **1991**, *179*, 195–201.
1851. Bakhmutov, V. I.; Bianchini, C.; Maseras, F.; Lledos, A.; Peruzzini, M.; Vorontsov, E. V. *Chem Eur J* **1999**, *5*, 3318–3325.
1852. Facey, G. A.; Fong, T. P.; Gusev, D.; Macdonald, P. M.; Morris, R. H.; Schlaf, M.; Xu, W. *Can. J. Chem.* **1999**, *77*, 1899–1910.
1853. Gusev, D. G.; Kuznetsov, V. F.; Eremenko, I. L.; Berke, H. *J. Am. Chem. Soc.* **1993**, *115*, 5831–5832.
1854. Kuhlman, R.; Gusev, D. G.; Eremenko, I. L.; Berke, H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1997**, *536*, 139–147.
1855. Halpern, J.; Cai, L. S.; Desrosiers, P. J.; Lin, Z. R. *J. Chem. Soc., Dalton Trans.* **1991**, 717–723.
1856. Saburi, M.; Aoyagi, K.; Kodama, T.; Takahashi, T.; Uchida, Y.; Kozawa, K.; Uchida, T. *Chem. Lett.* **1990**, 1909–1912.
1857. Michos, D.; Luo, X. L.; Crabtree, R. H. *Inorg. Chem.* **1992**, *31*, 4245–4250.
1858. Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876–4887.
1859. Albinati, A.; Klooster, W. T.; Koetzle, T. F.; Fortin, J. B.; Ricci, J. S.; Eckert, J.; Fong, T. P.; Lough, A. J.; Morris, R. H.; Golombek, A. P. *Inorg. Chim. Acta* **1997**, *259*, 351–357.
1860. Lough, A. J.; Morris, R. H.; Ricciuto, L.; Schleis, T. *Inorg. Chim. Acta* **1998**, *270*, 238–246.
1861. Cappellani, E. P.; Drouin, S. D.; Jia, G. C.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *J. Am. Chem. Soc.* **1994**, *116*, 3375–3388.
1862. Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1–2.
1863. Tenorio, M. J.; Puerta, M. C.; Salcedo, I.; Valerga, P. *J. Organomet. Chem.* **1998**, *564*, 21–28.
1864. Gusev, D. G.; Hubener, R.; Burger, P.; Orama, O.; Berke, H. *J. Am. Chem. Soc.* **1997**, *119*, 3716–3731.
1865. Gusev, D. G.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 13138–13147.
1866. Abdur-Rashid, K.; Gusev, D. G.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 1652.
1867. Chung, G.; Arliguie, T.; Chaudret, B. *New J. Chem.* **1992**, *16*, 369–374.
1868. Hubler, K.; Hubler, U.; Roper, W. R.; Schwerdtfeger, P.; Wright, L. J. *Chem Eur J* **1997**, *3*, 1608–1616.
1869. Yardy, N. M.; Lemke, F. R.; Brammer, L. *Organometallics* **2001**, *20*, 5670–5674.
1870. Parent, J. S.; McManus, N. T.; Rempel, G. L.; Power, W. P.; Marder, T. B. *J. Mol. Catal. A* **1998**, *135*, 285–293.
1871. Luther, T. A.; Heinekey, D. M. *Inorg. Chem.* **1998**, *37*, 127–132.
1872. Schlaf, M.; Lough, A. J.; Morris, R. H. *Organometallics* **1993**, *12*, 3808–3809.
1873. Fong, T. P.; Forde, C. E.; Lough, A. J.; Morris, R. H.; Rigo, P.; Rocchini, E.; Stephan, T. *J. Chem. Soc., Dalton Trans.* **1999**, 4475–4486.
1874. Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Onate, E.; Ruiz, N. *Inorg. Chem.* **1994**, *33*, 787–792.
1875. Braga, D.; De Leonardis, P.; Grepioni, F.; Tedesco, E. *Inorg. Chim. Acta* **1998**, *273*, 116–130.
1876. Rocchini, E.; Mezzetti, A.; Ruegger, H.; Burckhardt, U.; Gramlich, V.; Del Zotto, A.; Martinuzzi, P.; Rigo, P. *Inorg. Chem.* **1997**, *36*, 711–720.
1877. Mathew, N.; Jagirdar, B. R. *Inorg. Chem.* **2000**, *39*, 5404–5406.
1878. Mathew, N.; Jagirdar, B. R.; Gopalan, R. S.; Kulkani, G. U. *Organometallics* **2000**, *19*, 4506–4517.
1879. Albertin, G.; Antoniutti, S.; Bordignon, E.; Pegoraro, M. *J. Chem. Soc., Dalton Trans.* **2000**, 3575–3584.
1880. Field, L. D.; Hambley, T. W.; Yau, B. C. K. *Inorg. Chem.* **1994**, *33*, 2009–2017.
1881. Hill, G. S.; Holah, D. G.; Hughes, A. N.; Prokopchuk, E. M. *Inorg. Chim. Acta* **1998**, *278*, 226–228.
1882. Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288–293.
1883. Sleigh, C. J.; Duckett, S. B.; Mawby, R. J.; Lowe, J. P. *Chem. Commun.* **1999**, 1223–1224.
1884. Jessop, P. G.; Rastar, G.; James, B. R. *Inorg. Chim. Acta* **1996**, *250*, 351–357.
1885. Albertin, G.; Antoniutti, S.; Baldan, D.; Bordignon, E. *Inorg. Chem.* **1995**, *34*, 6205.
1886. Moldes, I.; Nefedov, S.; Lugan, N.; Mathieu, R. *J. Organometal. Chem.* **1995**, *490*, 11–19.
1887. Hampton, C. R. S. M.; Butler, I. R.; Cullen, W. R.; James, B. R.; Charland, J. P.; Simpson, J. *Inorg. Chem.* **1992**, *31*, 5509–5520.
1888. MacFarlane, K. S.; Joshi, A. M.; Rettig, S. J.; James, B. R. *Chem. Commun.* **1997**, 1363–1364.
1889. Perez-Cordero, E. E.; Campana, C.; Echegoyen, L. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 137–140.
1890. Ermer, S. P.; Shinomoto, R. S.; Deming, M. A.; Flood, T. C. *Organometallics* **1989**, *8*, 1377–1378.
1891. Ogasawara, M.; Macgregor, S. A.; Streib, W. E.; Folting, K.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1996**, *118*, 10189–10199.
1892. Werner, H.; Michenfelder, A.; Schulz, M. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 596–598.
1893. Werner, H.; Flugel, R.; Windmuller, B.; Michenfelder, A.; Wolf, J. *Organometallics* **1995**, *14*, 612–618.
1894. Flugel, R.; Windmuller, B.; Gevert, O.; Werner, H. *Chem Ber* **1996**, *129*, 1007–1013.

Comprehensive Coordination Chemistry II
ISBN (set): 0-08-0437486
Volume 5, (ISBN 0-08-0443273); pp 555–731

5.6 Ruthenium and Osmium: High Oxidation States

CHI-MING CHE
The University of Hong Kong, People's Republic of China
and
TAI-CHU LAU
City University of Hong Kong, People's Republic of China

5.6.1 INTRODUCTION

Ruthenium and osmium are unique among all the elements in displaying the widest range of oxidation states in their complexes, i.e., from +8 to −2, corresponding to d^0 to d^{10}. This chapter describes the coordination chemistry of ruthenium and osmium from oxidation state +8 to +4, covering the literature from 1982 to 2002. This field has greatly expanded since the early 1980s, and a review covering the literature up to 1992 has been published.[1] Other relevant reviews include a report on osmium chemistry in 1991[2] and a general discussion of transition metal nitrido complexes in 1992.[3]

The higher oxidation states of ruthenium and osmium are dominated by complexes containing metal–ligand multiple bonds, mainly oxo, nitrido, and imido complexes. Complexes containing

amido, alkoxo, sulfido, and fluoro ligands are also common, in which there is also multiple bonding between the metal and the ligand. An excellent book on metal–ligand multiple bonds has been published.[4]

Since the early 1980s there have been exciting developments in ruthenium and osmium oxo chemistry. A variety of oxo complexes have been developed which are active oxidants for organic substrates such as alcohols, alkenes, aromatic hydrocarbons, and alkanes.[5,6] Oxo complexes with porphyrin ligands have also been used as models for the highly unstable iron-oxo intermediates in cytochrome P450 and related enzymes. Efficient catalytic systems for the oxidation of organic substrates have been developed using terminal oxidants such as *N*-methylmorpholine *N*-oxide (NMO), pyridine *N*-oxides (pyNO), *t*-butyl hydroperoxides (TBHP), hydrogen peroxide (H_2O_2), and electrochemical oxidation. Remarkably dioxoruthenium(VI) complexes containing sterically bulky porphyrin ligands can also catalyze the aerobic epoxidation of alkenes. By varying the oxidation states and the nature of the ancillary ligands, the oxidizing power of the oxo complexes can be fine tuned to oxidize various organic substrates. For example, $(NPr^n_4)[RuO_4]$, a mild oxidant, is one of the best catalysts for the selective oxidation of alcohols, while cationic ruthenium oxo complexes with polypyridyl ligands can oxidize unactivated C—H bonds, including ethane and methane. *cis*-Dihydroxylation of alkenes with a ruthenium system has been reported. Asymmetric epoxidation of alkenes has also been achieved using chiral ruthenium oxo systems, with moderate to good ee (enantiomeric excess).

Ruthenium and osmium oxo complexes are also unique in displaying reversible, pH-dependent redox couples in cyclic voltammetry.[7] The availability of well-defined E° values has greatly helped in the elucidation of the mechanisms of oxidations by these metal oxo species. Mechanistic studies on the oxidation of substrates by ruthenium oxo species with polypyridyl and macrocyclic tertiary amine ligands have revealed a variety of reaction pathways, including one-electron transfer, oxygen atom transfer, hydrogen atom transfer, hydride transfer, and proton-coupled electron transfer. This information should be relevant to biological oxidations. Moreover, oxidation of alcohols and hydrocarbons often exhibits remarkably large kinetic isotope effects. There are a number of recent reviews on metal oxo species in catalytic and biological systems.[8–12]

μ-Oxo ruthenium complexes containing bipyridyl ligands are also efficient water oxidation catalysts, and there have been extensive mechanistic studies on this important reaction, which should contribute to the understanding of biological water oxidations.

Although osmium oxo complexes are much weaker oxidants than ruthenium oxo complexes, there has been significant development in their oxidation chemistry. Notably, practical methods for the asymmetric dihydroxylation of alkenes based on $[OsO_4]$ have been developed. Dioxo-osmium(VI) complexes containing macrocyclic tertiary amine ligands are luminescent both in the solid state and in fluid solutions. The excited states are strong oxidants ($E^\circ > 2\,V$), and these complexes can function as photooxidants for a variety of inorganic and organic substrates.

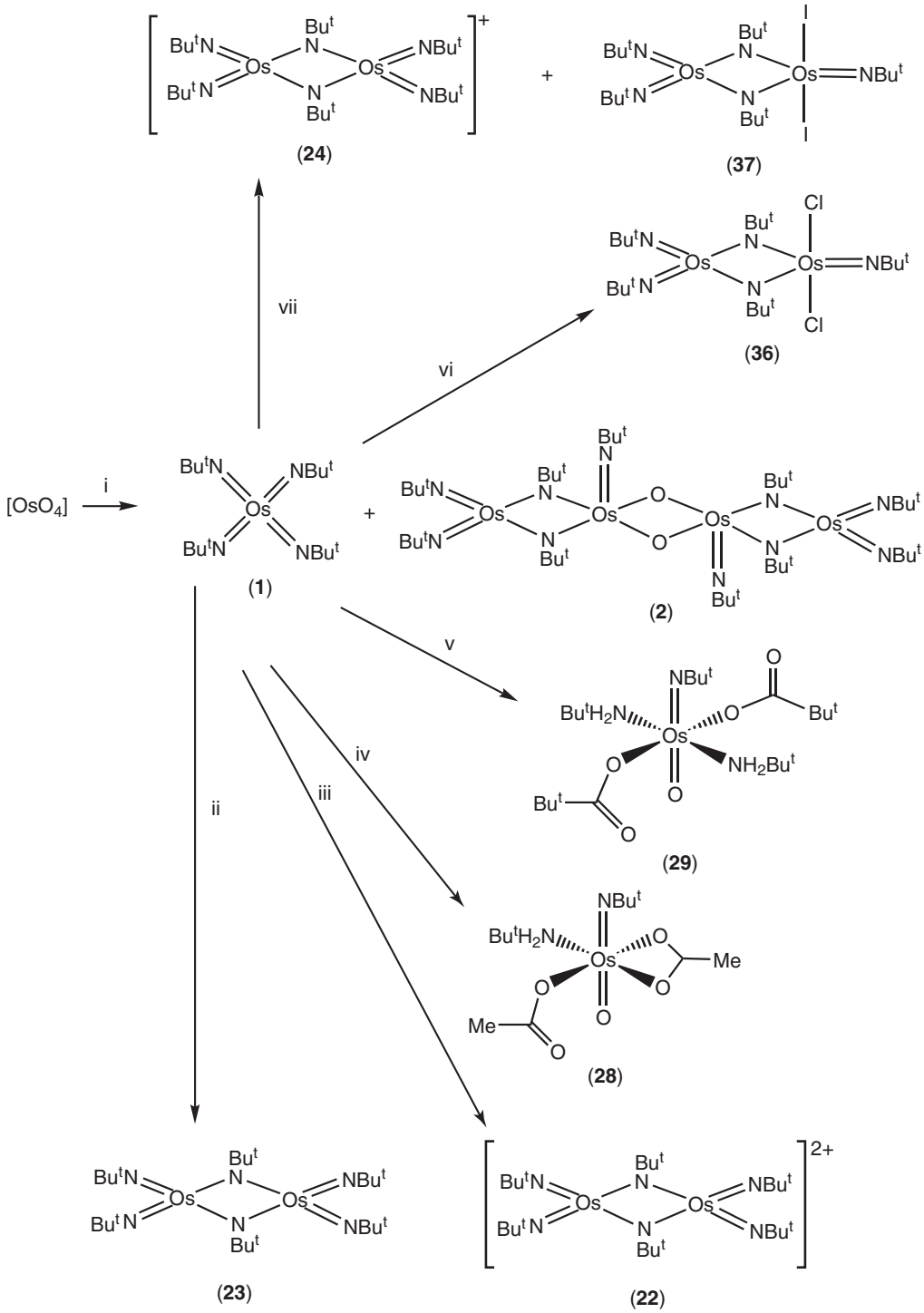
There have also been exciting developments in the chemistry of nitrido complexes. A number of electrophilic osmium(VI) nitrido complexes containing polypyridyl, trispyrazoylborate, and related ligands have been developed. They undergo a variety of redox reactions, many of them are unique to this class of osmium(VI) nitrido complexes. These reactions result in the formation of novel Os^{IV} and Os^{V} complexes; these can further react with various substrates to generate Os^{II} and Os^{III} complexes via atom/group transfer reactions, which may provide general routes for the synthesis of heteroatom compounds. These osmium(VI) nitrido complexes also show promise as reagents for C—N bond formation. Osmium nitrido complexes also undergo N···N coupling reactions to produce dinitrogen complexes; studies of this remarkable reaction should provide an insight into N≡N cleavage. A number of osmium(VI) nitrido complexes are luminescent and have long-live excited states both in the solid state and in fluid solutions at room temperature. These complexes are powerful one-electron oxidants in the excited states, with excited state redox potentials >2 V, and they should be useful as photooxidants. There has been much less development in the chemistry of ruthenium nitrido complexes; it may be anticipated that they are more reactive than osmium nitrido complexes.

There have also been significant advances in the imido chemistry of ruthenium and osmium. A variety of imido complexes in oxidation states +8 to +6 have been reported. Notably, osmium (VIII) imido complexes are active intermediates in osmium-catalyzed asymmetric aminohydroxylations of alkenes. Ruthenium(VI) imido complexes with porphyrin ligands can effect stoichiometric and catalytic aziridination of alkenes. With chiral porphyrins, asymmetric aziridination of alkenes has also been achieved. Some of these imido species may also serve as models for biological processes.[13] An imido species has been postulated as an intermediate in the nitrite reductase cycle.[14]

5.6.2 RUTHENIUM(VIII) AND OSMIUM(VIII)

5.6.2.1 Imido Complexes

No imido complexes of Ru^{VIII} have been reported.



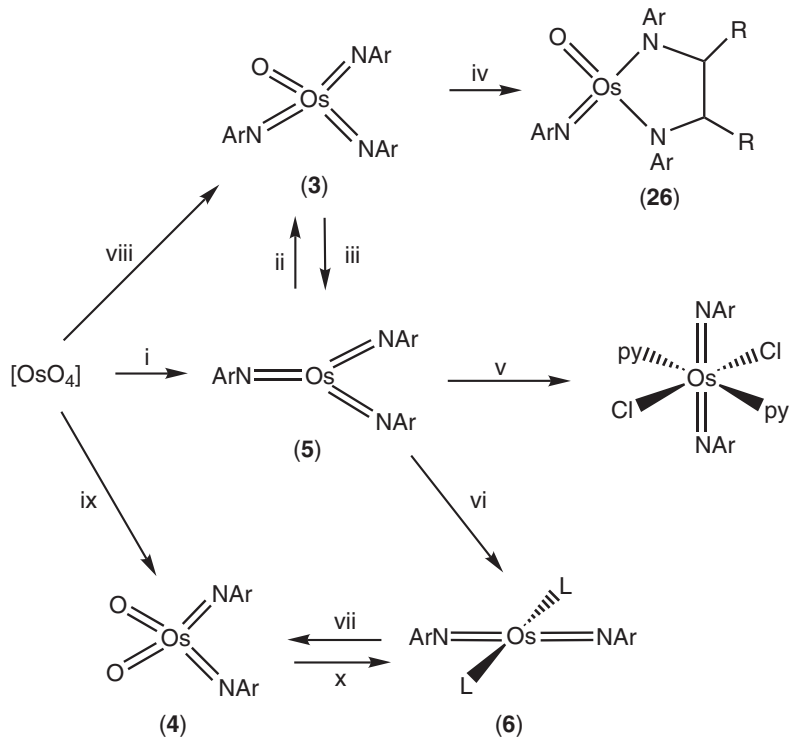
i, $Bu^tNH(SiMe_3)$; ii, PPh_3 or Na/Hg; iii, $(Me_3O)(BF_4)$; iv, MeCOOH; v, Me_3CCOOH; vi, PPh_4I, $ClCH_2CH_2Cl$; vii, I_2.

Scheme 1

Osmium(VIII) alkylimido complexes of the type $[Os(O)_3(NR)]$, $[Os(O)_2(NR)_2]$, and $[Os(O)(NR)_3]$ (R = *t*-butyl (Bu^t), *t*-amyl, *t*-octyl, or 1-adamantyl) have been well documented in *CCC* (1987).

The first homoleptic osmium(VIII) imido compound, $[Os(NBu^t)_4]$ (**1**), together with the tetranuclear osmium(VI) oxo-imido complex $[(NBu^t)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)(\mu\text{-}O)]_2$ (**2**) have been synthesized by the interaction of $[OsO_4]$ with neat $[NHBu^t(SiMe_3)]$ (Scheme 1). The IR spectrum of (**1**) shows a $\nu(Os{=}N)$ stretch at 1238 cm^{-1}.[15] The molecular structure of (**1**) has been determined in the gas phase by electron diffraction. The measured Os—N distance is 1.750 Å with a bent alkylimido ligand (Os—N—C = 156.4°).[16] The NBu^t groups are in a distorted tetrahedral arrangement around the central osmium atom, and bent in such a way that the overall molecular symmetry is reduced to S_4. The reactions of (**1**) with PR_3, I_2, PPh_4I, acetic acid, pivalic acid, and $(Me_3O)(BF_4)$ are summarized in Scheme 1.[15]

The arylimido complexes $[Os(O)(NAr)_3]$ (**3**) and $[Os(O)_2(NAr)_2]$ (**4**) ($Ar = C_6H_3Pr^i{}_2$-2,6) have been synthesized by the interaction of Me_3NO with $[Os(NAr)_3]$ (**5**) and $[Os(NAr)_2(PMe_2Ph)_2]$ (**6**), respectively (Scheme 2).[17] These complexes can also be prepared in high yields by an imido/oxo exchange reaction.[18] $[OsO_4]$ reacts smoothly with one equivalent of $[Mo(NAr)_2(OBu^t)_2]$ to give $[Os(O)_2(NAr)_2]$. If 1.5 equivalents of $[Mo(NAr)_2(OBu^t)_2]$ are used, then $[Os(O)(NAr)_3]$ is obtained in high yield. However, $[Os(NAr)_4]$ cannot be prepared.



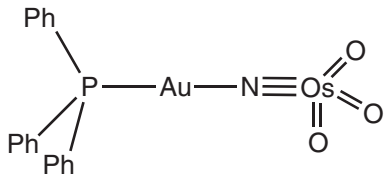
Ar = $C_6H_3Pr^i{}_2$-2,6; i, ArNCO; ii, Me_3NO; iii, PPh_3 or Zn; iv, $C_2H_2R_2$ = ethylene, norbornene or cyclopentene; v, py·HCl; vi, PR_3, L = PMe_3, PMe_2Ph, $P(OMe)_3$; vii, L = PMe_2Ph, Me_3NO; viii, 1.5 $[Mo(NAr)_2(OBu^t)_2]$; ix, $[Mo(NAr)_2(OBu^t)_2]$; x, PMe_2Ph.

Scheme 2

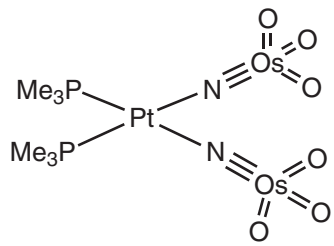
5.6.2.2 Nitrido Complexes

No nitrido complexes of ruthenium(VIII) have been isolated. For osmium, the only well-established osmium(VIII) nitrido species is $[Os(O)_3(N)]^-$, which has been well documented in *CCC* (1987). A number of heterometallic complexes formed by the interaction of $[Os(O)_3(N)]^-$ with a second metal center have been reported. In these complexes, the $[Os(O)_3(N)]^-$ ion acts as a

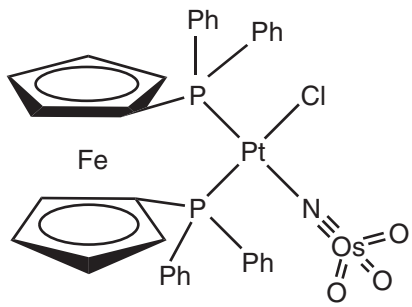
ligand and binds to a second metal center through the nitrogen atom to produce a —M—N≡$Os(O)_3$ linkage. Treatment of $(NBu^n_4)[Os(O)_3(N)]$ with $Au(PPh_3)(CF_3SO_3)$ and *cis*-$[(Me_3P)_2Pt(CF_3SO_3)_2]$ produces the species $[(PPh_3)Au\{(\mu\text{-}N)Os(O)_3\}]$ (**7**) and *cis*-$[(Me_3P)_2Pt\{(\mu\text{-}N)Os(O)_3\}_2]$ (**8**), respectively.[19] In (**7**) the mean Os—O, Os—N, and Au—N distances are 1.71 Å, 1.69 Å, and 2.02 Å, respectively, indicating that the Os≡N bond remains a triple bond. The Os—N—Au linkage is essentially linear (Au—N—Os = 168°). Other bimetallic nitrido-bridged complexes *cis*-$[(dppm)Pt\{(\mu\text{-}N)Os(O)_3\}_2]$ (dppm = bis(diphenylphosphino)methane), *trans*-$[Pt(4\text{-}Bu^tpy)_2\{(\mu\text{-}N)Os(O)_3\}_2]$, $[Ir(CO)(PPh_3)_2\{(\mu\text{-}N)Os(O)_3\}]$, and $[\{Rh(cod)\}\{(\mu\text{-}N)Os(O)_3\}_2]$ (cod = cycloocta-1,5-diene) are also known.[20] The reaction of $[Pt(dppf)(O_3SCF_3)(Cl)]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with $(NBu^n_4)[Os(O_3)(N)]$ affords the trimetallic complex $[Pt(dppf)\{(\mu\text{-}N)Os(O)_3\}(Cl)]$ (**9**), the mean Pt—N, Os—N, and Os—O distances are 2.06 Å, 1.66 Å, and 1.67 Å, respectively. The μ-nitrido complexes $[(OEP)(NO)Ru\{(\mu\text{-}N)Os(O)_3\}]$ (OEP = octaethylporphyr- inato dianion)[21] and $[Ru(CO)(Et_2dtc)(PPh_3)_2\{(\mu\text{-}N)Os(O)_3\}]$($Et_2dtc$ = N,N-diethyldithiocarbamato)[22] (**10**) have also been prepared, the Ru—N—Os linkage is bent with an angle of 138.4° and 155.1°, respectively. Treatment of $[OsN\{N(SPPh_2)_2\}_2](BF_4)$ with $(NBu_4)[OsO_3N]$ gives a μ-nitrido Os^{VIII}–Os^{VI} complex, $[OsN\{N(SPPh_2)_2\}_2(\mu\text{-}NOsO_3)]$ (**11**), in which the $[NOsO_3]^-$ is *trans* to the terminal nitrido ligand. The Os^{VI}—N, Os^{VI}—N(Os), and Os^{VIII}—N distances are 1.617 Å, 2.318 Å, and 1.719 Å, respectively; the Os—N—Os angle is 159.2°.[199]



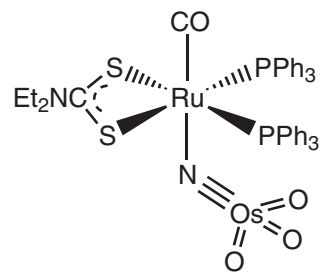
(**7**)



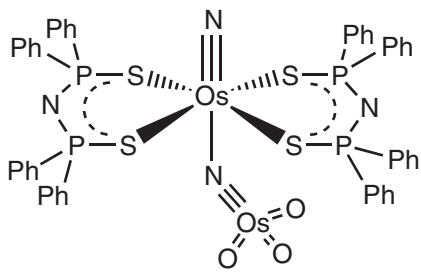
(**8**)



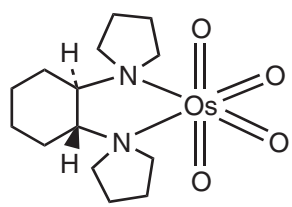
(**9**)



(**10**)



(**11**)



(**12**)

5.6.2.3 Oxo Complexes

5.6.2.3.1 Metal tetroxides

(i) RuO_4

$[RuO_4]$ is the only well-defined Ru^{VIII} species; its properties and chemistry have been reviewed in *CCC* (1987). It is a powerful oxidant that is able to oxidize a variety of organic substrates including alcohols, aldehydes, alkenes, alkynes, ethers, lactones, amines, aromatics, and sulfides.[23–25] The oxidation of cyclic sulfites to cyclic sulfates[26] and cycloalkanes to ring-opening products[27] with $[RuO_4]$ have also been reported.[26] An intriguing method for vicinal dihydroxylation of alkenes with $RuCl_3$ and $NaIO_4$ in a biphasic solution (ethyl acetate, acetonitrile, and water) has been described; the active intermediate is probably $[RuO_4]$.[28] $[RuO_4]$ oxidations have been used to determine the absolute stereochemistry of aromatic and heterocyclic alcohols.[29] Reactions of $[RuO_4]$ with the fullerenes C_{60} and C_{70} in 1,2,4-trichlorobenzene followed by acid hydrolysis produce the fullerene diols $C_{60}(OH)_2$ and $C_{70}(OH)_2$.[30]

$[RuO_4]$ has been used for the oxidative degradation of organochlorines such as polychlorinated biphenyls and organochlorine pesticides.[31–33] The oxidation of polycyclic aromatic hydrocarbons (PAHs) by $[RuO_4]$ has also been studied.[34] It is also used in the molecular characterization of kerogens by mild selective chemical degradations.[35]

There are a number of mechanistic studies on $[RuO_4]$ oxidations. The oxidation of 2-propanol by $[RuO_4]$ has been investigated. In 1–6.5 M $HClO_4$ hydride transfer appears to be the rate-determining step, while at high acid concentrations the rate-determining step seems to involve formation of carbocations.[36] The oxidation of methoxy-substituted benzyl phenyl sulfides by $[RuO_4]$, $[RuO_4]^-$, and $[RuO_4]^{2-}$ produces only sulfoxides and sulfones, and it is concluded that these oxidations occur by direct oxygen atom transfer rather than by single-electron transfer (followed by oxygen rebound).[37] The oxidation of thianthrene 5-oxide by $[RuO_4]$ to thianthrene 5,10-dioxide is also proposed to have an oxygen atom transfer mechanism.[38] The ruthenium-catalyzed oxidation of styrene and substituted styrenes by NaOCl has been studied. Electron donating groups retard the reaction but electron withdrawing groups accelerate the reaction. This trend is consistent with results of analysis by frontier MO theory. The mechanism of the oxidation of ethers to esters by RuO_4—$NaIO_4$ has also been investigated. Oxidation of cyclopropylmethyl methyl ether gives methyl cyclopropanecarboxylate with no rearranged products. No chlorinated products are observed in the presence of CCl_4. The rates of oxidation of a series of 4-substituted benzyl methyl ethers correlate with Hammett σ values to give a ρ value of -1.7, indicating only a moderate charge separation in the transition state. When $PhCHDOCH_3$ and $PhCD_2OCH_3$ are oxidized two deuterium isotope effects, one of 6.1 and another of 1.3, are obtained. It is proposed that the reaction proceeds by either a concerted reaction or a reversible oxidative addition of the ether to $[RuO_4]$ followed by a slow concerted step to give the product.[39] The oxidation of methyl and octyl α-D-glucopyranoside by $NaBrO_3$, catalyzed by three different high-valent ruthenium species, ruthenium tetroxide, perruthenate, and ruthenate, has been reported. At pH 4.5, $[RuO_4]$ appears to catalyze the oxidation of the alkyl glucopyranosides rapidly and produces alkyl glucuronic acid as the main product. Analysis of the kinetic and thermodynamic data suggests a hydride transfer mechanism.[40]

The photochemical decomposition of gaseous $[RuO_4]$ as a function of wavelength has been studied.[41]

The use of $[RuO_4]$ as a reagent for the preparation of epidermal samples for transmission electron microscopy has been investigated.[42,43]

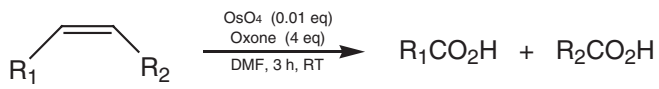
(ii) OsO_4

The most important compound is $[OsO_4]$; its properties, reactivities, and uses have been described in *CCC* (1987) . One of the most important reactions of $[OsO_4]$ is the *cis*-dihydroxylation of alkenes to vicinal glycols. Oxidations can be effected catalytically with a variety of cooxidants such as ClO_3^-, H_2O_2, TBHP, IO_4^-, NMO, and $[Fe(CN)_6]^{3-}$. Catalytic asymmetric dihydroxylation of alkenes to give optically active *cis*-glycols has been achieved by using a chiral amine ligand.[44] Chiral amines such as the acetates of quinidine and dihydroquinidine have been employed using NMO as the cooxidant.[45] A trioxoosmium(VIII) glycolato complex, $[OsO_3(O_2R)L]$ (L = chiral

amine), is thought to be involved in the oxidative cycle.[46,47] The X-ray crystal structure of the 1 : 1 OsO_4–(dimethylcarbamoyl)dihydroquinidine complex shows that it has a trigonal bipyramidal geometry with an axial amine ligand.[48] Chiral chelating diamines such as (−)-(*R*,*R*)-*N*,*N*,*N*′,*N*′-tetramethylcyclohexane-1,2-diamine have also been employed to promote asymmetric *cis*-hydroxylations.[49,50] A (*R*,*R*)-*trans*-1, 2-bis(*N*-pyrrolidino)cyclohexane–OsO_4 (**12**) complex has been isolated as a deep red crystalline solid at low temperature. This compound has a distorted octahedral structure; the diamine clearly functions as a bidentate ligand.[51] The two Os—N bonds are rather long (2.33 Å) indicating that the amine is weakly bound to the osmium. NMR studies indicate that this structure is retained in solution. This diamine is a much better ligand for asymmetric dihydroxylation catalysis (AD) than the related monoamine *N*-pyrrolidinocyclohexane. The complexes OsO_4·NMO (NMO = *N*-methylmorpholine *N*-oxide) and OsO_4·NMM (NMM = *N*-methylmorpholine) have been made and their crystal structures determined.[52] These species may play a role in the alkene–OsO_4–NMO reactions. AD of olefins has become one of the most general methods in asymmetric catalysis, and this topic has been extensively reviewed.[53–57]

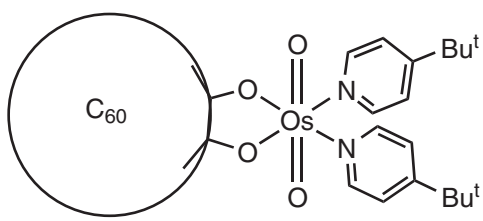
A closely related reaction, which has been discovered subsequently, is the catalytic asymmetric aminohydroxylation (AA) of alkenes.[58–60] The reaction is initiated by *in situ* formation of $[Os(O)_3(NR)]$ from $[OsO_4]$ and an appropriate nitrene source such as sulfonamides, carbamates, or amides. This is followed by the coordination of a chiral ligand L to form a five-coordinate species which adds to the alkene. Cinchona alkaloids are utilized as ligands as in the case of AD. *N*-toluenesulfonyl derivatives of α,β-hydroxyamino acids have been found to give better results both in AA and AD.[61] The AD reactions have been reviewed.[62,63]

A method for the catalytic oxidative cleavage of alkenes using $[OsO_4]$ and oxone in DMF has been reported.[64] This method provides a safer alternative to ozonolysis (Equation (1)).

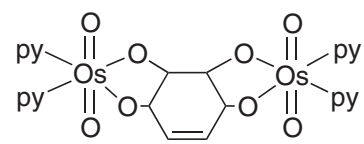


(1)

Reaction of one equivalent of $[OsO_4]$ with [60]fullerene in the presence of pyridine produces *trans*-$[C_{60}(OsO_4)(py)_2]$. In the presence of excess $[OsO_4]$ a two-to-one adduct can be obtained. The X-ray structure of *trans*-$[C_{60}(OsO_4)(4\text{-Bu}^t\text{py})_2]$ (**13**) has been determined, which provides the first crystallographic confirmation of the structure of C_{60}.[65–69]



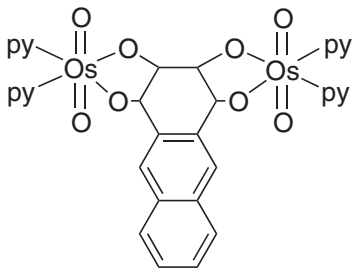
(**13**)



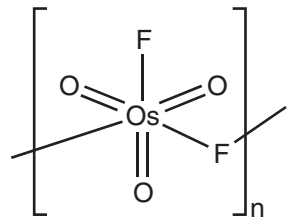
(**14**)

The photochemical and thermal "osmylation" of arenes have been reported.[70,71] Various types of arenes spontaneously form highly colored electron donor–acceptor (EDA complex) with $[OsO_4]$ in nonpolar solvents (Equation (2)). Charge transfer (CT) osmylation is effected by irradiation of the absorption bands of the EDA complexes. The molecular structures of the adducts of benzene (**14**) and anthracene (**15**) are elucidated by X-ray crystallography. The mechanism for CT osmylation is shown in Equation (3). The intermediate ion pair $[Ar^+, OsO_4^-]$ is detected by time-resolved picosecond spectroscopy. In the absence of light the EDA complexes of $[OsO_4]$ with electron-rich arenes such as naphthalene, anthracene, and phenanthrene slowly undergo direct thermal (DT) osmylation to produce the same series of adducts. Thus a similar mechanism is proposed for the thermal reactions (Scheme 3). It is likely that ligand-promoted thermal osmylation of arenes and dihydroxylation of alkenes also proceed with similar mechanisms.

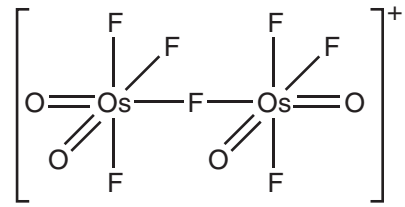
(2)



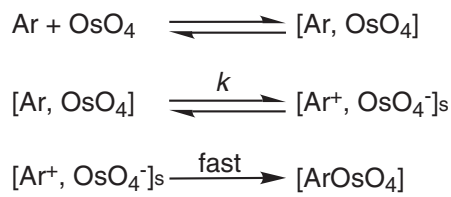
(15)



(16)



(17)



Scheme 3

$$[Ar, OsO_4] \underset{}{\overset{h\nu_{CT}}{\rightleftharpoons}} [Ar^{\cdot+}, OsO_4^{\cdot-}] \xrightarrow{\text{fast}} \text{adduct} \qquad (3)$$

The complex OsO_4(4-dimethylaminopyridine) has been synthesized.[72] It shows an absorption at 473 nm which is assigned to LMCT transition. Excitation of this band in ethanol leads to a reduction of Os^{VIII} to Os^{VI} and oxidation of ethanol to ethanal with a quantum yield of 0.1 at 436 nm.

There are a number of reports on the binding of $[OsO_4]$ to DNA in the presence of bpy (2,2′-bipyridine) and phen (1,10-phenanthroline).[73–81]

5.6.2.3.2 Oxo hydroxo complexes

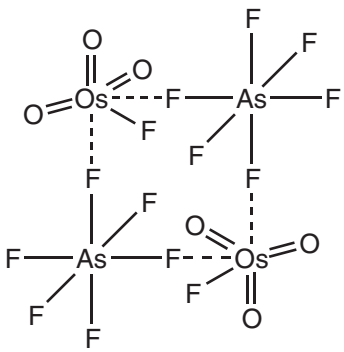
The Os^{VIII} complexes *cis*-$[OsO_4(OH)_2]^{2-}$, $[Os_2(O)_8(OH)]^-$, and $[Os(O)_5(H_2O)]^{2-}$ have been described in *CCC* (1987). The X-ray crystal structures of *cis*-$M^I_2[Os(O)_4(OH)_2]$ (M^I = Li, Na)[82,83] and *cis*-$M^{II}[Os(O)_4(OH)_2]$ (M^{II} = Ca, Sr, Ba)[84,85] have been determined. The X-ray structures of $M^I[Os_2(O)_8(OH)]$ (M^I = Rb, Cs)[86,87] show that the complexes have a trigonal bipyramidal geometry with a bridging hydroxo ligand in the apical position. The terminal Os=O bond lengths lie in the range 1.62–1.77 Å, and the Os—OH distances are 2.21 Å and 2.22 Å.[86]

5.6.2.3.3 Oxo halo complexes

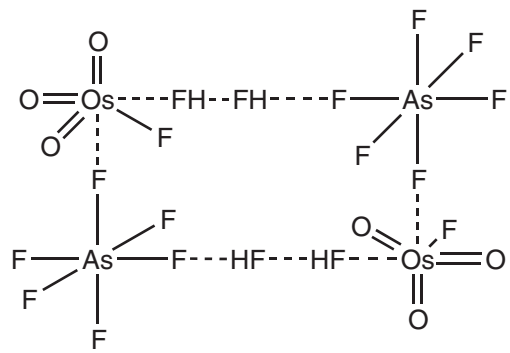
There are a few neutral oxo fluoro complexes of osmium(VIII), including $[Os(O)_3(F)_2]$ and $[Os(O)_2(F)_4]$.[88] The electronic and matrix IR spectra of $[Os(O)_3(F)_2]$ have been measured.[89] A new method for the preparation of $[Os(O)_3(F)_2]$, which involves the reaction of an excess of liquid ClF_3 with $[OsO_4]$, has been reported.[90a] X-ray crystal studies indicate a polymeric chain structure with a distorted octahedral geometry for the $[Os(O)_3(F)_2]$ units (**16**) and symmetrical, nonlinear fluoride bridges. The equilibrium geometries of $[OsO_4]$, $[Os(O)_3(F)_2]$, $[Os(O)_2(F)_4]$, and $[OsF_6]$ have been calculated by *ab initio* methods. The results show that $[Os(O)(F)_6]$ and $[OsF_8]$ are unlikely to exist.[90b] The results also predict a D_{3h} symmetry for $[Os(O)_3(F)_2]$, which is not in accord with experimental results.[90a] $[Os(O)_2(F)_4]$ was obtained from KrF_2 and $[OsO_4]$.[91] The X-ray crystal structure shows a helical chain arrangement of nearly octahedral *cis*-$[Os(O)_2(F)_4]$ molecules; however, the oxygen and fluorine atoms are partially disordered.[90a] The *cis* structure of this molecule is confirmed by electron diffraction, NMR, vibrational

spectroscopy, and DFT calculations.[92] The Os=O distance is 1.674 Å, and the Os—F distances are 1.883 Å and 1.843 Å.

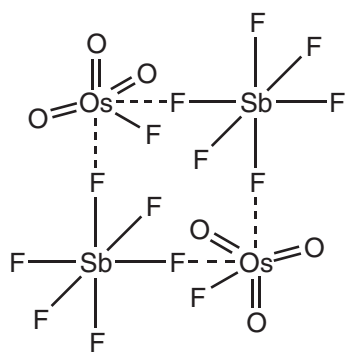
Cationic osmium(VIII) oxo fluoro species are also known. *cis*-$[Os(O)_2(F)_4]$ reacts with the strong fluoride ion acceptors AsF_5 and SbF_5 in anhydrous HF to produce $[\{cis\text{-}Os(O)_2(F)_3\}_2(\mu\text{-}F)]^+$ as the $[AsF_6]^-$ and $[Sb_2F_{11}]^-$ salts, respectively.[93] The structure of $[\{cis\text{-}Os(O)_2(F)_3\}_2(\mu\text{-}F)](Sb_2F_{11})$ consists of discrete fluoride bridged $[\{cis\text{-}Os(O)_2(F)_3\}_2(\mu\text{-}F)]^+$ (**17**) and $[Sb_2F_{11}]^-$. The species $[Os(O)_3(F)](AsF_6)$, $[Os(O)_3(F)](HF)_2(AsF_6)$, $[\{Os(O)_3(F)\}_2(\mu\text{-}F)](AsF_6)$, $[Os(O)_3(F)](HF)_2(SbF_6)$, and $[Os(O)_3(F)](HF)(SbF_6)$ have been prepared by the reaction of $[Os(O)_3(F)_2]$ with AsF_5 or SbF_5 in HF solvent.[94] The X-ray crystal structures of $[Os(O)_3(F)](AsF_6)$ (**18**), $[Os(O)_3(F)](HF)_2(AsF_6)$ (**19**), $[Os(O)_3(F)](SbF_6)$ (**20**), and $[Os(O_3)(F)](HF)(SbF_6)$ (**21**) have been determined. In these structures the $[Os(O)_3(F)]^+$ cations exhibit strong contacts to the anions and HF giving rise to cyclic, dimeric structures in which the osmium atoms have coordination numbers of six. The reaction of $[Os(O)_3(F)_2]$ with neat SbF_5 gives $[Os(O)_3(F)](Sb_3F_{16})$, which consists of well-isolated cations and anions and the osmium is four-coordinate.



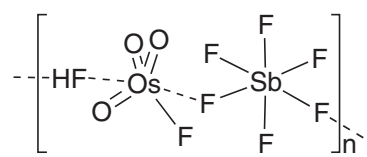
(**18**)



(**19**)



(**20**)



(**21**)

There are also a number of anionic osmium(VIII) oxo fluoro complexes. The salts $(NMe_4)[Os(O)_4(F)]$ and *cis*-$(NMe_4)_2[Os(O)_4(F)_2]$ are prepared by reacting $[OsO_4]$ with stoichiometric amounts of $(NMe_4)F$ in MeCN. The salts *fac*-$(NMe_4)[Os(O)_3(F)_3]$ and *fac*-$(NO)[Os(O)_3(F)_3]$ are prepared by reacting $[Os(O)_3(F)_2]$ with a stoichiometric amount of $(NMe_4)F$ in MeCN and with excess NOF, respectively. The structures of $(NMe_4)[Os(O)_4(F)]$ and $(NMe_4)[Os(O)_3(F)_3]$ have been determined by X-ray diffraction studies.[95]

Reaction of $[OsO_4]$ with $(PPh_4)Cl$ in CH_2Cl_2 gives $(PPh_4)[Os(O)_4(Cl)]\cdot CH_2Cl_2$ as orange-red crystals. The X-ray crystal structure shows a trigonal bipyramidal configuration (d(Os = O) = 1.72 Å, Os—Cl = 2.76 Å).[96]

Oxo imido and oxo nitrido complexes of Os^{VIII} are discussed in Sections 5.6.2.1 and 5.6.2.2, respectively.

5.6.3 RUTHENIUM(VII) AND OSMIUM(VII)

5.6.3.1 Imido Complexes

No imido complexes of ruthenium(VII) have been reported and there are only two examples for osmium.

An Os(VII)—Os(VII) dimer, $[(Bu^tN)_2Os^{VII}(\mu\text{-}NBu^t)]_2(BF_4)_2$ (**22**), is prepared by treatment of $[Os(Bu^tN)_4]$ (**1**) with $(Me_3O)(BF_4)$ (Scheme 1).[15] Its structure has been determined by X-ray crystallography (Os···Os = 2.68 Å, Os=N(terminal) = 1.715 Å, 1.710 Å, Os—N(bridge) = 1.902 Å, 1.927 Å). Cyclic voltammetry reveals a reversible two-electron couple at −0.07 V vs. Ag/AgCl, assigned to the $Os^{VII,VII}/Os^{VI,VI}$ couple.

A paramagnetic mixed-valence Os^{VI}—Os^{VII} compound $[(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)_2]^+$ (**24**) has been isolated from the interaction of $[Os(NBu^t)_4]$ (**1**) with I_2. X-ray crystal studies reveal that the two osmium atoms are structurally equivalent (Os···Os = 2.921 Å, Os=N(terminal) = 1.711 Å, Os—N(bridge) = 1.925 Å) (Scheme 1).[97]

5.6.3.2 Nitrido Complexes

No Ru^{VII} and Os^{VII} nitrido complexes have been isolated.

5.6.3.3 Oxo Complexes

5.6.3.3.1 $[RuO_4]^-$

The only well-defined complex of ruthenium(VII) is the perruthenate ion, $[RuO_4]^-$. This tetrahedral ion has long been known, and its properties and reactivities have been reviewed.[98] In aqueous solutions $[RuO_4]^-$ oxidizes alcohols and aldehydes to ketones and carboxylic acids, but it readily cleaves C=C double bonds.[99,100] The most important use of $[RuO_4]^-$ is as a mild and selective reagent for the catalytic oxidation of alcohols by NMO. There have been numerous publications in this area since 1984, including reviews.[5,6,101] A breakthrough in the oxidation chemistry of $[RuO_4]^-$ was the isolation of the organic-soluble tetrabutylammonium salt, $(NBu^n_4)[RuO_4]$, prepared by the fusion of $RuCl_3$ with KNO_3 and KOH, followed by oxidation with Cl_2 and addition of $(NBu^n_4)OH$. $(NBu^n_4)[RuO_4]$ is a remarkably mild and selective oxidant for alcohols without competing double-bond attack. This oxidation can be made catalytic by using NMO as a cooxidant.[102] This system becomes more useful when a more easily prepared tetra-*n*-propylammonium salt, $(NPr^n_4)[RuO_4]$, is reported.[101] This salt was first made by passing $[RuO_4]$ vapor into a solution of $(NPr^n_4)OH$ and NaOH.[102] An even simpler procedure was later developed, which involves generating $[RuO_4]^-$ from $NaBrO_3$ and RuO_2 and then precipitating with $(NPr^n_4)OH$.[103] The ESR spectrum of $(NPr^n_4)[RuO_4]$ has been measured.[104] Salts of other organic cations such as $(PPh_4)^+$ and $(PPN)^+$ have also been prepared.[104,105] In CH_2Cl_2, $(NPr^n_4)[RuO_4]$/NMO is an excellent oxidant of primary alcohols to aldehydes and of secondary alcohols to ketones, without affecting sensitive functions such as allylic, epoxy, lactone, indole, silyl ether, acetal, and tetrahydropyranyl functions. It has also been used for the oxidation of homoallylic alcohols to dienones, the selective oxidation of primary–secondary diols to lactones,[106,107] and the oxidation of secondary nitro compounds to the corresponding ketones.[108]

Kinetics studies on the oxidation of alcohols by $[RuO_4]^-$ in aqueous solutions have been reported.[109] The oxidation of cyclobutanol results in much C—C bond cleavage and the mostly likely mechanism involves one-electron processes with the formation of a radical intermediate.[109] On the other hand, in organic solvents using $(NPr^n_4)[RuO_4]$ both the stoichiometric and the catalytic (with NMO) oxidation of cyclobutanol produce almost exclusively cyclobutanone, suggesting that the oxidations proceed by two-electron processes, although $(NPr^n_4)[RuO_4]$ is a three-electron oxidant. A possible reaction sequence is shown in Equations (4)–(6).

$$Ru^{VII} + 2e \rightarrow Ru^{V} \tag{4}$$

$$2\,Ru^{V} \rightarrow Ru^{IV} + Ru^{VI} \tag{5}$$

$$Ru^{VI} + 2e \rightarrow Ru^{IV} \tag{6}$$

Various solid-supported perruthenate reagents have been designed for the oxidation of alcohols.[110–114] Solid-supported NMO has also been used.[115] A number of perruthenate systems employing O_2 as the terminal oxidant have also been reported.[113,116–119] The use of ionic liquids based upon substituted imidazolium cations as alternative solvent media for the selective oxidation of alcohols to aldehydes and ketones has also been investigated.[120,121]

The kinetics of the reduction of perruthenate(VII) by $[Fe(CN)_6]^{4-}$ and $[W(CN)_8]^{4-}$ and the oxidation of ruthenate(VI) by $[Mo(CN)_8]^{3-}$ and $[Ru(CN)_6]^{3-}$ have been studied in aqueous alkaline solutions. The cross-reaction data have been treated according to the Marcus relations and yield a self-exchange rate constant of $10\,M^{-1}\,s^{-1}$ at 25.0 °C and 1.0 M ionic strength for the perruthenate(VII)–ruthenate(VI) couple.[122] The oxidation of alkylthio and arylthioacetic acids ($RSCH_2CO_2H$) by $[RuO_4]^-$ has been studied. A reaction mechanism involving an expansion of the ruthenium coordination shell through incorporation of a hydroxide ion is proposed. Oxygen transfer is then initiated by action of a nonbonding pair of sulfur electrons with either a vacant ruthenium *d*-orbital or a Ru═O π^*-orbital.[38]

5.6.3.3.2 $[OsO_4]^-$

Reduction of $[OsO_4]$ with $(AsPh_4)I$ in CH_2Cl_2 produces $(AsPh_4)[OsO_4]$. The gray-green solid has a μ_{eff} of $1.37\mu_B$, the low value being attributed to spin–orbit coupling effects. The IR spectrum shows bands at 834 and 852 cm^{-1} assigned to $\nu_1(A_1)$ and $\nu_3(F_2)$, and the deformations ν_3 and ν_4 are at 240 cm^{-1}. A reversible OsO_4/OsO_4^- couple ($E^\circ = 0.1$ V vs. SCE) is observed in CH_2Cl_2.[123] The salt $(PPh_4)[OsO_4]$ is also known.[124] The $[OsO_4]^-$, like its ruthenium counterpart, functions as an oxidant for activated alcohols, converting them to aldehydes.[125]

5.6.3.3.3 Oxo fluoro species

The species $[Os(O)(F)_5]$ is well characterized. The ESR,[126] IR, and UV–vis spectra[89] of this complex have been measured. $[Os(O)_2(F)_3]$ is also known, but it is highly unstable. Matrix IR studies suggest that it has a D_{3h} structure.[127]

5.6.4 RUTHENIUM(VI) AND OSMIUM(VI)

The vast majority of ruthenium(VI) and osmium(VI) complexes are those stabilized by metal–ligand multiple bonds. These are mainly imido, nitrido, and oxo species.

5.6.4.1 Imido Complexes

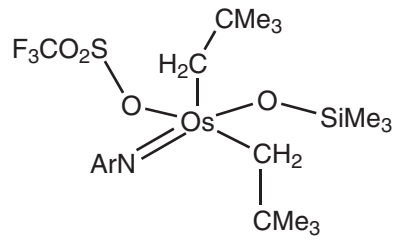
5.6.4.1.1 Mono imido complexes

Ruthenium(VI) imido complexes are rare in the literature. The reaction of $[Ru(N)(CH_2SiMe_3)_4]^-$ with $Me_3SiOSO_2CF_3$ leads to $[Ru(NSiMe_3)(CH_2SiMe_3)_4]$.[128] However, no elemental analysis can be obtained due to the extreme instability of the compound to air and moisture. The first cyclopentadienyl imido complex of osmium was prepared by alkylation of the nitrogen atom in $[(\eta^5\text{-}C_5H_5)Os(N)(CH_2SiMe_3)_2]$ by $CH_3OSO_3CF_3$ to give $[(\eta^5\text{-}C_5H_5)Os(NMe)(CH_2SiMe_3)_2](OSO_2CF_3)$, which was characterized by ^1H NMR spectroscopy ($\delta(NMe) = 2.8$ ppm).[129]

The complex $(PPh_4)[Os\{NC(CCl_3)NCCl(CCl_3)\}Cl_5]$ may be regarded as an imido complex of osmium(VI), made by the reaction of Os_2Cl_{10} with trichloroacetonitrile and has been characterized by X-ray structural studies.[130] The Os—N distance of 1.97 Å is slightly shorter than that expected for a single bond.

Reaction of [Os(N)(L)(Cl)] (L = 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridinato(2-)) with trifluoroacetic anhydride in the presence of a small amount of glacial acetic acid in dry CH_2Cl_2 gives the imido complex $[Os(L)(NCOCF_3)(O_2CCF_3)(Cl)]$ which has been characterized by IR spectroscopy ($\nu(Os{=}N) = 1197\,cm^{-1}$).[149] A similar trifluoroacetylimidomanganese(V) complex has been proposed as the active intermediate in imido transfer to alkenes.[14]

The reactions of $[Os(O)(NAr)(CH_2Bu^t)_2]$ with HCl, Me_3SiI, and $AlMe_3$ give $[Os(NAr)(CH_2Bu^t)_2(Cl)_2]$, $[Os(NAr)(CH_2Bu^t)_2(I)_2]$, and $[Os(NAr)_2(CH_2Bu^t)_2(Me)_2]$, respectively. $[Os(O)(NAr)(CH_2Bu^t)_2]$ reacts with Me_3SiX (X = Cl, OTf) to yield green crystalline $[Os(NAr)(CH_2Bu^t)_2(OSiMe_3)X]$. X-ray crystallography studies of $[Os(NAr)(CH_2Bu^t)_2(OSiMe_3)(OTf)]$ (**25**) show an approximate square pyramid with a neopentyl group in the apical position (d(Os=N) = 1.689 Å).[132]



(**25**)

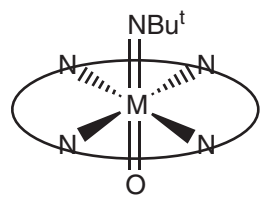
5.6.4.1.2 Oxo imido complexes

$[Os(O)(NAr)_3]$ reacts with alkenes $C_2H_2R_2$ to give $[Os(O)\{N(Ar)CHRCHRN(Ar)\}(NAr)]$ (**26**). An X-ray study of the complex made from ethene shows that it has a pseudo-tetrahedral geometry (Scheme 2).[17]

Complexes of the type $[Os(O)(NAr)(R)_2]$ (Ar = $C_6H_3Pr^i_2$-2,6; R = CH_2CMe_3, CH_2CMe_2Ph) are prepared via imido/oxo exchange reactions between $[Os(O)_2(R)_2]$ with 1 equivalent of $[Ta(NAr)(OBu^t)_3]$.[132]

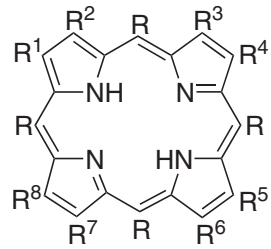
An osmium(VI) oxo imido complex, $[Os(O)(NBu^t)(mes)_2]$(mes = mesityl), has been isolated and has been discussed in reference 131.

The isolation of the first stable oxo-*t*-butylimido complexes of ruthenium(VI) and osmium(VI) porphyrins, $[M(O)(por)(NBu^t)]$ (**27**), by oxidative deprotonation of $[M(por)(Bu^tNH_2)_2]$ (por = TPP (*meso*-tetraphenylporphyrinato dianion)), 3,4,5-MeO-TPP (*meso*-tetrakis(3,4,5-trimethoxyphenyl)porphyrinato dianion), TTP (*meso*-tetrakis(p-tolyl)porphyrinato dianion), 4-Cl-TPP (*meso*-tetrakis(4-chlorophenyl)porphyrinato dianion), and 3,5-Cl-TPP (*meso*-tetrakis(3,5-dichlorophenyl)porphyrinato dianion) have been reported.[133,134] These complexes are diamagnetic and have been characterized by ^{1}H NMR and IR spectroscopy. $[Ru^{VI}(O)(por)(NBu^t)]$ can also be prepared by reacting $[Ru(O)_2(por)]$ with Bu^tNH_2.[135] It reacts rapidly with PPh_3 in solution to give $O{=}PPh_3$, $Ph_3P{=}NBu^t$, and $[Ru(por)(PPh_3)_2]$.[133] $[Os(O)(por)(NBu^t)]$ can also be prepared by air oxidation of $[Os(por)(H_2NBu^t)_2]$.[134] The X-ray crystal structure of (**27h**) has been



(**27**)

(**a**) M = Ru; N_4 = TPP
(**b**) M = Ru; N_4 = 3,4,5-MeO-TPP
(**c**) M = Ru; N_4 = TTP
(**d**) M = Ru; N_4 = 4-Cl-TPP
(**e**) M = Ru; N_4 = 3,5-Cl-TPP
(**f**) M = Os; N_4 = TPP
(**g**) M = Os; N_4 = 3,4,5-MeO-TPP
(**h**) M = Os; N_4 = TTP
(**i**) M = Os; N_4 = 4-Cl-TPP



H_2por: unspecified

H_2TPP: R = Ph, R^1-R^8 = H

H_2DPP: R = Ph, R^1-R^8 = Ph

H_2TTP: R = $C_6H_4CH_3$, R^1-R^8 = H

H_2TMP: R = 2,4,6-Me(C_6H_2), R^1-R^8 = H

$H_2$4-X-TPP: R = 4-XC_6H_4, R^1-R^8 = H

$H_2$2,6-Cl-TPP: R = 2,6-$Cl_2C_6H_3$, R^1-R^8 = H

$H_2$3,5-Cl-TPP: R = 3,5-$Cl_2C_6H_3$, R^1-R^8 = H

$H_2$2,4,6-MeO-TPP: R = 2,4,6-$(MeO)_3C_6H_2$, R^1-R^8 = H

$H_2$3,4,5-MeO-TPP: R = 3,4,5-$(MeO)_3C_6H_2$, R^1-R^8 = H

H_2OEP: R = H, R^1-R^8 = Et

Figure 1 Porphyrin abbreviations.

determined; the Os=O and Os=NBu^t distances are 1.772 Å and 1.759 Å, respectively.[134] Oxo arylimidoosmium(VI) complexes of the type [Os(O)(por)(NAr)] (Ar = 4-F-Ph, por = TPP, 3,4,5-MeO-TPP) have also been isolated by refluxing a solution of [Os^{IV}(por)(ArNH)$_2$] in aerated THF and Bu^{t}NH$_2$.[134] The various porphyrin structures are summarized in Figure 1.

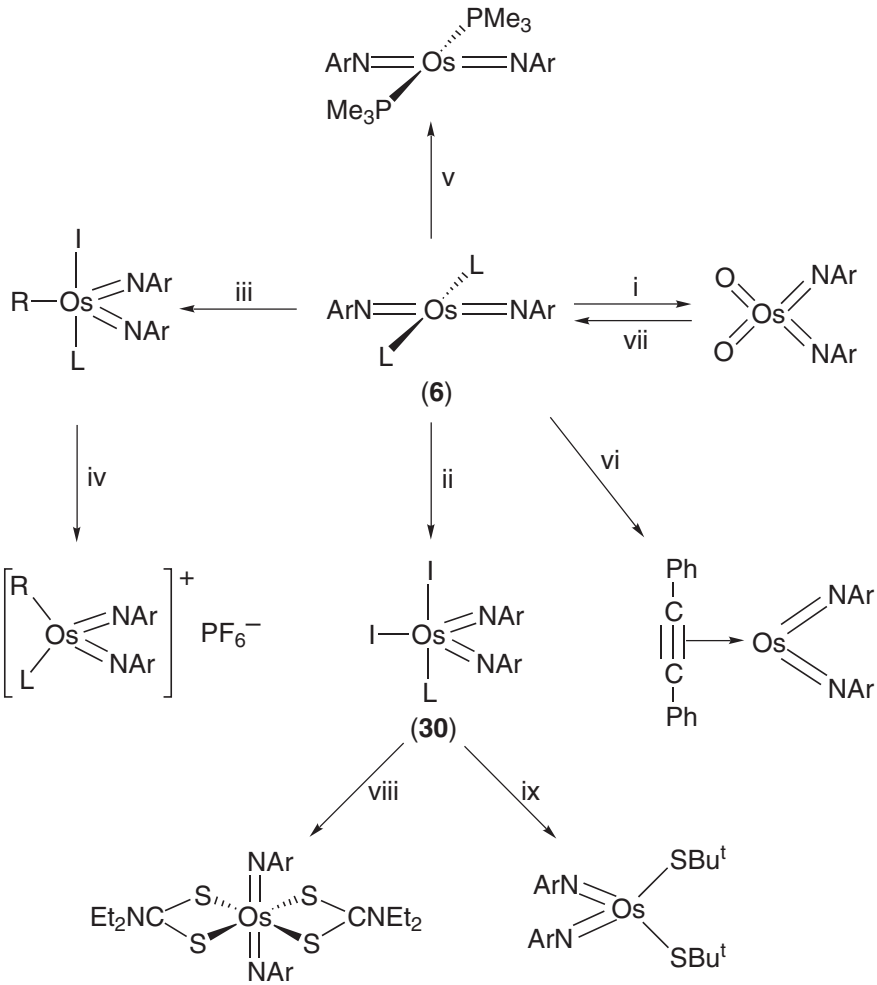
Reaction of [Os(NBu^t)$_4$] (**1**) with HOAc or pivalic acid in CH_2Cl_2 at low temperature gives the oxo imido osmium(VI) compounds [Os(O)(NBu^t)(O$_2$CMe)$_2$(NH$_2$Bu^t)] (**28**) and [Os(O)(NBu^t)-(O$_2$CBu^t)$_2$(NH$_2$Bu^t)$_2$] (**29**), respectively (Scheme 1).[97] The structure of (**29**) has been determined by X-ray crystallography (Os—N = 1.749 Å, Os—O = 1.761 Å). The shorter Os—N than Os—O distance reflects the greater π-donating capability of the organoimido function.[97]

5.6.4.1.3 Bis imido complexes

The imido/oxo exchange reaction between [Os(O)$_2$R$_2$] (R = CH$_2$Bu^t, CH$_2$CMe$_2$Ph) or [Os(O)$_2$(CH$_2$-SiMe$_3$)$_2$]$_n$ and 2 equivalents of [Ta(NAr)(OBu^t)$_3$] affords [Os(NAr)$_2$(R)$_2$] (Equation (7)).[132]

$$[Os(O)_2R_2] + 2[Ta(NAr)(OBu^t)_3] \longrightarrow [Os(NAr)_2R_2] + 2[Ta(O)(OBu^t)_3] \quad (7)$$

[Os(NAr)$_2$(I)$_2$(PMe$_2$Ph)] (**30**) is prepared by the reaction of *trans*-[Os(NAr)$_2$(PMe$_2$Ph)$_2$] (**6**) (Ar = $C_6H_3Pr^i_2$-2,6) with iodine followed by MeI (Scheme 4). X-ray crystallography studies of the complex reveal a trigonal bipyramidal structure; the average Os—N distance is 1.773 Å and the imido ligands are close to linear (Os—N—C = 168.2° and 171.2°). Replacement of iodides and phosphine by addition of K[S$_2$CNEt$_2$] gives *trans*-[Os(NAr)$_2$(S$_2$CNEt$_2$)$_2$]. Converting (**30**) to the acetato complex with AgOAc followed by the treatment of LiSBu^t gives [Os(NAr)$_2$-(SBu^t)$_2$].[17]



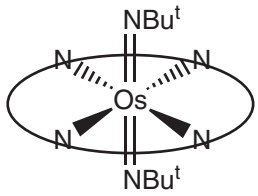
Ar = $C_6H_3Pr^i_2$-2,6, L = PMe_2Ph ; i, Me_3NO; ii, I_2, MeI; iii, RI, R = Me, Et; iv, R = Me, $AgPF_6$; v, PMe_3; vi, L = PPh_3, PhC ≡ CPh, CuCl; vii, PMe_2Ph; viii, KS_2CNEt_2; ix, AgOAc, $LiSBu^t$.

Scheme 4

Air oxidation of $[Os(por)(H_2NBu^t)_2]$ to give $[Os(O)(por)(NBu^t)]$ is described in Section 5.6.4.1.2. In the presence of H_2NBu^t, however, air oxidation of $[Os(por)(H_2NBu^t)_2]$ gives $[Os(por)(NBu^t)_2]$ (**31**). The mean Os═NBu^t distance in (**31c**) is 1.775 Å and the imido angles are 166.6° and 174.6°.[134]

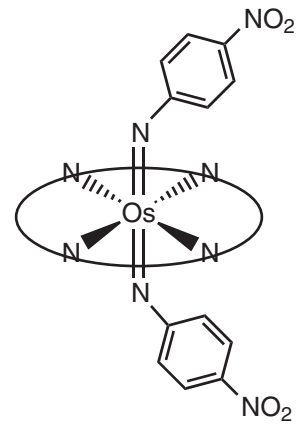
A bis(arylimido)osmium(VI) complex $[Os(TPP)(p\text{-}NC_6H_4NO_2)_2]$ (**32**) has been synthesized by reacting *p*-nitrophenyl azide with $[Os(TTP)]_2$.[136] The two axial ligands are nearly coplanar and the average imido Os—N distance is 1.821 Å, which is significantly shorter than a normal Os—N single bond, but is longer than other structurally characterized osmium organoimido bonds. The organoimido ligands are strongly bent with Os—N—C angles of 144.8° and 142.0°.[136]

Tosylimido complexes are key intermediates in the metal-catalyzed aziridination of alkenes by PhI═NTs.[137–144] The syntheses and reactivities of a series of bis(tosylimido)osmium(VI) and ruthenium(VI) porphyrin complexes are summarized in Scheme 5. Tosylimidoosmium(VI) complexes $[Os^{VI}(por)(NTs)_2]$ (**33**) (por = TPP, TTP, 4-Cl-TPP, 4-MeO-TPP; Ts = tosyl) are prepared by the treatment of $[Os^{II}(por)(CO)(MeOH)]$ with excess PhI═NTs in CH_2Cl_2.[145] The X-ray crystal study of (**33a**) reveals that the two tosylimido ligands are *anti* to each other, and the mean Os—N(Ts) distance and Os—N—S angle are 1.800 Å and 155.3°, respectively. (**33a**) is able to transfer its imido ligands to PPh_3 to yield Ph_3P═NTs and $[Os^{II}(TPP)(PPh_3)_2]$. Likewise



(**31**)

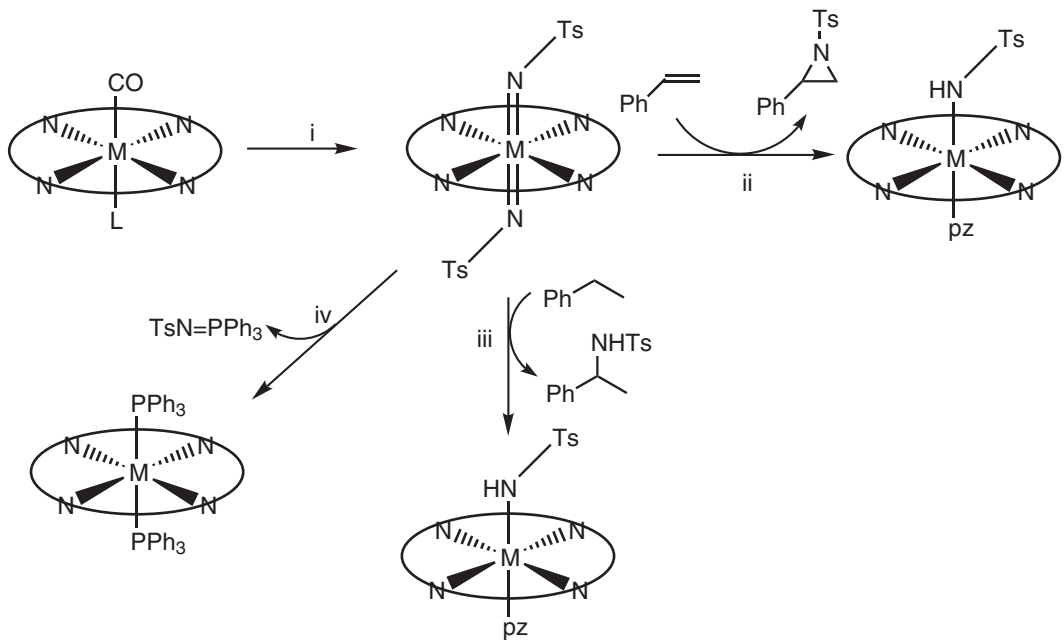
(**a**) N_4 = TPP
(**b**) N_4 = TTP
(**c**) N_4 = 4-Cl-TPP
(**d**) N_4 = 3,4,5-MeOTPF



(**32**)

N_4 = TTP

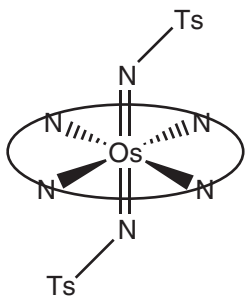
[Ru^{VI}-(por)$(NTs)_2$] (**34**) are prepared by the reaction of the corresponding [Ru^{II}(por)(CO)(MeOH)] (por = TPP, TTP, 4-Cl-TPP, 4-MeO-TPP, OEP) with PhI=NTs.[146,147] These ruthenium(VI) complexes are more reactive than the osmium analogs, they are able to transfer their imido groups to alkenes to yield aziridines, as well as to C—H bonds to afford amines.[146,147] The kinetics of the oxidation of a variety of alkenes by [Ru^{VI}(TPP)$(NTs)_2$] (**34a**) have been investigated. The second-order rate constants (k_2) range from 1.6×10^{-3} M^{-1} s^{-1} to 9.0×10^{-2} M^{-1} s^{-1} at 298 K. A carboradical intermediate is proposed based on the nonstereospecificity of the aziridination, a small slope of -1.7 V^{-1} in the plot of log k_2 vs. $E_{1/2}$ of the alkenes, and a small ρ^+ value of -1.1 in the Hammett plot for *para*-substituted styrenes.[146] The reactions between [Ru^{VI}(TPP)$(NTs)_2$] and alkylaromatics have k_2 in the range 3.3×10^{-4}–1.65×10^{-2} M^{-1} s^{-1}. A mechanism involving hydrogen atom abstraction by the imido group is proposed based on a large primary deuterium isotope effect ($k_H/k_D = 11$ for tosylamidation of ethylbenzene) and a linear Hammett correlation



N_4 = por, L = MeOH; i, M = Ru or Os, PhI=NTs; ii & iii, M= Ru, Hpz; iv, M = Os, PPh_3

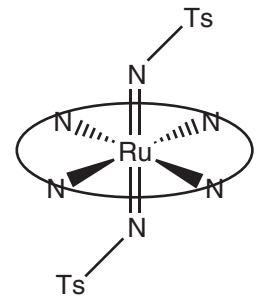
Scheme 5

between log k_R (k_R = relative rate) and TE (total effect parameters). A [Ru^{VI}(D_4-por*)$(NTs)_2$] complex bearing a D_4-symmetric chiral porphyrin ligand 5,10,15,20-tetrakis-{(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7, 8-octahydro-1,4:5,8-dimethanoanthracene-9-yl}porphyrin [H_2(D_4-por*)] (**35**) has also been isolated and it undergoes asymmetric aziridination of alkenes and amidation of C—H bonds with poor to moderate ee.[148] The bis(imido)ruthenium(VI) complex could be an active species in the [Ru^{II}(D_4-por*)(CO)(EtOH)]-catalyzed asymmetric aziridination of aromatic alkenes and asymmetric amidation of benzylic hydrocarbons by PhI=NTs and "$PhI(OAc)_2 + NH_2SO_2Me$."[148]



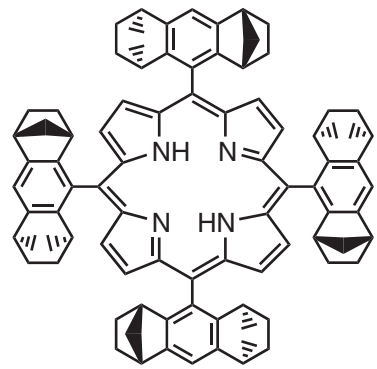
(**33**)

(**a**) N_4 = TPP
(**b**) N_4 = TTP
(**c**) N_4 = 4-Cl-TPP
(**d**) N_4 = 4-MeO-TPP



(**34**)

(**a**) N_4 = TPP
(**b**) N_4 = TTP
(**c**) N_4 = 4-Cl-TPP
(**d**) N_4 = 4-MeO-TPP
(**e**) N_4 = OEP



(**35**)

H_2D_4-Por*

Reaction of *cis*-[$Os^{VI}(O)_2(L)$] (L = 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridinato(2-)) with phenylisocyanate leads to the formation of [$Os^{VI}(L)(NPh)_2$], which has been characterized by IR spectroscopy (ν(Os=N(—Ph)) = 1,233 cm^{-1}).[149]

A highly reactive *cis*-bis(imido)ruthenium(VI) complex has been suggested in the oxidation of *cis*-[$Ru(bpy)_2(tmen)]^{2+}$ (tmen = 2,3-dimethylbutane-2,3-diamine) by Ce^{IV} in aqueous solutions.[150] This Ru^{VI} species decomposes rapidly in water to give [$Ru(bpy)_2$ $(ONCMe_2CMe_2NO)]^{2+}$.

5.6.4.1.4 Tris imido complexes

Reaction of [OsO_4] with 3 equivalents of ArNCO (Ar = $C_6H_3Pr^i_2$-2,6) for 20 h in refluxing heptane affords the unusual homoleptic tris(imido) complex [$Os(NAr)_3$] (**5**) (Scheme 2).[151] An X-ray study reveals a rare planar trigonal geometry. Two of the phenyl rings are oriented roughly perpendicular to the OsN_3 plane, while the third lies in the OsN_3 plane.[151] The two

crystallographically distinct imido ligands are linear (Os—N—C = 178.0° and 180°, *d*(Os═N) = 1.736 Å, 1.738 Å). (**5**) is stable to moist air in both the solid state and solution for days at 25 °C. It does not react at 25 °C with pyridine, THF, tertiary amines, PPh_3, HCl, or alkenes. However, it does react with PMe_2Ph in pentane to give $[Os(NAr)_2(PMe_2Ph)_2]$ (**6**) and $Me_2PhP{=}NAr$ in high yield. It also reacts with Me_3NO to give $[Os(O)(NAr)_3]$ (**3**), which readily transfers an oxygen atom to PPh_3 to give Ph_3PO and $[Os(NAr)_3]$. (**3**) also reacts with alkenes RCH═CHR to give [Os(O)(ArNCHRCHRNAr)(NAr)] (**26**).[17] The reactivities of $[Os(NAr)_3]$ are summarized in Scheme 2.

$[Os^{VI}(NAr)_3]$ (Ar = $C_6H_3Me_2$-2,6, $C_6H_3Pr^i_2$-2,6) can also be synthesized by reacting $[OsO_4]$ with neat $NHAr(SiMe_3)$ at 100–120 °C for 2–3 h.[15]

5.6.4.1.5 *Imido-bridged complexes*

The tetranuclear osmium(VI) oxo imido complex $[(Bu^tN)_2Os(\mu\text{-}NBu^t)_2Os(NBu^t)(\mu\text{-}O)]_2$ (**2**) is obtained as a side product in the reaction of $[OsO_4]$ with neat $NHBu^t(SiMe_3)$ (Scheme 1). Its structure can be described as a dimer of dimers with C_{2h} symmetry.[15]

The Os^{VI} dimer $[(Bu^tN)_2Os^{VI}(\mu\text{-}NBu^t)]_2$ (**23**) has been prepared by reduction of $[Os(NBu^t)_4]$ with PPh_3 or Na/Hg in THF (Scheme 1). The X-ray structure has been determined [Os···Os = 3.120 Å; Os—N(bridge) = 1.953 Å, 1.939 Å; Os—N(terminal) = 1.589 Å, 1.821 Å].[15] $[(Bu^tN)_2$-Os-$(\mu\text{-}NBu^t)_2Os(X)_2(NBu^t)]$ (X = Cl (**36**), I (**37**)) are also known (Scheme 1).

5.6.4.2 Nitrido Complexes

The bond lengths and the stretching frequencies of some M^{VI} nitrido complexes are summarized in Table 1.

5.6.4.2.1 *Carbon ligands*

(i) Cyano complexes

Reaction of $K[Os(O)_3(N)]$ with HCN in water has been known to produce $K[Os(N)(CN)_4(H_2O)]$.[152] Treatment of $(Ph_4As)[Os(N)Cl_4]$ with a slight excess of NaCN in THF/MeOH gives *trans*-$(Ph_4As)_2$ $[Os^{VI}(N)(CN)_4(OH)]$, isolated as a diamagnetic yellow crystalline solid. Recrystallization in methanol in the presence of NaCN affords $(Ph_4As)_2[Os^{VI}(N)(CN)_5]$ (**38**), the structure of which has been determined by X-ray crystallography (*d*(Os≡N) = 1.647 Å; Os—C(*trans*) = 2.353 Å).[153]

(ii) Alkyl complexes

There is a rich chemistry of alkyl nitrido complexes of ruthenium(VI) and osmium(VI), which has been well documented.[154]

5.6.4.2.2 *Nitrogen ligands*

Since the early 1980s rich thermal and photochemical redox chemistries of $Os^{VI}{\equiv}N$ species containing nonlabile oxidation-resistant nitrogen donor ligands have emerged. However, there are only a few examples of ruthenium(VI) nitrido complexes of this type, and their redox chemistry is largely unexplored.

(i) Syntheses

Oxidation of $[Os(NH_3)_5(Cl)]Cl_2$ with an excess of Ce^{IV} in water followed by the addition of 6 M HCl and MeOH affords $[Os^{VI}(N)(NH_3)_4]Cl_3$ as a bright yellow solid (ν (Os≡N) = 1,090 cm^{-1}).[155] Dissolving the chloride salt in neat CF_3SO_3H followed by the addition of ether produces the light

Table 1 Selected metal–nitrido bond distances and stretching frequencies for ruthenium and osmium complexes.

Complex	$d(M{\equiv}N)$ (Å)	$\nu(M{\equiv}N)$ (cm^{-1})	*References*
$[Ru(N)Cl_4](AsPh_4)$	1.570	1,092	*CCC* (1987)
$[Ru^{VI}(N)(Me)_3(SSiMe_3)](PPh_4)$		1,074	189
$[Ru^{VI}(N)(Me)_3(SH)](PPh_4)$	1.595(6)	1,073	189
$[Ru^{VI}(N)(Me)_4](PPh_4)$	1.58(1)	1,077	128
$[Ru^{VI}(N)\{Bu^tNC(O)NBu^t\}(Cl)_2](PPh_4)$	1.588(6)	1,067	159
$[Ru^{VI}(N)(NHC(O)CH_2CH_2S)_2](PPh_4)$	1.595(8)		202
$[Ru^{VI}(N)(NHC(O)CH_2CH_2S)_2](NBu^n{}_4)$		1,094	202
$[Ru^{VI}(N)(bdt)_2](NBu^n{}_4)$	1.613(5)	1,024	193
$[Ru^{VI}(N)(HBA\text{-}B)](NBu^n{}_4)$	1.594(4)		203
$[Ru^{VI}(N)(HBA\text{-}DCB)](NBu^n{}_4)$	1.609(6)		203
$[Ru^{VI}(N)(L)]\{Na(dme)_3\}$[a]	1.569(6)		209
$[Os^{VI}(N)(Cl)_5]K_2$	1.614(13)	1,073	*CCC* (1987)
$[Os^{VI}(N)(Cl)_4(H_2O)]K$	1.74(7)		*CCC* (1987)
$[Os^{VI}(N)(Cl)_4](AsPh_4)$	1.604(10)	1,123	*CCC* (1987)
$[Os^{VI}(N)(Br)_4](AsPh_4)$	1.583(15)	1,119	*CCC* (1987)
$[Os^{VI}(N)(I)_4](AsPh_4)$	1.626(17)		*CCC* (1987)
$[Os^{VI}(N)(CN)_5](AsPh_4)_2$	1.647(7)	1,050	153
trans-$[Os^{VI}(N)(CN)_4(OH)](AsPh_4)_2$		1,050	153
$[Os^{VI}(N)(CH_2SiMe_3)_4](NBu^n{}_4)$	1.631(8)	1,100	601,602
$[Os^{VI}(^{15}N)(CH_2SiMe_3)_4](NBu^n{}_4)$		1,073	602
$[Os^{VI}(N)(NH_3)_4](CF_3SO_3)_3$		1,090	155
$[Os(N)\{Bu^tNC(O)NBu^t\}Cl_2](PPh_4)$	1.629(7)	1,104	159
$[Os^{VI}(N)(tmen\text{-}H)(tmen)_2](CF_3SO_3)_2$	1.68(3)		161
$[Os^{VI}(N)(bpy)(Cl)_3]$		1,086	603
$[Os^{VI}(^{15}N)(bpy)(Cl)_3]$		1,051	163
$[Os^{VI}(N)(dmbpy)(Cl)_3]$	1.68(1)	1,084	162
$[Os^{VI}(N)(dpphen)(Cl)_3]$		1,081	162
$[Os^{VI}(N)(bpy)(Cl)_2(H_2O)](CF_3SO_3)$	1.630(7)		162
trans-$[Os^{VI}(N)(tpy)(Cl)_2]Cl$	1.663(5)		163
$[Os^{VI}(N)(tpy)(Cl)(CF_3SO_3)](CF_3SO_3)$	1.629(8)		162
$[Os^{VI}(N)(Tp)(Ph)_2]$	1.637(4)		167
$[Os^{VI}(N)(Tp^*)(Ph)_2]$	1.648(3)	1,094	604
$[Os^{VI}(N)(SCH_2Ph)_4](PPh_4)$		1,069	190a
$[Os^{VI}(N)(mnt)_2](NBu^n{}_4)$	1.639(8)	1,074	192
$[Os^{VI}(N)(bdt)_2](NBu^n{}_4)$	1.64(1)	1,063	196
$[Os^{VI}(N)(L_{OEt})(Cl)_2]$	1.58(1)		188
$[Os^{VI}(N)(HBA\text{-}B)](NBu^n{}_4)$	1.618(7)		203
$[Os^{VI}(N)(HBA\text{-}B)](Ph_3PNH_2)$	1.64(1)		204
$[Os^{VI}(N)(salophen)(MeOH)](ClO_4)$	1.651(7)		205
$[Os^{VI}(N)(salophen)(Cl)]$		1,072	205
$[Os^{VI}(^{15}N)(salophen)(Cl)]$		1,037	205
$[Os^{VI}(N)(5,5'\text{-}Cl_2salophen)(MeOH)](ClO_4)$	1.66(1)		205
$[Os^{VI}(N)(salen)(Cl)]$		1,094	205
$[Os^{VI}(N)\{N(SPPh_2)\}_2(Cl)]$	1.64(1)	1,064	198
$[Os^{VI}(N)\{N(SPPh_2)\}_2](BF_4)$	1.646(5)		198
$[Os^{VI}(N)\{N(SPPh_2)\}_2(OCOCF_3)]$	1.643(5)	1,082	198
$[Os^{VI}(N)\{N(SePPh_2)\}_2(Cl)]$		1,069	303

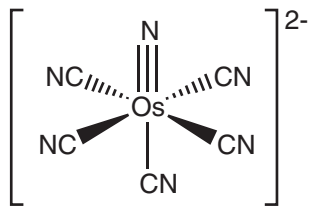
[a] H_4L = *meso*-octamethylporphyrinogen; dme = 1,2-dimethoxyethane.

yellow $[Os^{VI}(N)(NH_3)_4](CF_3SO_3)_3$. Both complexes are luminescent in the solid state and in fluid solutions (see Section 5.6.4.2.2(iii)).

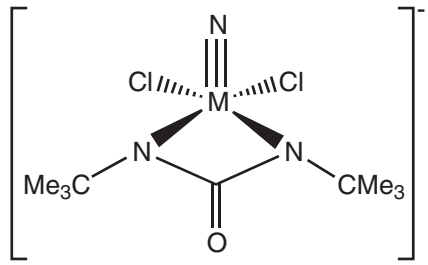
A series of complexes of the type $[Os^{VI}(N)(L)_2(Cl)_3]$ (L = py, 3-Mepy, 4-Mepy, 4-Etpy, 4-Bu^tpy) have been prepared by the reaction of $[Os(N)Cl_4]^-$ with L.[156–158]

$[M(N)\{Bu^tNC(O)NBu^t\}(Cl)_2]^-$ (M = Ru (**39a**) or Os (**39b**)) are prepared by the interaction of $[Ru(O)_2(Cl)_3]^-$, $[Ru(O)_2(Cl)_4]^{2-}$, or $[Os(O)_2(Cl)_4]^{2-}$ with excess *t*-butylisocyanate in acetonitrile.[159] X-ray diffraction studies show that the anions have distorted square pyramidal geometry with the

nitrido group in axial position (d(Ru≡N) = 1.588 Å, Ru—N(Bu^t) = 1.973 Å, 1.974 Å; d(Os≡N) = 1.629 Å, Os—N(Bu^t) = 1.980 Å, 1.977 Å) The nitrido ligand has been shown to arise from C—N bond cleavage of a *t*-butylimido intermediate accompanied by cycloelimination of $Me_2C{=}CH_2$ and HCl.



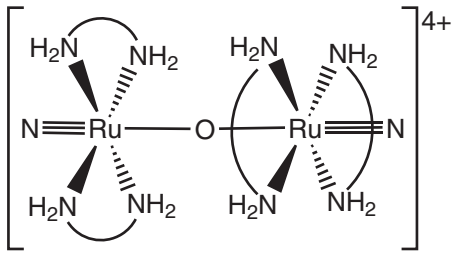
(**38**)



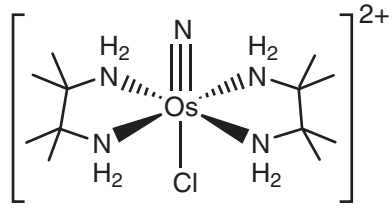
(**39**)

(**a**) M = Ru
(**b**) M = Os

A novel binuclear cationic ruthenium(VI) nitrido complex, $[\{Ru^{VI}(L)_2(N)\}_2(\mu\text{-}O)]Cl_4$ (**40**) (L = 2,5-dimethyl-2,5-hexanediamine), has been prepared by treatment of $(NBu_4)[Ru(N)Cl_4]$ with L in acetone. The X-ray crystal structure reveals a linear N≡Ru—O—Ru≡N unit. The measured bond lengths of Ru—N and Ru—O are 1.66 Å and 1.9896 Å, respectively.[160] The long Ru—N distance, compared with the Ru—N distance of 1.570 Å found in $[Ru(N)Cl_4]^-$, could be attributed to the competitive π-bonding of the Ru ion with the N^{3-} and $\mu\text{-}O^{2-}$ ligands.



(**40**)

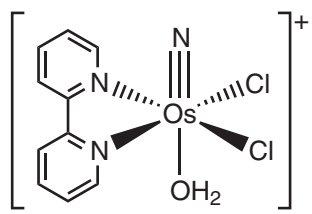


(**41**)

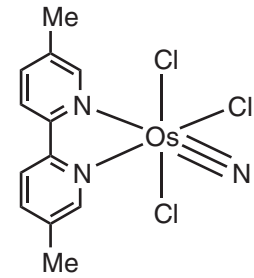
$H_2N\text{^}NH_2$ = 2,5-dimethyl-2,5-hexanediamine

Reaction of $[Os(N)Cl_4]^-$ with tmen in MeOH produces $[Os(N)(tmen)_2Cl]Cl_2{\cdot}2H_2O$ (**41**).[161] Addition of CF_3SO_3H under an inert atmosphere gives $[Os(N)(tmen)_2](CF_3SO_3)_3$ which on prolonged standing in MeCN becomes $[Os(N)(tmen\text{-}H)(tmen)_2](CF_3SO_3)_2$. The long osmium–nitrido distance of 1.797 Å in (**41**) may be due to problems of the disordered nitrido and chloro ligands. In 0.1 M CF_3CO_2H, $[Os(N)(tmen)_2](CF_3SO_3)_3$ shows a $3H^+/3e^-$ reduction wave at −0.34 V vs. SCE which is assigned to the reduction of $Os^{VI}{\equiv}N$ to $Os^{III}{-}NH_3$.[161]

A series of luminescent complexes $[Os^{VI}(N)(R\text{-}bpy)(Cl)_3]$ and $[Os^{VI}(N)(R\text{-}phen)(Cl)_3]$ (R-bpy = bpy, dmbpy (5,5′-dimethyl-2,2′-bipyridine), R-phen = phen, 5-Clphen (5-chlorophenanthroline), dpphen (4,7-diphenyl-1,10-phenanthroline)) have been prepared by reaction of $[Os(N)(Cl)_4]^-$ with the appropriate ligands in MeCN.[162] Treatment of $[Os(N)(bpy)(Cl)_3]$ with neat HOTf gives $[Os(N)(bpy)(Cl)_2(H_2O)](CF_3SO_3)$ (**42**). $[Os(N)(dmbpy)(Cl)_3]$ (**43**) adopts a distorted octahedral geometry with the three chlorides in a meridonal configuration (d(Os≡N) = 1.68 Å). The atoms *cis* to the nitrido ligand bend away from it with N(bpy)—Os—Cl and Cl—Os—Cl angles of 165.4° and 164.1°, respectively. By comparing with the structure of $[Os(N)(dmbpy)(Cl)_3]$ it seems that an isomerization has occurred during the conversion of $[Os(N)(bpy)(Cl)_3]$ to $[Os(N)(bpy)(Cl)_2(H_2O)](CF_3SO_3)$ (d(Os≡N) = 1.630 Å). These complexes have long-lived and emissive $^3[d_{xy},d_\pi]$ excited states in the solid state and in fluid solution at room temperature.



(**42**)



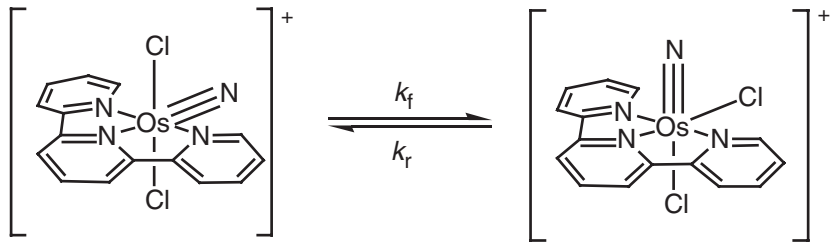
(**43**)

The cationic nitrido complexes $[Os^{VI}(N)(tpy)(X)_2]^+$ (tpy = 2,2′:6′,2″-terpyridine; X = Cl, Br) are prepared by the reaction of $[Os(N)(X)_4]^-$ with tpy in acetone or MeCN.[162,163] The complex has a severely distorted octahedral geometry, the *trans* angles being 150.4°, 165.0°, and 179.6°. The two chlorides are *trans* and bend away from the nitrido ligand. The Os≡N distance is 1.663 Å.[163]

This complex can be reduced reversibly in aqueous solution either electrochemically or chemically to give $[Os^{II}(tpy)(Cl)_2(NH_3)]$ (Equation (8)).

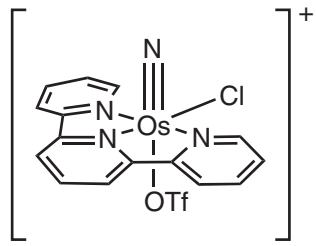
$$[Os^{VI}(tpy)(N)(Cl)_2]^+ \underset{-\,4e^-/3H^+}{\overset{4e^-/3H^+}{\rightleftharpoons}} [Os^{II}(tpy)(NH_3)(Cl)_2] \tag{8}$$

An equilibrium occurs between *trans*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$ (**44**) and *cis*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$ (**45**) in methanolic solution containing chloride with $K(20\,^\circ C) = 4.8$, $\Delta H^\circ = 22(2)$ kJ mol^{-1}, and $\Delta S^\circ = 88(6)$ J mol^{-1} (Equation (9)). The approach to equilibrium follows first-order kinetics with $k_f(20\,^\circ C) = 1.1 \times 10^{-4}$ s^{-1}, $k_r(20\,^\circ C) = 2.3 \times 10^{-5}$ s^{-1}, $\Delta H_f^{\ddagger} = 78(8)$ kJ mol^{-1}, $\Delta S_f^{\ddagger} = 79(10)$ J mol^{-1}, $\Delta H_r^{\ddagger} = 56(7)$ kJ mol^{-1}, and $\Delta S_r^{\ddagger} = -9(6)$ J mol^{-1}. In the absence of chloride a rapid solvolysis occurs to give a mixture of *trans*- or *cis*-$[Os(N)(tpy)(Cl)(MeOH)]^{2+}$.[164]

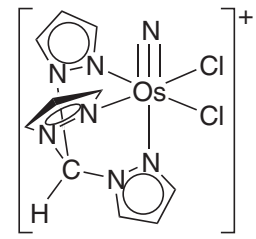


(**44**) (**45**) (9)

Dissolving (**44**) in neat HOTf followed by precipitation with ether converts the complex to $[Os(N)(tpy)(Cl)(OTf)]^+$ (**46**). The X-ray crystal structure shows that isomerization has occurred.[162]



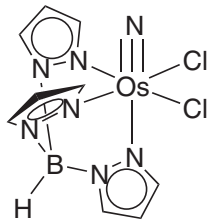
(**46**)



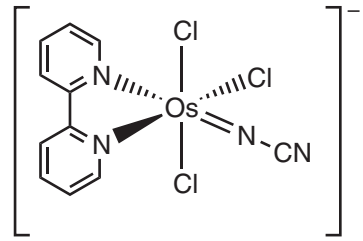
(**47**)

Nitridoosmium(VI) complexes containing facially coordinated polypyrazolyl ligands have been reported. $[Os^{VI}(N)(tpm)(Cl)_2]^+$ (**47**) (tpm = tris(1-pyrazolyl)methane) is prepared in a manner

similar to that of $[Os^{VI}(N)(tpy)(Cl)_2]^+$.[165] $[Os^{VI}(N)(Tp)(Cl)_2]$ (**48**) ($Tp^- =$ hydridotris (1-pyrazolyl)-borate anion) is prepared by the reaction of $[Os(N)(O)_3]^-$ with KTp in aqueous ethanolic HCl.[166,167] The crystal structure of (**47**)BF_4 and (**48**) have been determined.[165] Due to N/Cl disorder in the structures, precise bond lengths cannot not obtained. $[Os^{VI}(N)(Tp)(Ph)_2]$ and $[Os^{VI}(N)(Tp)(Ph)(Cl)]$ have also been obtained via the routes shown in Equations (10) and (11).[167]



(**48**)



(**49**)

$$(NBu^n_4)[Os(N)(Ph)_4] \xrightarrow[\text{acetone}]{\text{1. HI(aq)}\ \text{2. KTp}} [Os(N)(Tp)(Ph)_2] \quad (10)$$

$$[Os(N)(Tp)Ph_2] \xrightarrow[HCl\ CH_2Cl_2/Et_2O]{\Delta} [Os(N)(Tp)PhCl] \quad (11)$$

$[Os^{IV}(Tp)(OTf)(Cl)_2]$ can abstract the nitrogen atom from MeCN upon heating to give osmium nitrido compound $[Os^{VI}(N)(Tp)(Cl)_2]$[168a] (see M(IV) Section 5.6.6.4).

$[Os^{VI}(N)(tpm)(Cl)_2]^+$ and $[Os^{VI}(N)(Tp)(Cl)_2]$ can be reversibly reduced electrochemically or chemically in acidic solutions to give the corresponding ammine complexes of Os^{II}.[165]

Cyclic voltammetry of [Os(N)(Tp)(X)(Y)] (X, Y = Ph, Cl) shows a quasi-reversible or irreversible oxidation wave and an irreversible reduction wave. The potentials of the $Os^{VII/VI}$ couples have been compared with isoelectronic oxo and imido complexes of rhenium. The potentials follow the order Os(N) > Re(O) > Re(Ntolyl). The potentials also correlate with the sum of the Hammett σ values for X, Y. The oxidation potential decreases from 2.05 V for $[Os(N)(Tp)(Cl)_2]$ to 1.60 V for [Os(N)(Tp)(Cl)(Ph)] to 1.36 V vs. $Ag/AgNO_3$ for $[Os(N)(Tp)(Ph)_2]$.[168b]

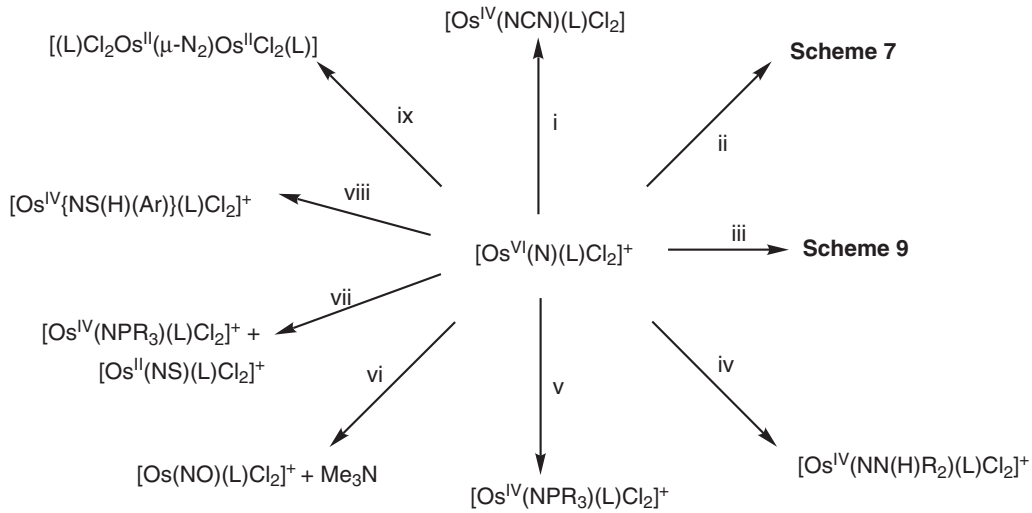
$[Os(N)(Tp)(OAc)_2]$ is formed upon treating $[Os(N)(Tp)(Cl)_2]$ with AgOAc.[169] Treatment of $[Os(N)(Tp)(OAc)_2]$ with protic acids give $[Os(N)(Tp)(X)_2]$ (X = trifluoroacetate, trichloroacetate, tribromoacetate, bromide, 1/2 oxalate or nitrate). Cyclic voltammetry of these complexes shows irreversible reductions of Os^{VI} to Os^V, varying over a range of 0.63 V. The Os≡N stretching frequencies occur in a narrow range (1059–1087 cm^{-1}).

(ii) Reactivities

The nitrido ligand can show nucleophilic and/or electrophilic behavior, depending on the nature of the ancillary ligands.[4] With strongly electron donating alkyl ligands, osmium(VI) nitrido complexes are nucleophilic. For example, $[Os(N)R_4]^-$ undergoes alkylation by MeI to give $[Os(NMe)R_4]$.[171] $BF_3{\cdot}Et_2O$ can be added to $[(Cp)Os(N)R_2]$ to form $[(Cp)Os(NBF_3)R_2]$ ($R = CH_2SiMe_3$).[129]

Neutral or cationic osmium(VI) nitrido complexes containing nitrogen ligands, including *cis*- and *trans*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$, $[Os^{VI}(N)(tpm)(Cl)_2]^+$, $[Os^{VI}(N)(Tp)(Cl)_2]$, and $[Os^{VI}(N)(bpy)(Cl)_3]$, are electrophilic. In general they are unreactive toward the electrophiles MeOTf, $[CF_3C(O)]_2O$, $BF_3{\cdot}Et_2O$, and $[Ph_3C](BF_4)$. However, they undergo a variety of redox reactions that are initiated by nucleophilic attack at the nitrido ligand to produce N—C, N—N, N—P, and N—E (E = O, S, Se) bonds. Many of these reactions are unprecedented, and the resulting

osmium(IV) or osmium(V) complexes can further react with various substrates to generate osmium(II) or osmium(III) complexes via atom/group transfer reactions, which may provide general routes for the synthesis of heteroatom compounds (Scheme 6; see Section 5.6.6.4). Kinetic data for the nitrogen atom transfer reactions by osmium(VI) nitrido complexes are summarized in Table 2.



i) L = tpy, CN^-; ii) alkenes; iii) N_3^-; iv) L= tpy/ tpm, HNR_2 (R = Et, 1/2$(CH_2)_4O$, 1/2$(CH_2)_4CH_2$); v) L = tpy, PR_3; vi) L = tpy, Me_3NO; vii) L = tpy/tpm, $SPPh_3$; viii) L = tpy, ArSH (Ar = 3,5-$Me_2C_6H_3$); ix) L = tpy, e^-.

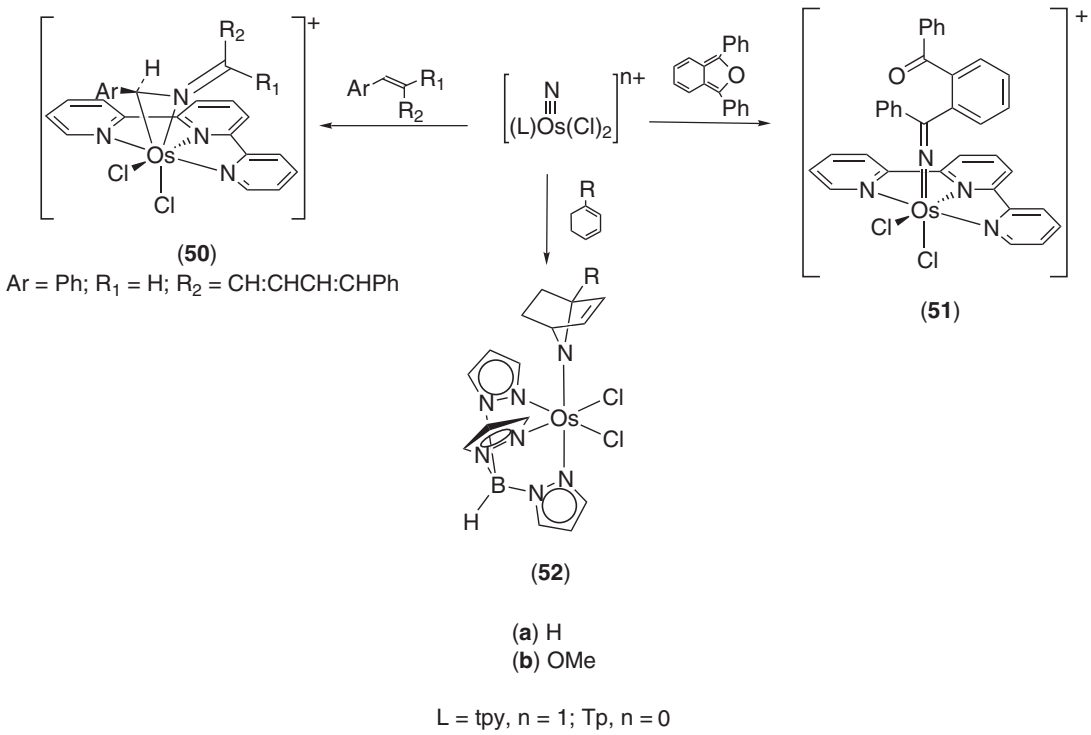
Scheme 6

Table 2 Representative kinetic data for the nitrogen atom transfer reactions by osmium(VI) nitrido complexes.

Complex	*k at 298 K*[a] (M^{-1} s^{-1})[a]	*References*
Reaction: $[Os^{VI}(N)] + PPh_3 \rightarrow [Os^{IV}(NPPh_3)]$		
$[Os(N)(salophen)(MeOH)]^+$	$(2.53 \pm 0.11) \times 10^4$ (MeCN)	205
$[Os(N)(5,5'\text{-}Cl_2salophen)(MeOH)]^+$	$(1.05 \pm 0.02) \times 10^5$ (MeCN)	205
$[Os(N)(5,5'\text{-}Me_2salophen)(MeOH)]^+$	$(1.16 \pm 0.02) \times 10^4$ (MeCN)	205
$[Os(N)(5,5'\text{-}(MeO)_2salophen)(MeOH)]^+$	$(1.51 \pm 0.08) \times 10^4$ (MeCN)	205
trans-$[Os(N)(tpy)(Cl)_2]^+$	$(1.36 \pm 0.08) \times 10^4$ (MeCN)	379,455
Reaction: $[Os^{VI}(N)] + SPPh_3 \rightarrow 1/2[Os^{II}(NS)] + 1/2[Os^{IV}(NPPh_3)]$		
trans-$[Os(N)(tpy)(Cl)_2]^+$	$(2.46 \pm 0.06) \times 10^1$ (MeCN)	605
cis-$[Os(N)(tpy)(Cl)_2]^+$	$(8.4 \pm 0.9) \times 10^{-1}$ (MeCN)	605
Reaction: $[Os^{VI}(N)] + CN^- \rightarrow [Os^{IV}(NCN)]$		
$[Os(N)(bpy)(Cl)_3]$	$(8.44 \pm 0.02) \times 10^1$ (295 K, MeCN)	606
Reaction: $[Os^{VI}(N)] + NO \rightarrow [Os^{II}(NO)] + N_2O$		
$[Os(N)(Tp)(Cl)_2]$	$\sim 3 \times 10^{-4}$ (294 K, CD_2Cl_2)	182
Reaction: $2[Os^{VI}(N)] + 2HN(CH_2)_4O \rightarrow [Os^{V}(NN(CH_2)_4O)] + 1/2[Os^{II}(\mu\text{-}N_2)Os^{II}] + H_2N(CH_2)_4O^+$		
trans-$[Os(N)(tpy)(Cl)_2]^+$	$(5.81 \pm 0.12) \times 10^1$ [b] (MeCN)	178
$[Os(N)(tpm)(Cl)_2]^+$	$(2.683 \pm 0.04) \times 10^2$ [b] (MeCN)	178
Reaction: $[Os^{VI}(N)] + 3,5\text{-}Me_2C_6H_3SH \rightarrow [Os^{IV}(NSAr)] + H^+$		
trans-$[Os(N)(tpy)(Cl)_2]^+$	$(3.60 \pm 0.08) \times 10^{-2}$ (MeCN)	446
cis-$[Os(N)(tpy)(Cl)_2]^+$	(3.21 ± 0.06) (MeCN)	446

[a] Unless specified. [b] Units = M^{-2} s^{-1}.

(a) Reaction with CN^-. $[Os^{VI}(N)(bpy)(Cl)_3]$ reacts readily with CN^- to generate a novel osmium(IV) cyanoimido complex, $[Os^{IV}(bpy)(Cl)_3(NCN)]^-$ (**49**), which is described in Section 5.6.6.4.1. The same reaction occurs with $[Os(N)(tpy)(Cl)_2]^+$.[606]



Scheme 7

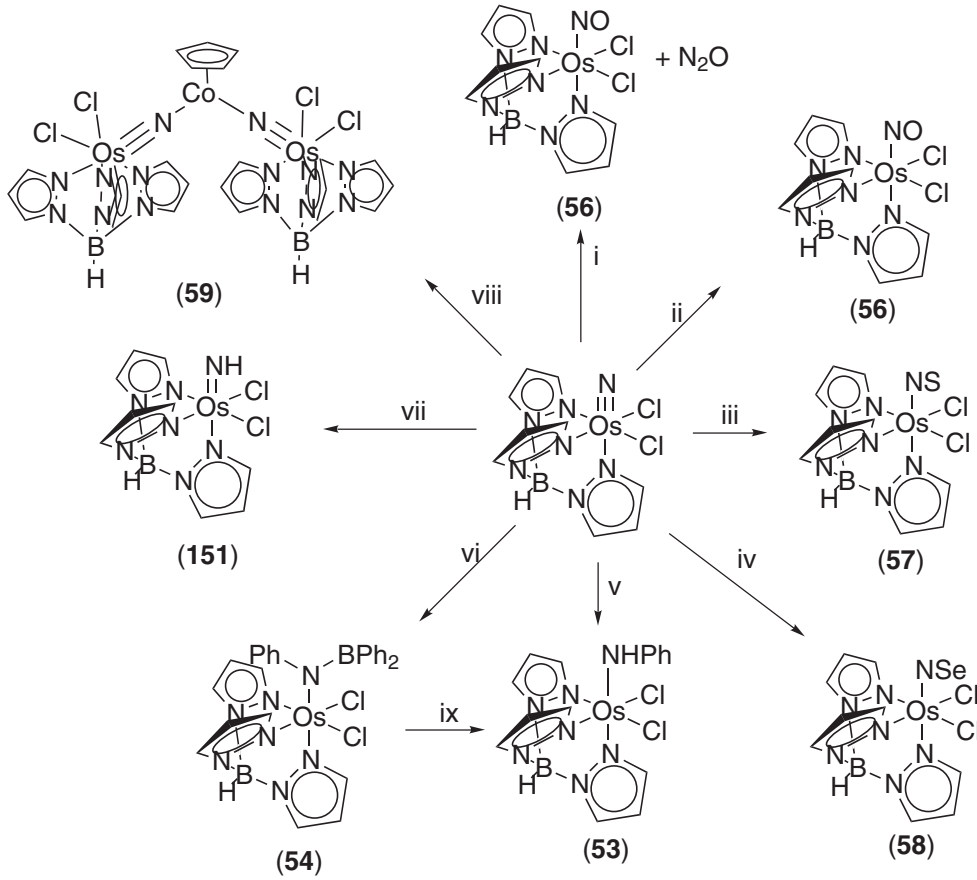
(b) Reaction with alkenes (Scheme 7). *cis*- and *trans*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$ react with aryl substituted alkenes in MeCN to form η^2-azaallenium complexes.[172] The alkene C═C double bond is completely ruptured, forming two new C—N bonds and a new Os—C bond. The structure of *cis*-$[(tpy)Os(1,2\text{-}\eta^2\text{-}PhCH{=}N{=}CHCH{=}CHCH{=}CHPh)(Cl)_2]^+$ (**50**) has been determined (Os—N = 2.006 Å, Os—C = 2.182 Å, *d*(C═N) = 1.293 Å). The product may be regarded as an osmium(II) azaallenium complex or an osmium(IV) azametallocyclopropane.

cis- and *trans*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$ also react with the electron-rich alkene 1,3-diphenylisobenzofuran to form azavinylidene complexes (**51**).[173]

The azavinylidene moieties are linear (175.5° and 168.2° for the *trans* and *cis* isomers, respectively) and have short Os═N (1.812 Å and 1.806 Å) and C═N bonds (1.273 Å and 1.264 Å). The formation of azavinylidene is presumably initiated by nucleophilic attack of isobenzofuran at the nitrido ligand.[173]

The nitrido complexes $[Os^{VI}(N)(Tp)(Cl)_2]$, $[Os^{VI}(N)(tpm)(Cl)_2]^+$, and *cis*- and *trans*-$[Os(N)(tpy)(Cl)_2]^+$ undergo 1,4-addition reactions to 1,3-cyclohexadienes to generate bicyclic osmium(IV) amido complexes (**52**) (Section 5.6.6.1).[425]

(c) Reaction with Grignard reagents and boranes. Treatment of $[Os^{VI}(N)(Tp)(Cl)_2]$ with PhMgBr followed by H_2O produces an osmium(IV) anilido complex $[Os^{IV}(Tp)(NHPh)(Cl)_2]$ (**53**).[166,167] (Section 5.6.6.1) With 2 and 3 equivalents of PhMgCl, $[Os^{IV}(Tp)(NHPh)(Ph)(Cl)]$ and $[Os^{IV}(Tp)(NHPh)(Ph)_2]$ are produced, respectively. A similar reaction occurs with tolylmagnesium bromide or *p*-toluidine to give $[OsTp(NHTol)(Cl)_2]$.[167] These reactions probably occur by direct attack of carbanions on the nitrido ligand. $[Os^{VI}(N)(Tp)(Cl)_2]$ also reacts with BPh_3 to give the borylanilido compound (**54**) which hydrolyzes rapidly in H_2O to give the anilido compound (**53**) (Scheme 8).[174] The Lewis acid–base interaction between the two reactants is probably not important but rather the driving force comes from nucleophilic attack by the phenyl group of the borane at the nitrido ligand.

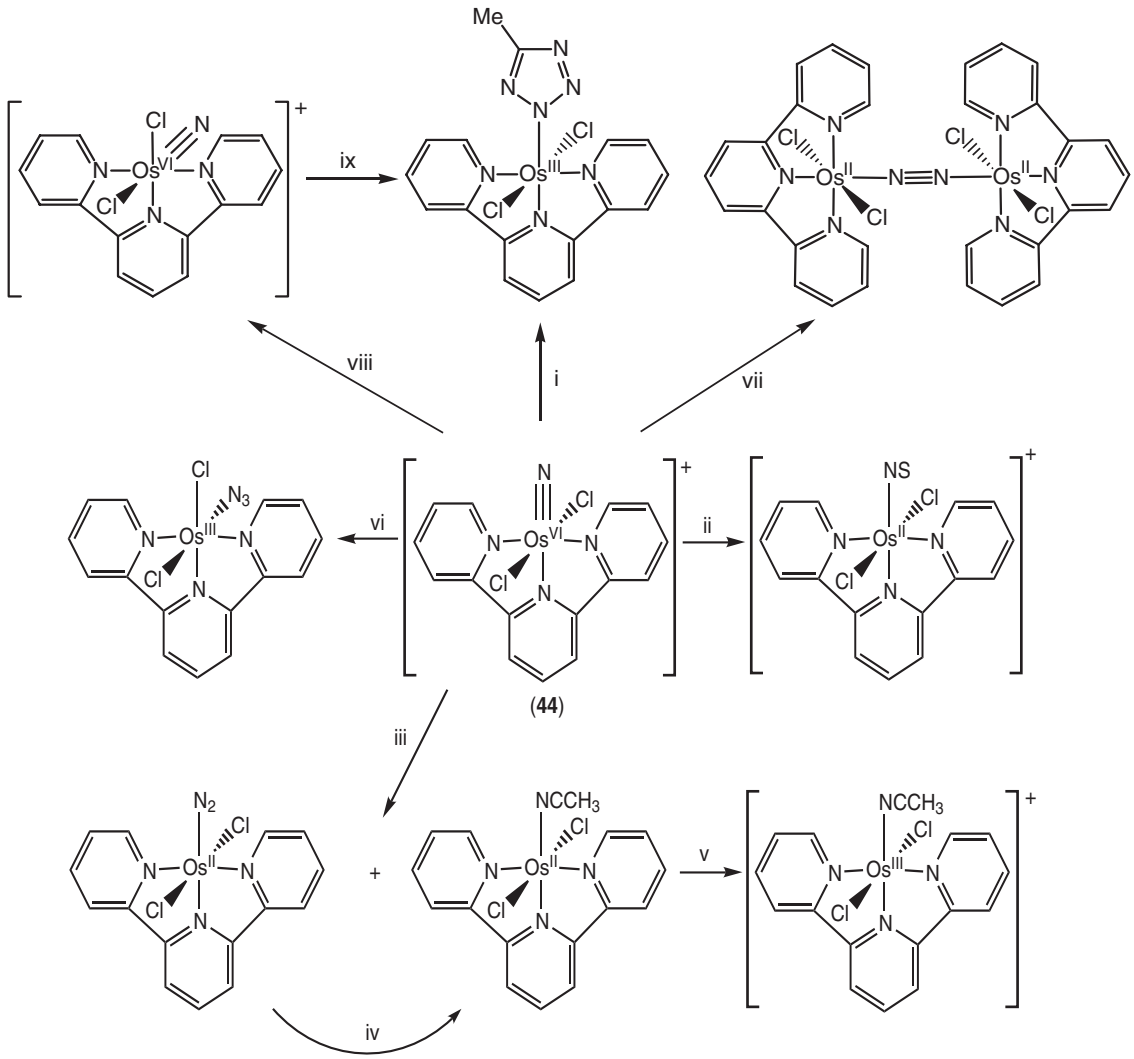


i, NO; ii, Me_3NO; iii, S_8 or ethylene sulfoxide; iv, Se; v, PhMgBr, H_2O; vi, BPh_3; vii, H^+/e viii, $[CpCo(C_5H_5C_6F_5)]$; ix, H_2O.

Scheme 8

(d) Reaction with N_3^-. The nitrido ligand in these complexes is readily attacked by N_3^-; the nature of the products, however, depends highly on the solvent and the nitrido species. $[Os^{VI}(N)(bpy)(Cl)_3]$ reacts with N_3^- to give the stable osmium(IV) azidoimido complex $[Os^{IV}(NN_3)(bpy)(Cl)_3]^-$ (see also Section 5.6.6.4.3). The reactions of *trans*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$ (**44**) and $[Os^{VI}(N)(tpm)(Cl)_2]^+$ with N_3^- do not give an azidoimido osmium(IV) complex (although it may be an intermediate), but produce a variety of products depending on the solvent and other reaction conditions.[175,176] In nonpolar solvents such as acetone or CH_2Cl_2, electron transfer occurs from N_3^- to (**44**) to give $[(tpy)(Cl)_2Os^{II}(\mu\text{-}N_2)Os^{II}(Cl)_2(tpy)]$ in acetone and CH_2Cl_2. In CH_3CN, *trans*-$[Os^{II}(N_2)(tpy)(Cl)_2]$ is produced which undergoes solvolysis to give *trans*-$[Os^{II}(tpy)(Cl)_2(CH_3CN)]$. In CH_3CN with excess N_3^-, the $[Os^{II}(tpy)(Cl)_2(CH_3CN)]$ formed reacts further with N_3^- followed by air oxidation to give $[Os^{III}(tpy)(Cl)_2(5\text{-}CH_3\text{-tetrazolate})]$. (**44**) also reacts with N_3^- and CS_2 to give *trans*-$[Os^{II}(tpy)(Cl)_2(NS)]^+$. In H_2O with 2 equivalents of N_3^- *cis*-$[Os^{III}(tpy)(Cl)_2(N_3)]$ is produced (Scheme 9).[176]

(e) Reaction with amines. $[Os^{VI}(N)(L)(Cl)_2]^+$ (L = tpy or tpm) react rapidly with secondary amines R_2NH ($R_2NH = HN(CH_2)_4O$ (morpholine), $HN(CH_2)_4CH_2$ (piperidine), $HN(C_2H_5)_2$ (diethylamine)) to give Os(V)–hydrazido complexes $[Os^{V}(L)(Cl)_2(NNR_2)]^+$ (Sections 5.6.5.3.1 and 5.6.6.4.4; Equation (12)).[177,178] The rate law for the reaction with morpholine is first order in Os^{VI} and second order in amine. The rate constants at 298 K in CH_3CN are 58.1 M^{-2} s^{-1} and 268.3 M^{-2} s^{-1} for L = tpy and tpm, respectively. The proposed mechanism involves nucleophilic attack of R_2NH at $Os^{VI}{\equiv}N$ to give $Os^{IV}{-}NN(H)R_2$, followed by deprotonation and oxidation by Os^{VI} to give $Os^{V}{-}NNR_2$.[177]



i) 2 N_3^-, CH_3CN, air oxidation; ii) N_3^-, CS_2, acetone; iii) N_3^-, CH_3CN; iv) recrystallization from CH_3CN/Et_2O;
v) Fc^+, CH_3CN; vi) $2N_3^-$, H_2O, air oxidation; vii) N_3^-, acetone or CH_2Cl_2; viii) H_2O or CH_3OH, Cl^-;
ix) $2N_3^-$, CH_3CN.

Scheme 9

$$2\,trans\text{-}[Os^{VI}(N)(L)(Cl)_2]^+ + 2\,HNR_2 \longrightarrow trans\text{-}[Os^{V}(tpy)(Cl)_2(NNR_2)]^+ + 1/2\,trans,trans\text{-}[(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)] + H_2NR_2^+ \quad (12)$$

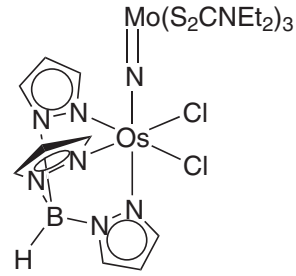
The Os^V complex can be chemically or electrochemically oxidized to Os^{VI} (Section 5.6.5.3.1) or reduced to Os^{IV} (Section 5.6.6.4.4).

(f) N···N coupling reactions. N···N coupling of Os≡N complexes to generate N_2 has been observed in a number of cases. These reactions are important because any factors that control the rates of these reactions should also be applicable to N≡N cleavage. The first evidence for nitrido coupling is the formation of $[Os_2(NH_3)_8(CO)_2(N_2)]^{4+}$ from the oxidation of $[Os(NH_3)_5(CO)]^{2+}$.

The product is proposed to arise from the coupling of the $[Os^{V}(N)(NH_3)_4(CO)]^{2+}$ intermediate (see also Section 5.6.5.2). The first direct observation of N···N coupling of Os≡N came from laser flash photolysis experiments on $[Os^{VI}(N)(NH_3)_4]^{3+}$ in the presence of electron donors such as 1,4-dimethoxybenzene. This produces the nucleophilic $Os^{V}{\equiv}N$ which undergoes N···N coupling with the electrophilic $Os^{VI}{\equiv}N$[179] (Equation (13)).

$$Os^{V}{\equiv}N + Os^{VI}{\equiv}N \longrightarrow [Os^{II}\text{---}N{\equiv}N\text{---}Os^{III}] \tag{13}$$

One-electron reduction of $[Os^{VI}(N)(tpy)(Cl)_2]^{+}$ in nonaqueous media generates $Os^{V}{\equiv}N$ which also undergoes N···N coupling (see also Section 5.6.5.2). A coupling reaction between the nucleophilic $[Mo^{VI}(N)(Et_2NCS_2)_3]$ and the electrophilic $[Os^{VI}(N)(Tp)(Cl)_2]$ has also been reported.[180] This reaction produces N_2; ^{15}N labeling experiments reveal that the N_2 produced comes from Mo≡N and Os≡N coupling. The major transition metal-containing product of the reaction is the μ-nitrido complex $[(Tp)(Cl)_2Os(\mu\text{-}N)Mo(S_2CNEt_2)_3]$ (**55**), where the bridging nitride is derived primarily (82%) from the Os≡N. X-ray crystallography reveals a nearly linear nitrido bridge (Mo—N = 1.721 Å, Os—N = 1.906(3) Å, Os—N—Mo = 173.7°).



(**55**)

(g) Reaction with PR_3. The nitrido ligand in these complexes are subject to rapid nucleophilic attack by PR_3 to form stable osmium(IV) phosphoraniminato complexes, which are described in Sections 5.6.5.3.2 and 5.6.6.4.6.

(h) Atom transfer reactions to give chalconitrosyls. An unusual four-electron change at the metal center occurs in the reaction of $[Os^{VI}(N)(tpy)(Cl)_2]^{+}$ with Me_3NO to give $[Os^{II}(NO)(tpy)(Cl)_2]^{+}$ (Scheme 6, reaction vi).[170]

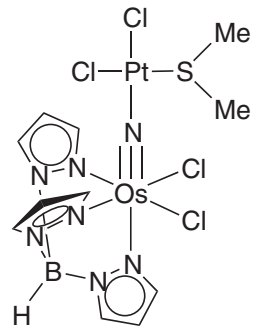
Similarly $[Os^{VI}(N)(Tp)(Cl)_2]$ reacts with various chalcogen compounds to give chalconitrosyls, $[Os^{II}(Tp)(NE)(Cl)_2]$ (E = O (**56**), S (**57**), and Se (**58**)) as outlined in Scheme 8.[181] The X-ray crystal structures of $[Os(Tp)(NO)(Cl)_2]$ (**56**) and $[Os(Tp)(NSe)(Cl)_2]$ (**58**) have been determined.[181] (**58**) is the first transition metal selenonitrosyl complex. (**56**) is also formed in an unusual reaction of $[Os^{VI}(N)(Tp)(Cl)_2]$ with NO (Scheme 8).[182] The reaction is probably initiated by addition of NO to the nitrido ligand to form an osmium–N_2O complex, $[TpOs(NNO)Cl_2]$. The loss of N_2O would give $[(Tp)Os(Cl)_2]$, which would be converted to (**56**) by excess NO.

(i) Reaction with thiophenols. $[Os^{VI}(N)(L)(Cl)_2]^{+}$ (L = tpy or tpm) react rapidly with thiophenols (3,5-$Me_2C_6H_3SH$) to give Os(IV)–sulfimido complexes, $[Os^{IV}(L)(Cl)_2(NSAr)]$ (Scheme 6, reaction viii) (see Sections 5.6.5.3.3 and 5.6.6.4.5).

(j) Reaction with electron-rich metal centers. $[Os(N)(Tp)(Cl)_2]$ reacts with $[(Cp)Co(\eta^4\text{-}C_5H_5C_6F_5)]$ to give a trimetallic species $[(Cp)Co\{Os(Tp)(N)(Cl)_2\}_2]$ (**59**) (Scheme 8).[183] X-ray crystallography studies show Os—N distances of 1.704 and 1.741 Å, which are longer than typical Os≡N bonds (average 1.629 Å). The Co—N distances are short (1.696(11) and 1.737(9) Å), indicating that the osmium nitrido complex acts as a π-acid ligand for $[(Cp)Co(\eta^4\text{-}C_5H_5C_6F_5)]$. A similar reaction occurs with $[Pt(Cl)_2(Me_2S)_2]$ to afford $[Pt(Cl)_2(SMe_2)\{(\mu\text{-}N)Os(Tp)(Cl)_2\}]$ (**60**), which has a short Pt—N distance of 1.868 Å. The Os—N distance is 1.687 Å.

(iii) Electronic absorption and emission spectroscopy

The electronic absorption spectra of $Os^{VI}{\equiv}N$ have been extensively studied by Gray and co-workers. The lowest energy excited state is ligand field in nature, arising from the $d_{xy} \rightarrow (d_{xz}, d_{yz})$



(**60**)

transition. The charge transfer transition, $p_{\pi}(N^{3-}) \rightarrow Os^{VI}$, probably occurs in the UV region and conclusive assignment has not been made.[184]

The species $[Os(N)(X)_4]^-$ (X = Cl, Br) exhibit intense red luminescence.[184] Vibronically resolved emission spectra have been obtained at 5 K. The spectra are dominated by a progression in a high-frequency ($\sim$1,120 cm^{-1}) mode that corresponds to ν(Os$\equiv$N) (IR/Raman: X = Cl, ν = 1,123 cm^{-1}; X = Br, ν = 1,119 cm^{-1}).[185] There is also a long, well-defined subprogression in a lower frequency mode (X = Cl, ν = 151 cm^{-1}; X = Br, ν = 112 cm^{-1}). The polarized single-crystal absorption spectrum of $(Ph_4As)[Os(N)(Cl)_4]$ at 5 K also showed vibronic structure but these features are extremely weak, consistent with the long emission lifetime of $\sim$20 μs at 77 K and $\sim$500 ns at 300 K. The observation of long emission lifetimes and very weak absorptions, together with a large geometric distortion along the OsN coordinate support the assignment of the excited state to B_1, $B_2(^3E)[(d_{xy})^1(d_{xz,yz})^1]$ (C_{4v} ground state).[184]

The luminescent properties of $[Os^{VI}(N)(NH_3)_4]X_3$ (X = Cl, CF_3SO_3)[155] and $(Ph_4As)_2[Os^{VI}(N)(CN)_5]$[153] have also been reported (Table 3). The complexes are emissive and have long excited state lifetimes both in the solid state and in fluid solutions at room temperature (λ_{em} = 550 nm in MeCN). $[Os(N)(NH_3)_4]Cl_3$ is a powerful one-electron oxidant in the excited state, with an excited state redox potential of $\sim$2.1 V vs. NHE. The emitting state has been suggested to be $^3[(d_{xy})^1(d_{\pi}*)^1]$ in origin.

The electronic absorption spectra and luminescent properties of $[Os^{VI}(N)(OEP)(X)]$ (X = OMe, $OClO_3$) have also been studied.[207a] The emission spectra of $[Os^{VI}(N)(OEP)(X)]$ and

Table 3 Photophysical data of selected osmium(VI) oxo and nitrido complexes in acetonitrile at room temperature.

Complex	λ_{max} *(Em)*(nm)	*Lifetime*, τ(μs)	*References*
trans-$[Os^{VI}(O)_2(14\text{-TMC})](ClO_4)_2$	620	1.0[a]	214
trans-$[Os^{VI}(O)_2(15\text{-TMC})](ClO_4)_2$	625	1.0[a]	214
trans-$[Os^{VI}(O)_2(16\text{-TMC})](ClO_4)_2$	600	1.6[a]	214
trans-$[Os^{VI}(O)_2(CRMe_3)](ClO_4)_2$	710	0.9[a]	214
trans-$[Os^{VI}(O)_2(CN)_4](Ph_4As)_2$	710	0.40[a]	214
$[Os^{VI}(N)(CN)_5](Ph_4As)_2$	550	2.49[b]	153
$[Os^{VI}(N)(NH_3)_4](CF_3SO_3)_3$	545	1.5[b]	155
$[Os^{VI}(N)(dmbpy)(Cl)_3]$	730	0.48[b]	162
$[Os^{VI}(N)(5\text{-Clphen})(Cl)_3]$	732	0.49[b]	162
$[Os^{VI}(N)(dpphen)(Cl)_3]$	728	0.57[a]	162
$[Os^{VI}(N)(tpy)(Cl)_2](ClO_4)$	700	5.64[a]	162
$[Os^{VI}(N)(tpy)(Br)_2](ClO_4)$	700	2.33[a]	162
$[Os^{VI}(N)(tpy)(Cl)(CF_3SO_3)](CF_3SO_3)$	660	0.2[a]	162
$[Os^{VI}(N)(bpy)(Cl)_2(H_2O)](CF_3SO_3)$	637	[c]	162
$[Os^{VI}(N)(tmen)_2(Cl)](Cl)_2$	550	5.0	161
$[Os^{VI}(N)(tmen\text{-}H)(tmen)](CF_3SO_3)_2$	560	2.0[d]	161
$[Os^{VI}(N)(mnt)_2](NBu^n_4)$	653	0.097[d]	192
$[Os^{VI}(N)(mnt)_2](NBu^n_4)$	610	0.097[d,e]	192

[a] Concentration of osmium complex $\sim 10^{-3}$ mol dm^{-3}. [b] Extraplated from the plot of $1/\tau$ vs. $[Os^{VI}\equiv N]$. [c] lifetime of the complex varied from sample to sample. [d] Concentration of osmium complex $\sim 10^{-4}$ mol dm^{-3}. [e] Measured in dichloromethane.

$[Os^{VI}(O)_2(OEP)]$ are similar and they have comparable lifetimes. The phosphorescence has been assigned to derive from a triplet $T_1(\pi, \pi^*)$ level.

5.6.4.2.3 Phosphorus, arsenic, and antimony donor ligands

Ruthenium(VI) and osmium(VI) nitrido complexes containing $AsPh_3$ and $SbPh_3[M(N)(X)_3(L)_2]$ ($\nu(M{\equiv}N) \sim 1{,}030$–$1{,}070\,cm^{-1}$) have been described in *CCC* (1987). The complex $[Os^{VI}(N)(Ph_2As\text{-}CH_2\text{-}CH_2AsPh_2)(Cl)_3]$ is also known.[186] The measured $d(Os{\equiv}N)$ of the two crystallographical independent molecules are 1.70 Å and 1.66 Å. The reaction of $[Os(N)(Cl)_4]^-$ with PPh_3 involves a nucleophilic attack on the nitride in addition to substitution to give $[Os^{IV}(NPPh_3)(Cl)_3(PPh_3)_2]$ (*CCC*, 1987). However, alkylosmium(VI) nitrido complexes of PMe_3, PPh_3, and $Ph_2PCH_2CH_2PPh_2$ (dppe) are known. The reaction of $(NBu_4)[Os(N)(CH_2SiMe_3)_4]$ with HBF_4 in the presence of either PMe_3 or PPh_3 produces $[Os(N)(CH_2SiMe_3)_3(PR_3)]$.[187] The addition of L (L = PMe_3, 1/2 dppe) to $(NBu_4)[Os(N)(CH_2SiMe_3)_2(Cl)_2]$ produces $[Os(N)(CH_2SiMe_3)_2(L)_2(Cl)]$.[187]

5.6.4.2.4 Oxygen and sulfur ligands

(i) Oxygen ligands

An anionic tetraalkoxide complex of nitridoosmium(VI), $(PPh_4)[Os(N)(OCH_2Ph)_4]$, has been reported. Thermolysis of the complex results in β-H elimination to produce benzaldehyde and benzyl alcohol.[190a]

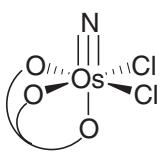
$[Os(N)(L_{OEt})(Cl)_2]$ (**61**) is prepared by the treatment of $(NBu_4)[Os(N)Cl_4]$ with NaL_{OEt} ($d(Os{\equiv}N) = 1.58$ Å).[188] The complex is relatively inert to alkylating agents such as MeOTf, $PhCH_2Br$, and $(CPh_3)^+$ and nucleophile such as N_3^-, Me_3NO, and propylene sulfide when compared with its Re analog $[Re(N)(L_{OEt})(PPh_3)(Cl)]$.

(ii) Sulfur ligands

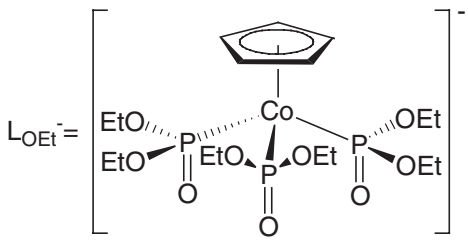
(a) Thiolate ligands. $(PPh_4)[Ru(N)(Me)_3(Br)]$ reacts with $NaSSiMe_3$ to give $(PPh_4)[Ru(N)\text{-}(Me)_3(SSiMe_3)]$, which on treatment with CsF or PPh_4Cl affords $(PPh_4)[Ru(N)(Me)_3(SH)]$, which has been structurally characterized by X-ray diffraction.[189] The $d(Ru{\equiv}N)$ of 1.595 Å in $(PPh_4)[Ru(N)(Me)_3(SH)]$ is slightly longer than the $d(Ru{\equiv}N)$ of 1.58 Å in $(PPh_4)[Ru(N)(Me)_4]$. Alternatively, $(PPh_4)[Ru(N)(Me)_3(SH)]$ can be synthesized directly from the reaction between $(PPh_4)[Ru(N)(Me)_3(Br)]$ and NaSH. $(PPh_4)[Ru(N)(Me)_3(SSiMe_3)]$ also reacts with $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}Cl)]_2$ to form a heterobimetallic complex $(PPh_4)[Me_3(N)Ru(\mu\text{-}S)Os(N)(CH_2\text{-}SiMe_3)_2(NCCH_3)]$.[189]

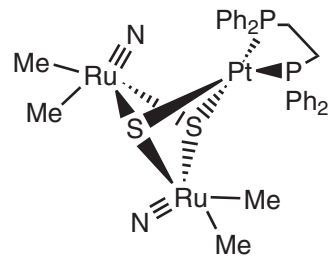
$[Os(N)(CH_2SiMe_3)_2(Cl)]_2$ reacts with alkali metal thiolates to give $[Os(N)(CH_2SiMe_3)_2(\mu\text{-}SR)]_2$ (R = Et, CMe_3, $CHMe_2$, CH_2CHMe_2, CH_2Ph), which have been characterized by spectroscopic means.[190a] The complexes are air and water stable and unreactive toward nucleophiles and electrophiles.

Reaction of $(PPh_4)[Os(N)(Cl)_4]$ with $Na(SCH_2Ph)$ in refluxing THF produces $(PPh_4)[Os(N)(SCH_2Ph)_4]$. Thermolysis of $(PPh_4)[Os(N)(SCH_2Ph)_4]$ gives benzyl disulfide, probably via reductive elimination.[190a]



(**61**)

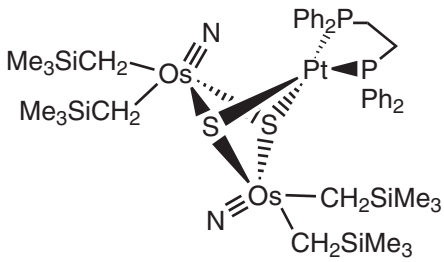




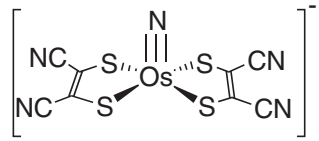
(**62**)

(b) Sulfido ligands. An osmium complex containing a terminal sulfido ligand, $(NBu^n_4)[Os^{VI}(N)(S)(CH_2SiMe_3)_2]$, has been prepared by the reaction of $(NBu^n_4)[Os(N)(CH_2SiMe_3)_2(Cl)_2]$ with Li_2S. It has been characterized by ^1H NMR, MS, and IR (ν (Os≡N) = 1,097 cm^{-1}, ν(Os=S) = 613 cm^{-1}).[190b]

The osmium(VI) and ruthenium(VI) μ_3-sulfido clusters (Y)[{M(N)R_2}$_3$(μ_3-S)$_2$] (Y = NBu_4, PPh_4; M = Os, R = CH_2SiMe_3; M = Ru, R = CH_3, CH_2SiMe_3) have been described in reference 131. A number of μ_3-sulfido heterobimetallic complexes [(L)M(μ_3-S)$_2${Ru(N)(Me)$_2$}$_2$] (M = Pt, L = dppe, cod; M = Pd, L = dppe) have been prepared by the reactions of [Pt(dppe)($SSiMe_3$)$_2$], [Pt(cod)($SSiMe_3$)$_2$], or [(dppe)Pd($SSiMe_3$)$_2$] with $(PPh_4)[Ru(N)(Me)_2(Cl)_2]$; the Os analog [(dppe)Pt(μ_3-S)$_2${Os(N)(CH_2SiMe_3)$_2$}$_2$] is also known.[191] The X-ray structures of [(dppe)Pt(μ_3-S)$_2${Ru(N)Me_2}$_2$] (**62**) and [(dppe)Pt(μ_3-S)$_2${Os(N)(CH_2SiMe_3)$_2$}$_2$] (**63**) have been determined.



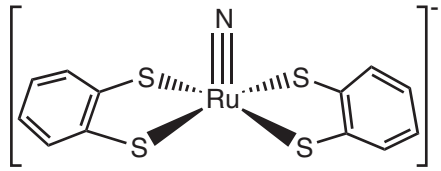
(**63**)



(**64**)

(c) Dithiolene complexes. The luminescent $(NBu_4)[Os(N)(mnt)_2]$ (**64**) (mnt = maleonitriledithiolate) is prepared by the treatment of $(NBu_4)[Os(N)(Cl)_4]$ with 2 equivalents of Na_2(mnt).[192] The X-ray structure reveals a square pyramidal geometry with the nitrido ligand at the axial position and the osmium atom is displaced above the S_4 plane by 0.651 Å; the Os—N distance is 1.639 Å.

$(NBu_4)[Ru(N)(bdt)_2]$ (**65**) (H_2bdt = 1,2-benzenedithiol) was first prepared by the interaction of $(NBu_4)[Ru(NO)(bdt)_2]$ with $NaBH_4$ in MeOH.[193] This reaction is extraordinary because the reduction of the nitrosyl ligand is accompanied by an oxidation of the metal center even in the presence of a strong reducing agent. Alternatively, (**65**) can be synthesized by interaction of $[Ru(N)(OSiMe_3)_4]^-$ with the ligand in the presence of base.[194] The osmium analogs $[Os(N)(L)_2]^-$ ($H_2L = H_2$bdt (**66a**) or 3,4-toluenedithiol (H_2tdt) (**66b**)) are also known.[195,196]

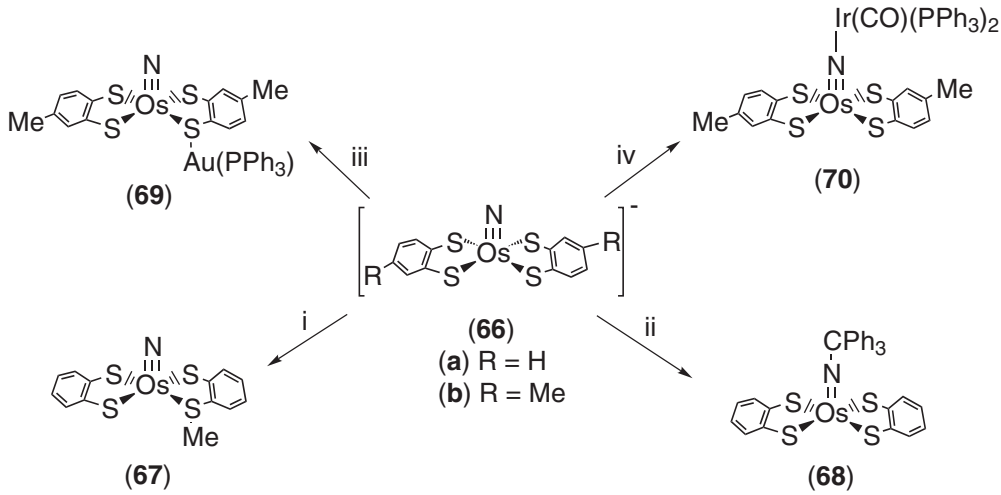


(**65**)

K[Os(N)(CH_2SiMe_3)$_2$(bdt)] and $(NBu_4)[Os(N)(CH_2SiMe_3)_2(dmit)]$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) have also been reported.[194]

Alkylation of $(NBu_4)[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]$ occurs at the more basic sulfur site to give $[Os(N)(CH_2SiMe_3)_2\{SCH_2CH_2S(Me)\}]$.[197] The position of alkylation for $(NBu_4)[Os(N)(C_6H_4S_2)_2]$ (**66a**) is dependent on the entering electrophiles. $(Me_3O)(BF_4)$ alkylates the sulfur atom of the benzenedithiolate ligand (**67**), whereas the bulky $(CPh_3)^+$ preferentially attacks the less hindered nitrido ligand (**68**) as shown in Scheme 10.[196]

A similar observation is found in the reaction of $(NBu_4)[Os(N)(L)_2]$ (**66b**) with electrophiles. Reaction with $[Au(PPh_3)(OTf)]$ in CH_2Cl_2 affords $[Os(N)(L)\{SC_7H_6S(AuPPh_3)\}]$ (**69**) (d(Os≡N) = 1.65 Å). Reaction with $[Ir(CO)(PPh_3)_2(OTf)]$ in CH_2Cl_2 gives $[(L)_2Os\{(N)Ir(CO)(PPh_3)_2\}]$ (**70**) (d(Os≡N) = 1.676(5) Å).[195] The less bulky electrophile $[Au(PPh_3)]^+$ attacks the more basic S-atom while the more bulky $[Ir(CO)(PPh_3)_2]^+$ is added to the less hindered nitrido ligand.



i, $(Me_3O)(BF_4)$; ii, $[CPh_3]^+$; iii, $[Au(PPh_3)(OTf)]$; iv, $[Ir(CO)(PPh_3)_2(OTf)]$.

Scheme 10

(d) Imidodiphosphinochalcogenido ligands. The nitrido complexes containing imidodiphosphinochalcogenido ligands, *trans*-$[Os(N)\{N(QPR_2)_2\}_2Cl]$ (R = Ph, Q = S (**71a**); R = Pr^i, Q = S (**71b**); R = Ph, Q = Se (**71c**)), are prepared by reactions of $(NBu_4)[Os(N)(Cl)_4]$ with $K[N(QPR_2)_2]$; $[Os(N)\{N(PSPh_2)_2\}_2](BF_4)$ is also known.[198,199] The μ-nitrido Os^{VIII}—Os^{VI} complex $[Os(N)\{N(SPPh_2)_2\}_2(\mu\text{-}NOsO_3)]$ is known (see Section 5.6.2.2). Heterometallic μ-oxo complexes *trans*-$[Os(N)\{N(SPPh_2)_2\}_2\{(O)Re(O)_3\}]$ and *trans*-$[\{Os(N)[N(SPPh_2)_2]\}_2(M_6(O)_{19})]$ (M = Mo or W) have also been reported and have been characterized by spectroscopic means.[199]

5.6.4.2.5 Halogen ligands

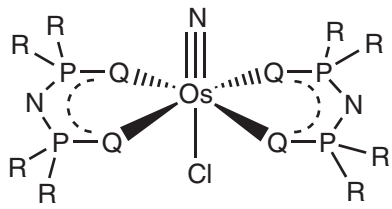
The preparation, bonding, and reactivities of anionic nitrido halo complexes of ruthenium(VI) and osmium(VI), including $[M(N)(X)_4]^-$, $[M(N)(X)_5]^{2-}$ (M = Ru, Os; X = Cl, Br, I), and $[Os(N)(X)_4(H_2O)]^-$ (X = Cl, Br), have been well documented in *CCC* (1987). These complexes, especially $[M(N)(X)_4]^-$, are important starting materials for the preparation of a variety of M^{VI} nitrido complexes.

Approximate density functional theory calculations have been used to investigate the *trans* influence in $[Os(N)(X)_4]^-$ (X = Cl, Me, SMe) and $[Os(N)(Cl)_5]^{2-}$.[200] By using the transition state method the relative effects of steric and electronic stabilization on the *trans* influence in these complexes have been quantitatively assessed. It is found that the electronic stabilization is greater than the steric stabilization for these complexes.

The reactions of $[Os(N)(Cl)_4]^-$ with L (L = pyrazine, *p*-dioxane) give the osmium dimers $[(Cl)_4(N)Os(\mu\text{-}L)Os(N)(Cl)_4]^{2-}$. The Os≡N distance in $[(Cl)_4(N)Os(\mu\text{-pyz})Os(N)(Cl)_4]^{2-}$ is 1.630 Å.[156]

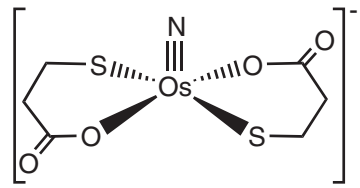
5.6.4.2.6 Mixed donor atom ligands

Ru^{VI} and Os^{VI} nitrido complexes containing amino acids and derivatives are known. Complexes containing cysteine(2-) and related ligands have been prepared by the reactions of $[Ru(N)(CH_2SiMe_3)_4]^-$, $[Ru(N)(OSiMe_3)_4]^-$, or $[Os(N)(Cl)_4]^-$ with *N*-acetyl-L-cysteine, 3-mercaptopropionic acid, and 3-mercaptopropionamide.[202] The X-ray crystal structures of $[Os(N)(O_2CCH_2CH_2S)_2]^-$ (**72**) and $[Ru(N)(NHCOCH_2CH_2S)_2]^-$ (**73**) have been determined (d(Os≡N) = 1.608 Å, d(Ru≡N) = 1.595 Å).[202]

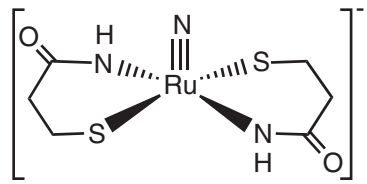


(**71**)

(**a**) R = Ph; Q = S
(**b**) R = Pr^{i}; Q = S
(**c**) R = Ph; Q = Se



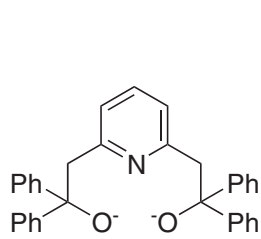
(**72**)



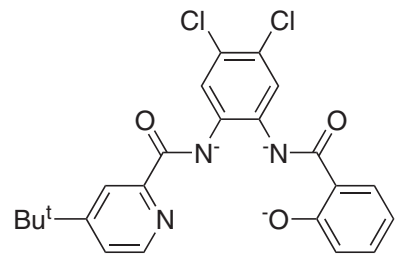
(**73**)

A number of air-stable, diamagnetic ruthenium(VI) and osmium(VI) nitrido complexes containing multidentate di-, tri-, and tetraanionic ligands (L) are known (**74**–**78**) (Figure 2). In general these complexes are synthesized by the reaction of $[M(N)(Cl)_4]^-$ with the protonated ligand H_nL in organic solvent at ambient conditions in the presence of 2,6-dimethylpyridine which functions as a mild base.[149,203] $[Os(N)(\mathbf{76a})]^-$ can also be prepared by the reaction of $[Os(HBA–B)(PPh_3)_2]$ with trimethylsilyl azide in benzene at room temperature.[204] The structures of these complexes have been established by X-ray crystallography. The pyridine–amide ligand derived from α-substituted pyridine (**77**) is a potentially tetradentate ligand. However, interaction of $[M(N)(Cl)_4]^-$ (M = Ru, Os) with (**77**) gives distorted octahedral complexes $[M(N)(\mathbf{77})(Cl)_3]$ where (**77**) is bound to the M≡N moiety in a bidentate fashion via the N—O pair of the ligand. The Ru≡N (1.594–1.615 Å) and the Os≡N (1.612–1.640 Å) distances are insensitive to the electron-donating power of the ancillary ligands.[149,203,204] All the nitridoruthenium(VI) complexes react spontaneously with PPh_3 and the intermediate $[Ru^{IV}(NPPh_3)(\mathbf{74})(py)(Cl)]$ has been isolated and characterized spectroscopically. However, for those nitridoruthenium(VI) complexes bearing the trianionic $(\mathbf{75})^{3-}$ and tetraanionic ligands (**76a**) and (**76b**), the phosphoraniminatoruthenium(IV) intermediate undergoes further reaction with pyrazole to generate a bis(pyrazole)ruthenium(IV) complex as the product.[203]

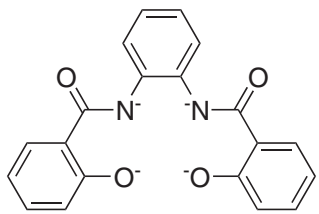
Os(VI) nitrido complexes containing Schiff base ligands, $[Os^{VI}(N)(L)(Cl)]$ (L = salophen or salen), have also been reported. The ν(Os≡N) for the salophen complexes occur at ~1,070 cm^{-1} and are insensitive to the nature of the substituents present on the Schiff base ligand. The X-ray structures of $[Os(N)(salophen)(MeOH)]ClO_4$ and $[Os(N)(5,5'\text{-}Cl_2salophen)(MeOH)]ClO_4$ have been obtained and the Os≡N bond distances are 1.651 Å and 1.66 Å, respectively. The Os^{VI} nitrido complexes react rapidly with PPh_3 to produce the corresponding Os^{IV} phosphoraniminato complexes $[Os^{IV}(NPPh_3)(L)(Cl)]$. The reactions are first order in both the ruthenium complex and PPh_3. The reactivities of the complexes follow a linear Hammett correlation of $\log(k_X/k_H)$ with σ_p, with a ρ value of 1.9. The positive ρ value is consistent with a transition state involving electrophilic attack by the nitrido ligand on the P-atom.[205] Interestingly, [Os(N)(salophen)(Cl)] undergoes facile nucleophilic addition of CN^- (**79**), H^- (**80**), or $CF_3C(O)CH_2^-$ (**81**) to the salophen ligand instead of the nitrido ligand to generate a number of osmium(VI) nitrido complexes containing trianionic modified salophen ligands (Scheme 11). The results suggest that



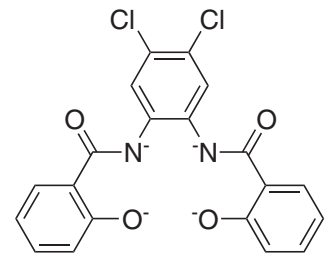
(74)



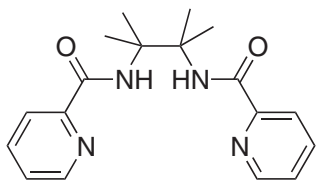
(75)



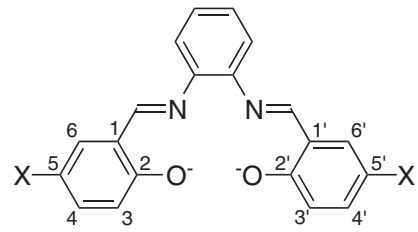
HBA-B
(76a)



HBA-DCB
(76b)



(77)



(78)

salophen, X = H
5,5′-$(OMe)_2$salophen, X = OMe
5,5′-Me_2salophen, X = Me
5,5′-Cl_2salophen, X = Cl

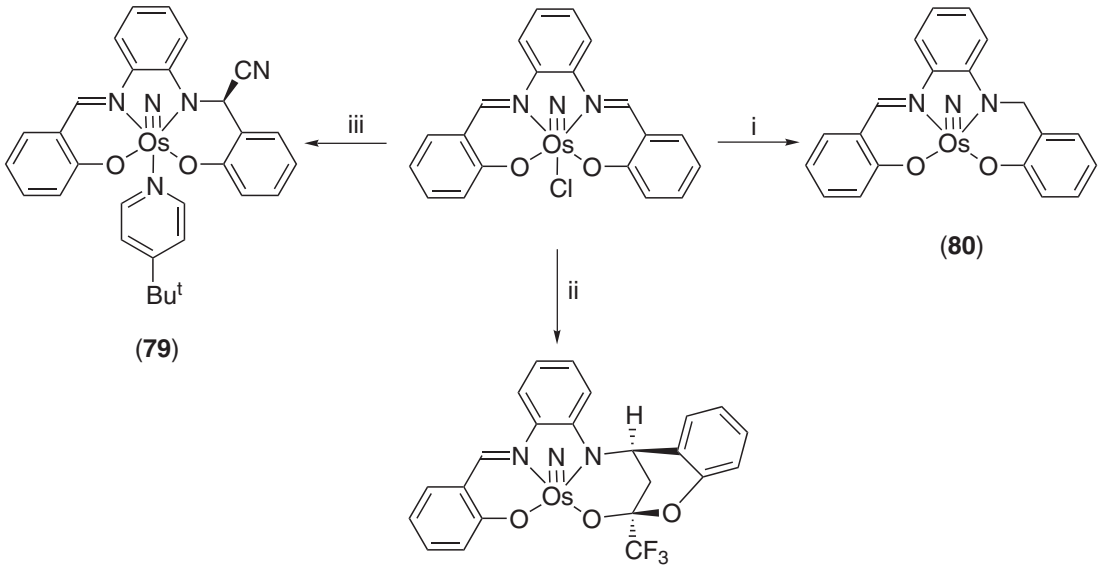
Figure 2 Mixed N, O-donor ligands.

nucleophilic attack at salen and salophen coordinated to a high-valent metal center could be very facile.[206]

5.6.4.2.7 Porphyrins and related complexes

Osmium(VI) nitrido porphyrin complexes [Os(N)(OEP)(X)] (X = F, ClO_4, OMe) are made from $[Os(O)_2(OEP)]$ and $N_2H_4 \cdot H_2O$ in the presence of HF, $HClO_4$, or MeOH.[207a] [Ru(N)(por)(OH)] (por = TMP, 3,4,5-MeO-TPP have been prepared by the reaction of $[Ru(O)_2(por)]$ with excess $HN{=}CBu^t_2$ in CH_2Cl_2. The X-ray structure of [Ru(N)(3,4,5-MeO-TPP)(OH)] reveals a Ru≡N distance of 1.656 Å.[207b] [Os^{VI}(N)(por)(OH)] (por = TPP, TTP, and 4-Cl-TPP) are synthesized by the oxidation of $[Os(por)(NH_3)_2]$ with *m*-CPBA.[208]

A ruthenium(VI) nitrido complex containing a tetrapyrrolic macrocycle ligand, $[Ru^{VI}(N)(L)]^-$ (**82**) (H_4L = *meso*-octamethylporphyrinogen), has been synthesized by the reaction of diphenyldiazomethane with $[Ru^{II}(L)]^{2-}$, which is prepared from $[Ru(cod)(Cl)_2]$ and $Na_4(L) \cdot 4THF$.[209] X-ray crystal studies reveal that $[Ru^{VI}(N)(L)]^-$ has a C_{2v} symmetry, and it has the usual saddle conformation, with the metal atom displaced 0.482 Å out of the N_4 mean plane. The reactivities and redox chemistry of this complex are summarized in Scheme 12 (see also Section 5.6.5.2).



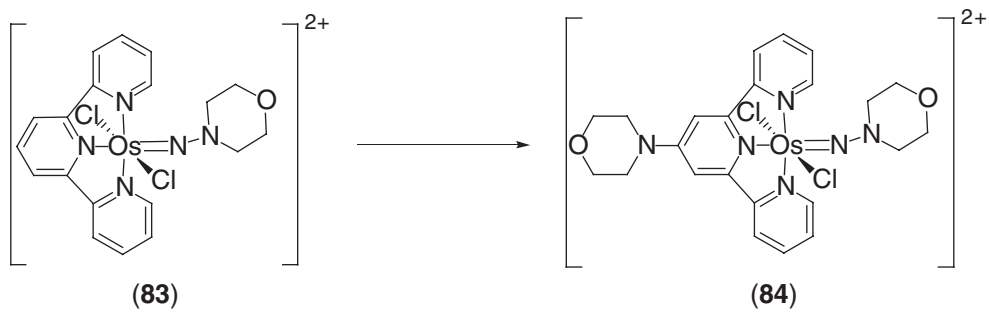
i, CH_3O^-; ii, $(CF_3CO)_2CH^-$; iii, CN^-, Bu^tpy.

Scheme 11

5.6.4.3 Hydrazido Complexes

Osmium(VI) hydrazido complexes can be generated by electrochemical oxidation of the corresponding osmium(V) hydrazido complexes (Section 5.6.5.3.1).[210,211] The complex *trans*-$[Os^{VI}(tpy)(Cl)_2(NN(CH_2)_4O)]^{2+}$ (**83**) is able to oxidize benzyl alcohol to benzaldehyde. It also oxidizes PPh_3 to PPh_3O, and R_2S to give R_2SO; the source of O atoms is presumably H_2O in the solvent.

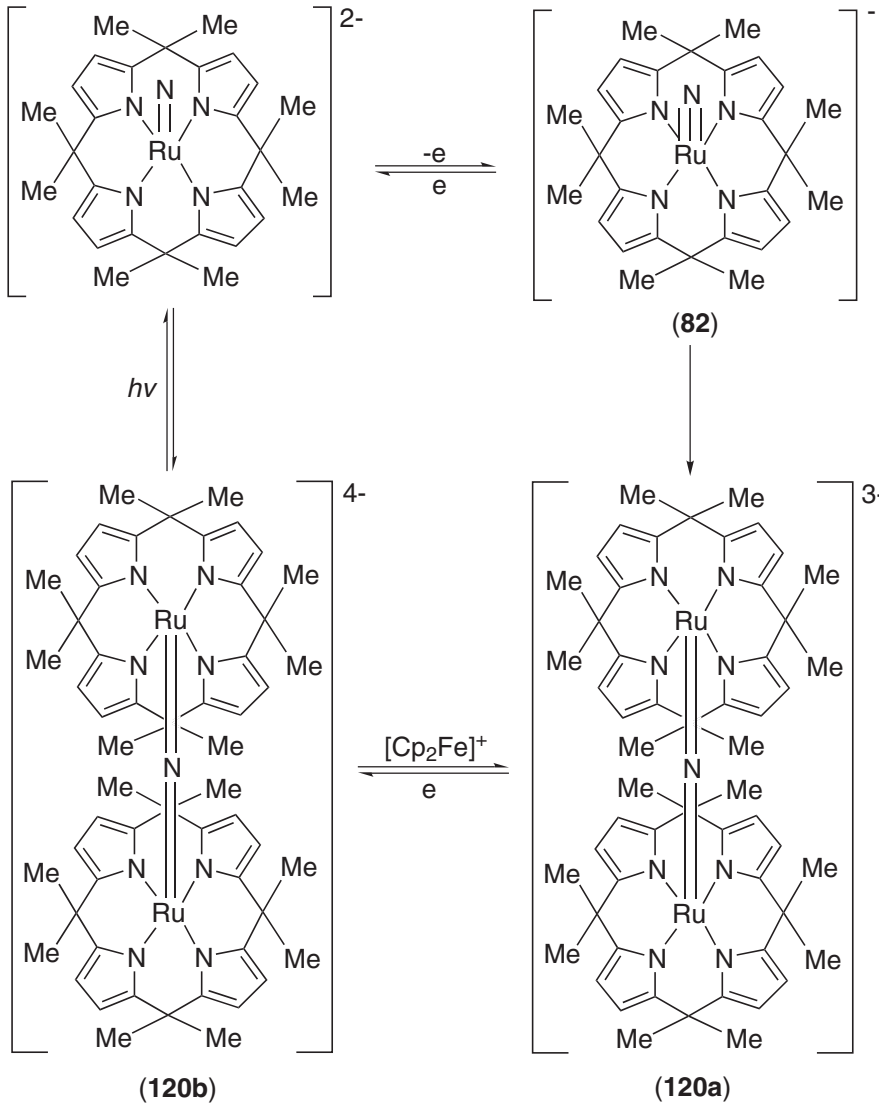
(**83**) also reacts with N or O bases such as $[HN(CH_2)_4O]$ to give a remarkable ring-substituted product, *trans*-$[Os^{VI}(4'\text{-}O(CH_2)_4Ntpy)(Cl)_2(NN(CH_2)_4O)]^{2+}$ (**84**) (Equation (14)).[212] The X-ray structure of the complex shows that the C(4′) position remains sp^2-hybridized. The Os—N-(hydrazido) bond length of 1.778 Å, N—N bond length of 1.237 Å, and Os—N—N angle of 172.5° are all consistent with an Os^{VI} hydrazido complex.



(14)

5.6.4.4 Oxo Complexes

Monooxo and *cis*- and *trans*-dioxo complexes of ruthenium(VI) and osmium(VI) are known, with the *trans*-dioxo species being most common.[1] In general, these complexes are all diamagnetic and are characterized by vibrational spectroscopy and/or X-ray crystallography. One intense metal–oxo stretch is usually observed for monooxo and *trans*-dioxo complexes while two metal–oxo stretches, $\nu_s(M(O)_2)$ and $\nu_{as}(M(O)_2)$, are found for the *cis*-dioxo species in the IR spectra. The structural and vibrational data are listed in Table 4.



Scheme 12

Table 4 Selected metal–oxo bond distances and stretching frequencies for ruthenium and osmium oxo complexes.

Complex	$d(M{=}O)$ (Å)	$\nu_{as}(M{=}O)$ (cm^{-1})	*References*
$[Ru^{IV}(O)(bpy)_2(py)](ClO_4)_2$		792	474
$[Ru^{IV}(^{18}O)(bpy)_2(py)](ClO_4)_2$		752	474
$[Ru^{IV}(O)(tpy)(bpy)](ClO_4)_2$		792	481
$[Ru^{IV}(O)(bpy)_2(PEt_3)](ClO_4)_2$		790	489
$[Ru^{IV}(^{18}O)(bpy)_2(PEt_3)](ClO_4)_2$		750	489
$[Ru^{IV}(O)(bpy)_2(PPr^i{}_3)](ClO_4)_2$		790	489
$[Ru^{IV}(O)(bpy)(biq)(PPr^n{}_3)](ClO_4)_2$		785	475
$[Ru^{IV}(O)(tpy)(TMEA)](ClO_4)_2$		773	476
$[Ru^{IV}(O)(tpy)(6,6'\text{-}Cl_2bpy)](ClO_4)_2$		780	269
$[Ru^{IV}(O)(Me_3tacn)(bpy)](ClO_4)_2$	1.815(6)	780	498
$[Ru^{IV}(O)(PPz^*)(bpy)]^{2+}$		788	515
$[Ru^{IV}(O)(tpy)(cxhn)](ClO_4)_2$	1.827(14)	775	484
$[Ru^{IV}(O)(Me_3tacn)(cbpy)](ClO_4)_2$		796	484

Table 4 continued

Complex	$d(M{=}O)$ (Å)	$\nu_{as}(M{=}O)$ (cm^{-1})	References
$[Ru^{IV}(O)(tpy)(S\text{- or }R\text{-bpop})](ClO_4)_2$		792	485
$[Ru^{IV}(O)(14\text{-TMC})(NCO)]ClO_4$	1.765(5)	815	240
$[Ru^{IV}(O)(14\text{-TMC})(N_3)]ClO_4$	1.765(5)	815	240
$[Ru^{IV}(O)(15\text{-TMC})Cl]ClO_4$		820	240
$[Ru^{IV}(O)(16\text{-TMC})Cl]ClO_4$	1.75(1)	840	497
$[Ru^{IV}(O)(TMEA)_2Cl]ClO_4$		820	240
$[Ru^{IV}(O)(CRMe_3)(NCO)]ClO_4$	1.777(2)	790	243
$[Ru^{IV}(O)(H_2O)(N_2O_2)](ClO_4)_2$	1.739(2)	845	247
$[Ru^{IV}(O)(TMP)]$		823	477
$[Ru^{IV}(^{18}O)(TMP)]$		782	477
$[Ru^{VI}(O)_2(bpy)\{IO_3(OH)_3\}]$	1.727	815	284,285
$[Ru^{V}(O)(PHAB)](NPr^n_4)$	1.702(3)		389
$[Ru^{V}(O)(O_2COCEt_2)_2](NPr^n_4)$	1.687(6)	900	395
$[Ru^{V}(O)(N_4O)](ClO_4)_2$		872	492
$[Ru^{V}(O)(CH_2SiMe_3)_3]_2$	1.733(6)	908	372
$[L_{OEt}(O)Ru(\mu\text{-}O)_2Ru(O)L_{OEt}]$	1.725(3)	848	413
trans-$[Ru^{V}(O)_2(14\text{-TMC})]ClO_4$		840–860	240
cis-$[Ru^{V}(O)_2(Tet\text{-}Me_6)]ClO_4$	1.751(3), 1.756(4)	850	260
$[Ru^{VI}(O)_3(OH)_2]Ba$	1.751, 1.759	820	279
$[Ru^{VI}(O)_2Cl_3][N(PPh_3)_2]$	1.658(5), 1.694(9)	878 (ν_{sym} 891)	304
$[Ru^{VI}(O)_2Cl_4][N(PPh_3)_2]_2$	1.709(4)	830	304
$[Ru^{VI}(O)_2(HIO_6)_2]NaK_5{\cdot}8H_2O$	1.732(8)	820	283
$[Ru^{VI}(O)_2(H_2TeO_6)_2]K_6{\cdot}4H_2O$		825	283
trans-$[Ru^{VI}(O)_2(14\text{-TMC})](ClO_4)_2$		850	245
trans-$[Ru^{VI}(O)_2(15\text{-TMC})](ClO_4)_2$	1.718(5)	855	245
trans-$[Ru^{VI}(O)_2(16\text{-TMC})](ClO_4)_2$	1.705(7)	860	245
trans-$[Ru^{VI}(O)_2(CRMe_3)](ClO_4)_2$		860	243
trans-$[Ru^{VI}(O)_2(pytn)](ClO_4)_2$		860	244
trans-$[Ru^{VI}(O)_2(N_2O_2)](ClO_4)_2$		865	247
trans-$[Ru^{VI}(O)_2(py)_2(OAc)_2]$	1.726(1)	840	224
trans-$[Ru^{VI}(O)_2(bpy)_2](ClO_4)_2$		850	227
trans-$[Ru^{VI}(O)_2(H_2O)(tpy)](ClO_4)_2$	1.661	834,841	235
trans-$[Ru^{VI}(O)_2(TMP)]$		821	320
trans-$[Ru^{VI}(O)_2(TPP)]$		819	318
trans-$[Ru^{VI}(O)_2(OEP)]$		821	318
trans-$[Ru^{VI}(O)_2(DPP)]$		818	317
trans-$[Ru^{VI}(O)_2(2,6\text{-Cl-TPP})]$		824	317
trans-$[Ru^{VI}(O)_2(4\text{-Cl-TPP})]$		821	317
trans-$[Ru^{VI}(O)_2(4\text{-Me-TPP})]$		823	317
trans-$[Ru^{VI}(O)_2(4\text{-MeO-TPP})]$		821	317
cis-$[Ru^{VI}(O)_2(6,6'\text{-}Cl_2bpy)_2](ClO_4)_2$		790 (ν_{sym} 840)	229
cis-$[Ru^{VI}(O)_2(2,9\text{-}Me_2phen)_2](PF_6)_2$		787 (ν_{sym} 839)	230
cis-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)](ClO_4)$	1.795(9)	859 (ν_{sym} 874)	260
$[Ru_2{}^{VI}O_6(py)_4]{\cdot}3.5H_2O$	1.72(1)	826 (ν_{sym} 810)	222
trans-$[Os^{V}(O)_2(14\text{-TMC})](ClO_4)_2$		873, 879	251
$[Os^{VI}(O)\{NHC(Me)_2C(Me)_2NH\}\text{-}\{NH_2C(Me)_2C(Me)_2NH_2\}]ClO_4$	1.72(2)	920	250
cis-$[Os^{VI}(O)_2(OAc)_3]K{\cdot}2AcOH$	1.711	845	290,201
cis-$[Os^{VI}(O)_2(S_2O_3)_2]Na_2$	1.692(3)	915 (ν_{sym} 931)	300
trans-$[Os^{VI}(O)_2(bpy)_2]^{2+}$		872	237
cis-$[Os^{VI}(O)_2(bpy)_2]^{2+}$		863 (ν_{sym} 883)	237
trans-$[Os^{VI}(O)_2(14\text{-TMC})](ClO_4)_2$		876	251,252
trans-$[Os^{VI}(O)_2(15\text{-TMC})](ClO_4)_2$		875	251
trans-$[Os^{VI}(O)_2(16\text{-TMC})](ClO_4)_2$		872	251
trans-$[Os^{VI}(O)_2(4\text{-Me-TPP})]$	1.743(3)	843	349
trans-$[Os^{VI}(O)_2(3\text{-}Bu^t\text{-saltmen})]$	1.760(7), 1.722(8)	845	311
trans-$[Os^{VI}(O)_2(CHBA\text{-Et})]K_2$		820	314
trans-$[Os^{VI}(^{18}O)_2(CHBA\text{-Et})]K_2$		788	314
trans-$[Os^{VI}(O)_2\{N(SPPh_2)_2\}_2]$	1.739	848	303
trans-$[Os^{VI}(O)_2\{N(SPPr^i_2)_2\}_2]$	1.748(3)	842	303
trans-$[Os^{VI}(O)_2\{N(SePPh_2)_2\}_2]$	1.734(3)	844	303

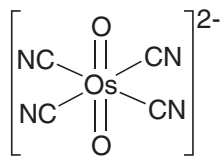
5.6.4.4.1 Carbon ligands

(i) Carbonyl complexes

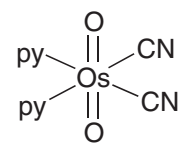
An unusual high-valent carbonyl complex, formulated as $[Os(O)_2(CO)_4](Sb_2F_{11})_2$, has been isolated by the reaction of $[OsO_4]$ with CO in SbF_5 at room temperature. The complex was characterized by vibrational spectroscopy. Unfortunately, because of its extreme sensitivity to moisture, satisfactory elemental analysis and X-ray crystal structures have not been obtained.[213]

(ii) Cyano complexes

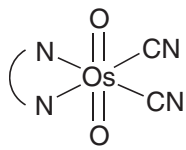
There are a number of osmium(VI) oxo complexes containing cyanide ligand, but none have been reported for ruthenium. The ion $[Os(O)_2(CN)_4]^{2-}$ can be prepared by reaction of $[OsO_4]$ with aqueous KCN. The X-ray crystal structure of $Cs_2[Os(O)_2(CN)_4]$ (**85**) shows that it has *trans*-dioxo groups with Os=O distances of 1.750 Å.[608] $[Os(O)_2(CN)_4]^{2-}$ is luminescent both in the solid state and in fluid solutions at room temperature, and the photochemistry of the organic-soluble $(AsPh_4)_2[Os(O)_2(CN)_4]$ has been studied in MeCN.[214–217] Reaction of $K_2[Os(O)_2(OH)_4]$ with KCN in water followed by the addition of acetic acid and $(NBu^n_4)(Br)$ produces $(NBu^n_4)_2[Os^{VI}(O)_2(OH)_2(CN)_2]$, which can be used as a precursor for the preparation of $[Os^{VI}(O)_2(L)(CN)_2]$ (L = $(py)_2$ (**86**), tmen (**87a**), 4,4′-Me_2bpy (**87b**), 4,4′-Bu^t_2bpy (**87c**)).[218] The crystal structures of $[Os^{VI}(O)_2(py)_2(CN)_2]$ and $[Os^{VI}(O)_2(tmen)(CN)_2]$ have been determined.[218] Like $(AsPh_4)_2[Os(O)_2(CN)_4]$, $[Os^{VI}(O)_2(py)_2(CN)_2]$ have long-lived and emissive excited states in solution at room temperature. The related species $[Os(O)_2(dpphen)(CN)_2]$ (**87d**) has also been prepared; this complex is able to catalyze the oxidation of alkanes by O_2 upon irradiation with UV light.[219] A μ-cyano species, $[Os(O)_2(mes)_2(\mu\text{-NC})Ru(bpy)_2(CN)]$ (**88**) (mes = mesityl), can be obtained from the reaction of $[Os^{VI}(O)_2(mes)_2]$ with $[Ru^{II}(bpy)_2(CN)_2]$; its photophysical properties have been studied.[220a]



(**85**)



(**86**)



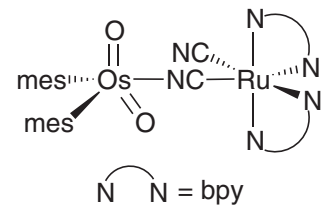
(**87**)

(**a**) tmen

(**b**) 4,4'-Me_2bpy

(**c**) 4,4'-Bu^t_2bpy

(**d**) dpphen

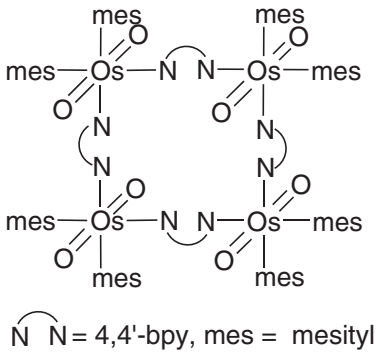


(**88**)

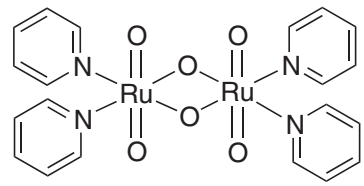
(iii) Alkyl and aryl complexes

There are a number of oxo species containing alkyl ligands, including $[Os(O)_2(mes)_2]$, $[M(O)(Me_3SiCH_2)_4]$ (M = Ru, Os), $[Os(O)(R_1)_2(R_2)_2]$ ($R_1 = R_2 =$ Me or Et; $R_1 =$ Me, $R_2 = Me_3SiCH_2$), $[Os(O)_2Me_2(py)_2]$, $[Os(O)_2(L)(mes)_2]$ (L = bpy, $CNC_6H_3Me_2$-2,6, $PMePh_2$), $[Os(O)_2(py)_2(Me_3SiCH_2)_2]$,

$[(Me)_2Os(O)_2(py)]_3$, $[(Me)_2(O)Os\{OC(Me)_2C(Me)_2O\}]$, and $[Os_3(O)_6(py)_3(Me)_6]$. These compounds are described in ref. 131, Volume 6, Chapter 7. $[Os(O)_2(tmen)(mes)_2]$ is also known.[218] A tetramer with a square planar structure, $[Os(O)_2(mes)_2(\mu\text{-}4,4'\text{-bpy})]_4$ (**89**) has been prepared by the reaction of $[Os(O)_2(mes)_2]$ with 4,4′-bpy in $CHCl_3$.[220b] An aryl $Os^{VI}{=}O$ species, $Os(O)(C_7H_7)_4$ (C_7H_7 = 2-methylphenol; Os=O bond length = 1.652 Å), has also been reported.[221]



(**89**)



(**90**)

5.6.4.4.2 Nitrogen ligands

Extensive work on *cis*- and *trans*-dioxo complexes of ruthenium(VI) and osmium(VI) containing nonlabile, oxidation-resistant nitrogen donor ligands has been reported.

(i) Syntheses

(a) Complexes with py, bpy, phen, tpy, and related ligands. A variety of *cis*- and *trans*-dioxoruthenium(VI) and osmium(VI) complexes containing pyridine and polypyridyl ligands are known. These ligands are frequently employed because they are oxidation resistant and are good σ-donors.

A number of mononuclear and binuclear *trans*-dioxoruthenium(VI) complexes containing pyridine ligands of the type $[Ru_2(O)_6(L)_4]$ (L = py, 4-Bu^{t}py, nicotinic acid, isonicotinamide, pyridine-2-carboxylic acid, 1/2bpy), *trans*-$[Ru(O)_2(py)_4]^{2+}$, *trans*-$[Ru(O)_2(pyca)_2]$ (pyca = py-2-carboxylate), *trans*-$[Ru(O)_2(L)_2(Cl)_2]$ (L = py, 4-Bu^{t}py, 4-Clpy), and *trans*-$[Ru(O)_2(Cl)_3(L)]^-$ (L = py, 4-Bu^{t}py, 3-Mepy, 3,4-Me_2py) are known.[222,223] The different types of complexes are made by the interaction of RuO_4 or $[Ru(O)_3(OH)_2]^{2-}$ with L (and Cl^-) in water under slightly different conditions; apparently higher pH favors the formation of binuclear species. The dark green solid produced by the reaction of $[RuO_4]$ in CCl_4 with pyridine, which was originally formulated as $[Ru(O)_4(py)_2]$, has now been determined to be $[Ru_2(O)_6(py)_4]$ by X-ray crystallography.[222] The X-ray crystal structure of $[Ru_2(O)_6(py)_4]\cdot 3.5H_2O$ (**90**) shows a planar $[Ru_2(O)_2]$ bridge (Ru—O = 1.93 Å) in which the Ru—O—Ru angle is 100.0° and the terminal Ru=O bond length is 1.72 Å. While for most *trans*-dioxoruthenium(VI) complexes the O=Ru=O angle is 180°, this compound is distinctly nonlinear, with an O=Ru=O angle of 160.5°.

All the monomeric and dimeric *trans*-dioxoruthenium(VI) complexes are characterized by vibrational spectroscopy. They display typically a strong IR band near 830 cm^{-1} corresponding to the asymmetric stretch $\nu_{asym}(RuO_2)$ and a strong Raman band near 850 cm^{-1} corresponding to the symmetric stretch $\nu_{sym}(RuO_2)$. These complexes all function as overall four-electron oxidants, converting primary alcohols into aldehydes and secondary alcohols into ketones. These oxidations can also be made catalytic by using *N*-methylmorpholine *N*-oxide as the terminal oxidant. *trans*-$[Ru_2(O)_6(py)_4]$, *trans*-$[Ru_2(O)_6(4\text{-}Bu^tpy)_4]$, *trans*-$[Ru(O)_2(py)_4]^{2+}$, and *trans*-$[Ru(O)_2(Cl)_3(4\text{-}Bu^tpy)]^-$ can also catalyze the aerobic oxidation of alcohols.[222]

A series of *trans*-dioxoruthenium(VI) complexes containing mixed pyridine–carboxylate ligands, *trans*-$[Ru^{VI}(O)_2(py)_2(RCO_2)_2]$ (R = Me, Et, Pr, Pr^i, Ph), have been prepared from $Ba[Ru(O)_3(OH)_2]$, carboxylic acid, and pyridine in acetonitrile at 0 °C.[224,225]

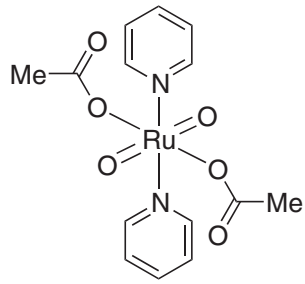
X-ray crystallography of $[Ru^{VI}(O)_2(py)_2(OAc)_2]$ (**91**) established that the complex has an octahedral geometry with the ligands in *trans* configurations (Ru—O = 1.726 Å).[224] The oxidative

reactivity of these dioxoruthenium(VI) complexes toward various organic substrates including phosphines, alkenes, phenols, alkanes, and ethers has been studied. These complexes are active but nonselective oxidants.

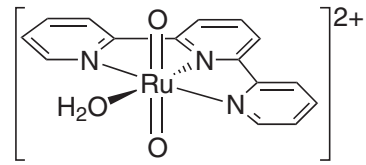
A series of cationic dioxoruthenium(VI) complexes of the form *trans*-$[Ru^{VI}(O)_2(L)_2]^{2+}$ (L = dmbpy,[226] bpy,[227] phen[226]) and *cis*-$[Ru^{VI}(O)_2(L')_2]^{2+}$ (L′ = 6,6′-Cl_2bpy,[229] 2,9-Me_2phen[230]) have also been isolated. Oxidation of *trans*-$[Ru^{III}(L)_2(OH)(H_2O)]^{2+}$ or *cis*-$[Ru^{II}(L')_2(H_2O)_2]^{2+}$ by electrochemical methods or by cerium(IV) in water produces the respective dioxoruthenium(VI) species.[226–229] The diamagnetic *trans*-$[Ru^{VI}(O)_2(L)_2]^{2+}$ complexes exhibit an intense $\nu_{as}(RuO_2)$ stretch at around 850 cm^{-1}. The UV–vis absorption spectra of *trans*-$[Ru^{VI}(O)_2(L)_2]^{2+}$ in MeCN show a characteristic weak vibronically structured absorption band at ~400 nm, which has been assigned as the p_π $(O^{2-}) \rightarrow Ru^{VI}$ charge transfer transition.[226] These cationic *trans*-dioxoruthenium(VI) complexes are strong oxidants with $E°(Ru^{VI/IV})$ of around 1.0 V vs. SCE at pH = 1; they can oxidize a wide variety of organic substrates, including alkanes.[226] The complex *trans*-$[Ru^{VI}(O)_2(phen)_2]$ $(ClO_4)_2$ has been found to catalyze the oxidation of cyclohexene and norbornene by PhIO.[228]

The IR spectra of *cis*-$[Ru^{VI}(O)_2(2,9\text{-}Me_2phen)_2]^{2+}$ and *cis*-$[Ru^{VI}(O)_2(6,6'\text{-}Cl_2bpy)_2]^{2+}$ show two $\nu(RuO_2)$ stretch bands at[230] 839 cm^{-1} and 787 cm^{-1} and at[229] 840 cm^{-1} and 790 cm^{-1}, respectively. An O—Ru—O angle of about 90° has been suggested from the IR data of *cis*-$[Ru^{VI}(O)_2(2,9\text{-}Me_2phen)_2]^{2+}$. Thermodynamically these *cis*-dioxoruthenium(VI) complexes are stronger oxidants than the corresponding *trans*-dioxoruthenium(VI) species. *cis*-$[Ru^{VI}(O)_2(2,9\text{-}Me_2phen)_2]^{2+}$ is found to catalyze the oxidation of alkenes such as norbornene, cyclohexene, and *trans*-β-methylstyrene with oxygen under pressure (2.7 atm) at 55 °C.[230] This complex is also able to catalyze hydroxylation of methane (at 4 atm and 75 °C) by H_2O_2.[231] Methane is oxidized to a 4:1 mixture of methanol and formaldehyde at a rate of 125 and 140 turnovers per day in water and acetonitrile, respectively. Under the same conditions ethane is oxidized to a mixture of ethanol and acetaldehyde, and propane to 1-propanol, propanal, and 2-propanol.[231] *cis*-$[Ru^{VI}(O)_2(6,6'\text{-}Cl_2bpy)_2]^{2+}$ is also able to oxidize a variety of substrates at room temperature, including chloride to chlorine, tetrahydrofuran to γ-butyrolactone, cyclohexane to cyclohexanone, toluene to benzaldehyde, and alkenes to epoxides.[229] Moreover, it is an active and robust catalyst for the electrochemical oxidation of MeOH, EtOH, propan-2-ol, and tetrahydrofuran;[232] and for the hydroxylation of alkanes by TBHP.[233] This complex has also been incorporated into a Nafion-coated basal-plane pyrolytic graphite electrode to produce a robust and active electrocatalyst for organic oxidations.[229,234]

A *trans*-dioxoruthenium(VI) complex containing the tpy ligand is also known. Oxidation of $[Ru^{II}(tpy)(C_2O_4)(H_2O)]$ by Ce^{IV} in 2 M $HClO_4$ produces *trans*-$[Ru^{VI}(O)_2(tpy)(H_2O)]^{2+}$ (**92**), whose structure has been characterized by X-ray crystallography.[235] The coordination geometry is approximately octahedral, the two oxo groups being *trans* to each other with an average Ru=O distance of 1.661 Å and an O=Ru=O angle of 171.3°. The complex is an active oxidant for a variety of organic substrates. The oxidation of the diphosphine 1,2-bis(diphenylphosphino)ethane (dppe) produces the corresponding diphosphine dioxide and a mechanism involving intramolecular rearrangement of the oxo group from an axial coordination position to one in the tpy plane following reduction from Ru^{VI} to Ru^{IV} is proposed (Equation (15)).

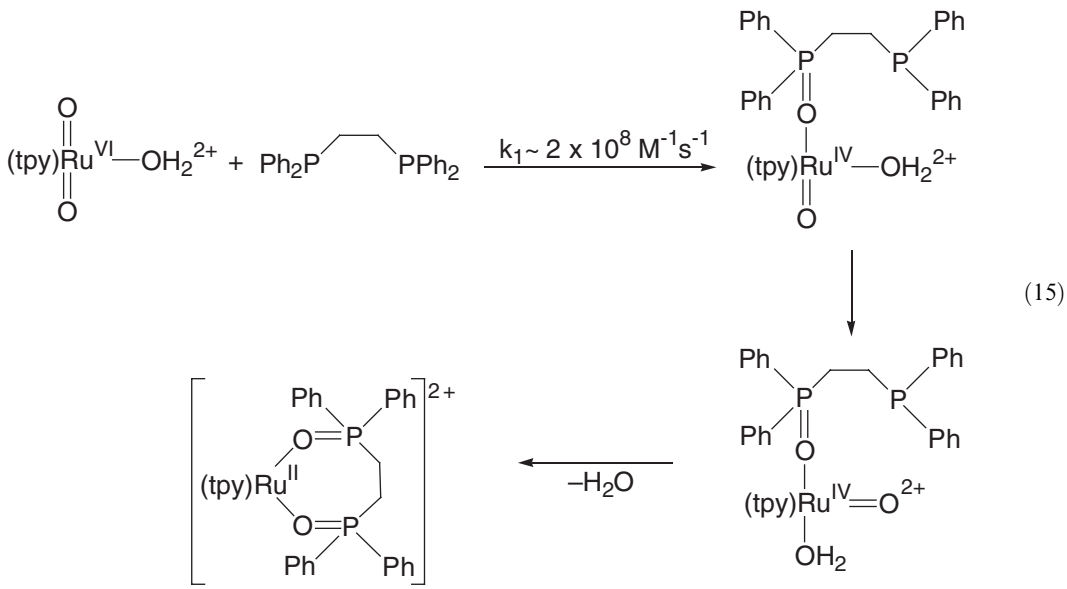


(**91**)



(**92**)

The kinetics and mechanisms of the oxidation of various other phosphines by *trans*-$[Ru^{VI}(O)_2(tpy)(H_2O)]^{2+}$ and *trans*-$[Ru^{VI}(O)_2(tpy)(MeCN)]^{2+}$ have also been investigated.[236]

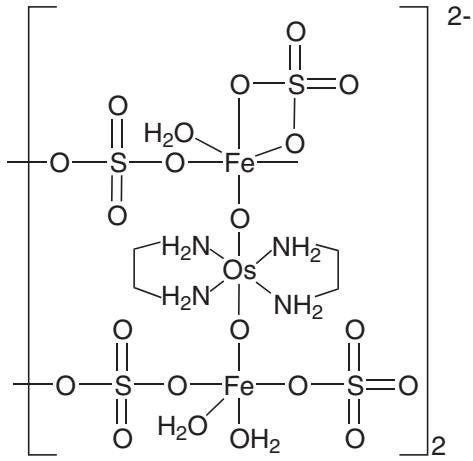


(15)

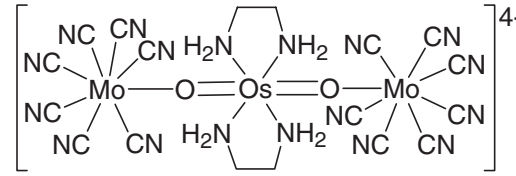
There are also a number of *cis*- and *trans*-dioxoosmium(VI) complexes containing pyridine and bipyridine ligands. These are in general much weaker oxidants than their ruthenium counterparts. The complexes *trans*-$[Os^{VI}(O)_2(py)_3(H_2O)]^{2+}$ and *trans*-$[Os^{VI}(O)_2(py)_2(X)_2]$ (X = Cl, Br) have been prepared by the reaction of $K_2[Os(O)_2(OH)_4]$ with pyridine followed by addition of HBF_4 and HX, respectively.[223] These complexes are characterized by vibrational spectroscopy ($\nu_{sym}(OsO_2)$ ~ 900 cm^{-1}). The electronic absorption spectra show bands at ~367 nm and 310–320 nm, characteristic of the *trans*-dioxoosmium(VI) moiety. *trans*-$[Os^{VI}(O)_2(bpy)(Cl)_2]$ ($\nu_{sym}(OsO_2) = 857\ cm^{-1}$) and *trans*-$[Os^{VI}(O)_2(4,4'\text{-}Bu^t{}_2bpy)(Cl)_2]$ ($\nu_{sym}(OsO_2) = 846\ cm^{-1}$) are also known.[218] *cis*- and *trans*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$ have also been prepared. Oxidation of *cis*-$[Os(bpy)_2(OH_2)_2]^{2+}$ (generated by acidification of *cis*-$[Os(bpy)_2(CO_3)]$) by Ce^{IV} produces *cis*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$, which isomerizes to *trans*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$ upon refluxing in dry acetonitrile. Both complexes are characterized by ^1H NMR and IR spectroscopy.[237] As in the case of the ruthenium analog, the *cis* complex shows two peaks in the IR at 883 cm^{-1} and 863 cm^{-1} assigned to the symmetric and asymmetric $\nu(OsO_2)$ stretches, respectively. As expected, the *trans* complex shows a single $\nu_{asym}(OsO_2)$ stretch in the IR at 872 cm^{-1}.

An interesting intensely blue complex ion is formed by the reversible reaction of $[Os(O)_2(en)_2]^{2+}$ with Fe^{2+}.[238] In the presence of sulfate ions the complex $[Os(O)_2(en)_2]_2[Os_2Fe_4(O)_4(SO_4)_8(en)_4(H_2O)_6]\cdot 12H_2O$ (**93**) can be isolated. The X-ray structure shows the linear ion $[(SO_4)_2Fe(\mu\text{-}O)Os(en)_2(\mu\text{-}O)Fe(SO_4)_2]^{2-}$, which is bridged by SO_4^{2-} to form an infinite one-dimensional planar ribbon-like array separated by cations.[238] The Os=O bond (average 1.845 Å) is much longer than that of the parent ion (average 1.734 Å), while the Fe—O bond (average 1.800 Å) is much shorter than the average single bond distance of 2.05 Å. Coordination of the oxo ligands in $[Os(O)_2(en)_2]^{2+}$ to Mo^{IV} is also reported.[239] Photolysis of yellow aqueous solutions of $[Mo(CN)_8]^{4-}$ leads to an orange-red species, thought to be $[Mo(CN)_7(OH_2)]^{3-}$, which quickly reacts with aqueous $[Os(O)_2(en)_2]^{2+}$ to produce a blue ion, $[Mo(CN)_7(\mu\text{-}O)Os(en)_2(\mu\text{-}O)Mo(CN)_7]^{4-}$ (**94**). The structure of $(AsPh_4)^+$ has been established by X-ray crystallography;[239] there is a remarkable change of the Os—O distances from 1.74 Å to 1.829 Å.

(b) Macrocyclic tertiary amine ligands. Apart from pyridine and polypyridyl ligands, macrocyclic tertiary amine ligands are also found to be oxidation resistant upon coordination and can stabilize high-valent ruthenium and osmium oxo complexes. A series of *trans*-dioxoruthenium(VI) complexes with macrocyclic tertiary amine ligands, *trans*-$[Ru^{VI}(O)_2(L)]^{2+}$ (L = 14-TMC, 15-TMC, 16-TMC, $CRMe_3$) (Figure 3),[240–243] *trans*-$[Ru^{VI}(O)_2(TMEA)_2]^{2+}$ (TMEA = *N*,*N*,*N*′,*N*′,-tetramethyl-1,2-diaminoethane),[240] and *trans*-$[Ru^{VI}(O)_2(pytn)]^{2+}$,[244] have been prepared by the following method. Reaction of *trans*-$[Ru^{III}(L)Cl_2]^+$ {L = 14-TMC, 15-TMC, 16-TMC, $CRMe_3$, $(TMEA)_2$} with Ag^+ followed by oxidation with H_2O_2 yields *trans*-$[Ru^{VI}(O)_2(L)]^{2+}$, which can be isolated as the ClO_4^- or the PF_6^- salt (Equations (16) and (17)).[240]



(**93**)



(**94**)

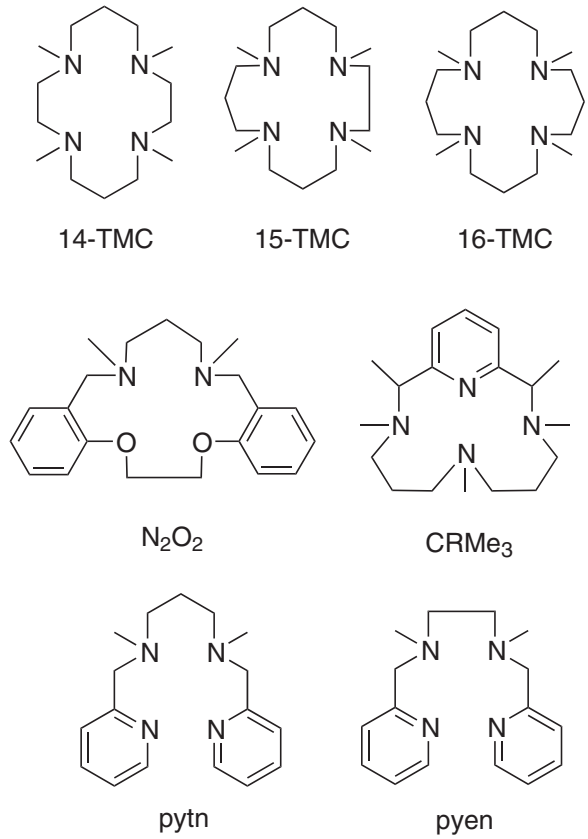


Figure 3 Macrocyclic ligands and related ligands.

$$trans\text{-}[Ru^{III}(L)(Cl)_2]^{+} \xrightarrow{Ag^{+},\, H_2O} trans\text{-}[Ru^{III}(L)(OH)(OH_2)]^{2+} \tag{16}$$

$$trans\text{-}[Ru^{III}(L)(OH)(OH_2)]^{2+} \xrightarrow{H_2O_2} trans\text{-}[Ru^{IV}(O)_2(L)] \tag{17}$$

The X-ray structures of *trans*-$[Ru^{VI}(O)_2(15\text{-TMC})](ClO_4)_2$ ($d(Ru{=}O) = 1.718$ Å) and *trans*-$[Ru^{VI}(O)_2(16\text{-TMC})](ClO_4)_2$ ($d(Ru{=}O) = 1.705$ Å) have been determined.[245] *trans*-$[Ru^{VI}(O)_2(pytn)]^{2+}$ has also been prepared by a similar route.[244] The IR spectral data of these complexes are listed in Table 4.

These *trans*-dioxoruthenium(VI) complexes have characteristic UV–vis absorption spectra. The σ-saturated nature of the macrocyclic tertiary amine ligands enables the high-energy metal-localized transition to be observed.[240] The weak vibronic structured band at ~370–400 nm has been assigned to $p_\pi\ (O^{2-}) \rightarrow Ru^{VI}$ charge transfer transition that is vibronically coupled to the Ru=O stretch. The position of this band is insensitive to the nature of the macrocyclic amine ligand, in accord with the formulation that the electronic transition involves the nonbonding d_π orbitals (Table 5, Figure 4). Similar electronic absorption bands have also been found for *trans*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$ [227] and *trans*-$[Ru^{VI}(O)_2\ (phen)_2]^{2+}$.[228] A very weak shoulder at ~430–450 nm could be due to the $(d_{xy})^2 \rightarrow (d_{xy})^1(d_\pi{*})^1$ transition. Bands in the region 220–320 nm are charge transfer transitions with substantial $\sigma N(L) \rightarrow Ru(VI)$ charge transfer character, as evidenced by the variation of the position and the relative intensity of these bands with the nature of the macrocyclic amine ligand.[240]

In general, tertiary amines are better σ-donors than pyridines. Hence dioxoruthenium(VI) complexes of macrocyclic tertiary amines are more stable and weaker oxidants than those of polypyridyls.

Although *trans*-$[Ru^{VI}(O)_2(CRMe_3)]^{2+}$ is a weak oxidant, upon irradiation with UV light it is able to oxidize a variety of substrates, including alcohols and alkenes.[246]

A dioxoruthenium(VI) complex containing a macrocyclic ligand with mixed N,O donor atoms, N_2O_2, is known. Oxidation of *trans*-$[Ru^{III}(N_2O_2)(OH)(OH_2)]^{2+}$ with Ce^{IV} gives *trans*-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$.[247] Because of the weaker donor strength of N_2O_2, *trans*-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$ is a stronger oxidant than *trans*-$[Ru^{VI}(O)_2(L)]^{2+}$ (L = 14-TMC, 15-TMC, 16-TMC, $CRMe_3$). The $E^\circ(Ru^{VI/IV})$ value is 0.92 V vs. SCE (at pH = 1.0) for *trans*-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$, which is 0.26 V higher than that of *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$, and is comparable to that of *trans*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$. It is capable of oxidizing a variety of organic substrates including alcohols, alkenes, aromatic hydrocarbons, and alkanes.[247]

There are two examples of *cis*-dioxoruthenium(VI) complexes containing tertiary amine ligands: *cis*-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$ (**95**) and *cis*-$[Ru^{VI}(O)_2(Me_3tacn)(CF_3CO_2)]^{+}$ (**96**).[249,260] Both have rather large O—Ru—O angles of >110°. Although both are active oxidants for organic substrates, they react with alkenes in non-protic solvents to give epoxides rather than vicinal diols. *cis*-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)](ClO_4)_2$ is prepared by the oxidation of *cis*-$[Ru^{III}(Tet\text{-}Me_6)(OH)(OH_2)]^{2+}$ in water with Ce^{IV}, followed by the addition of $NaClO_4$.[260] It is a green diamagnetic complex with IR bands at 874 and 859 cm^{-1} assigned to $\nu(RuO_2)$ stretches. Its structure has been characterized by X-ray crystallography ($d(Ru{=}O) = 1.795$ Å, O—Ru—O = 112.0°). *cis*-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$ is a strong oxidant ($E^\circ(Ru^{VI/IV}) = 0.80$ V vs. SCE at pH = 1.0), and is capable of oxidizing a variety of substrates including

Table 5 UV–visible spectral data of *trans*-dioxo(macrocyclic tertiary amine) complexes of Ru(VI), Ru(V), Os(VI), and Os(V) in acetonitrile.[240,251]

	λ_{max} (ε_{max}) (nm ($dm^3\ mol^{-1}\ cm^{-1}$))	
Complex	$^1[(d_{xz},d_{yz}) \leftarrow (d_{xy})]$	$^3[(d_{xz},d_{yz}) \leftarrow (d_{xy})]$
trans-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$	388 (560)	455sh (50)
trans-$[Ru^{VI}(O)_2(15\text{-TMC})]^{2+}$	377 (550)	430sh (50)
trans-$[Ru^{VI}(O)_2(16\text{-TMC})]^{2+}$	375 (670)	425sh (80)
trans-$[Ru^{V}(O)_2(14\text{-TMC})]^{+}$	422 (240)	525sh (20)
trans-$[Ru^{V}(O)_2(15\text{-TMC})]^{+}$	420 (260)	530sh (20)
trans-$[Ru^{V}(O)_2(16\text{-TMC})]^{+}$	448 (170)	550sh (10)
trans-$[Os^{VI}(O)_2(14\text{-TMC})]^{2+}$	312 (1260)	355 (340)
trans-$[Os^{VI}(O)_2(15\text{-TMC})]^{2+}$	307 (1815)	347 (475)
trans-$[Os^{VI}(O)_2(16\text{-TMC})]^{2+}$	306 (1915)	346 (345)
trans-$[Os^{V}(O)_2(14\text{-TMC})]^{+}$	335 (490)	410 (100)
trans-$[Os^{V}(O)_2(15\text{-TMC})]^{+}$	332 (540)	410 (120)
trans-$[Os^{V}(O)_2(16\text{-TMC})]^{+}$	330 (550)	410 (160)

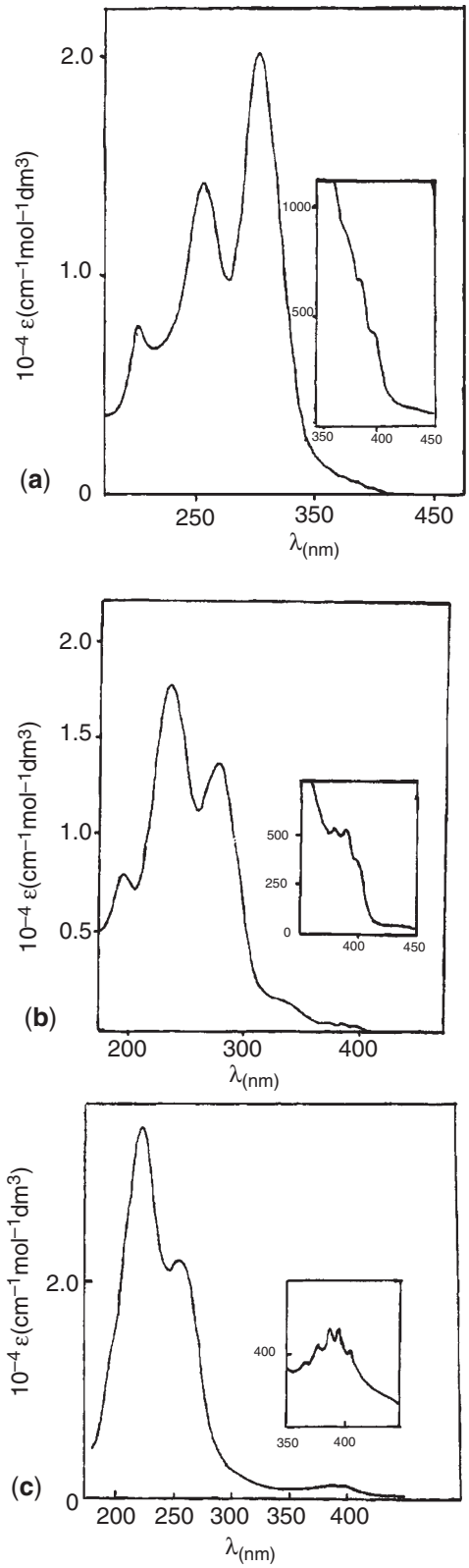
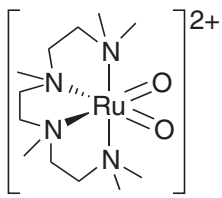
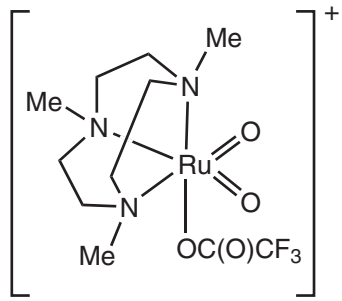


Figure 4 UV–vis spectra in CH_3CN: (a) *trans*-$[Ru^{VI}(O)_2(16\text{-TMC})]^{2+}$; (b) *trans*-$[Ru^{VI}(O)_2(15\text{-TMC})]^{2+}$; (c) *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$.

alcohols, alkenes, and alkanes.[260] The other *cis*-dioxoruthenium(VI) complex, *cis*-$[Ru^{VI}(O)_2(Me_3tacn)(CF_3CO_2)]ClO_4$, is similarly prepared as follows. Reaction of $[Ru(Me_3tacn)(Cl)_3]$ with $AgCF_3SO_3$ in aqueous CF_3CO_2H produces $[Ru(Me_3tacn)(CF_3CO_3)(OH_2)_2]^{2+}$, which is oxidized by Ce^{IV} to give *cis*-$[Ru^{VI}(O)_2(Me_3tacn)(CF_3CO_2)]^+$, isolated as a perchlorate salt.[249] The ν_{asym} and $\nu_{sym}(RuO_2)$ stretches of this green diamagnetic solid occur at 842 cm^{-1} and 856 cm^{-1}, respectively. The two Ru=O bond distances are identical (1.717 Å) and the O—Ru—O angle is 118.3°. This complex is able to stoichiometrically oxidize a variety of organic substrates, including alkenes and alkanes. In the oxidation of dimethyl sulfide, it functions as a four-electron oxidant. It can carry out catalytic oxidation of alkenes and alkanes using PhIO or TBHP as the terminal oxidant.

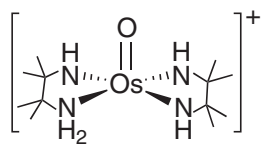


(**95**)



(**96**)

The six-coordinate *trans*-$[Os(O)_2(tmen)_2]^{2+}$ and five-coordinate $[Os(O)(tmen\text{-}2H)(tmen\text{-}H)]^+$ (**97a**) complexes have been prepared and are found to be in equilibrium in solution.[250] The X-ray structure of the five-coordinate square pyramidal Os^{VI}=O complex has been determined with a measured Os=O distance of 1.72 Å.[250]



(**97a**)

As in the case of ruthenium, a series of *trans*-dioxoosmium(VI) complexes with macrocyclic tertiary amine ligands, *trans*-$[Os^{VI}(O)_2(L)]^{2+}$ (L = 14-TMC, 15-TMC, 16-TMC, $CRMe_3$), have been synthesized by the method shown in Scheme 13.[251,252]

$$Na_2[Os^{IV}(Cl)_6] + L \xrightarrow[\text{reflux}]{\text{Sn/EtOH}} \textit{trans}\text{-}[Os^{III}(L)(Cl)_2]^+ \xrightarrow[\text{ii)}H_2O_2,\ 60^\circ C,\ 5\ min]{\text{i)}\ H_2O,\ 80^\circ C,\ 20\ min} \textit{trans}\text{-}[Os^{VI}(O)_2(L)]^{2+}$$

Scheme 13

It is likely that the dichloro species undergoes aquation in hot water to give an aqua species, which is then oxidized by H_2O_2 to give the dioxo species. Their IR spectra show a $\nu_{asym}(OsO_2)$ stretch at around 875 cm^{-1} (Table 4). Their UV–vis spectra are characterized by two vibronic structured electronic absorption bands centered at ~310 nm and 350 nm that are due to spin-allowed and spin-forbidden $p_\pi(O^{2-}) \rightarrow Os^{VI}$ charge transfer transitions (Table 5). Very weak absorptions are also observed in the tail of the low-energy band, which are due to ligand-field $d_{xy} \rightarrow d_\pi^*(d_{xz}, d_{yz})$ transitions. As in the case of ruthenium, the relative insensitivity of the LMCT transition to the nature of the equatorial ligands is in agreement with the lack of involvement of d_σ^* electrons. The much higher extinction coefficients of the $d_{xy} \rightarrow d_\pi^*$ transition for the osmium complexes than that of ruthenium, which appears as a weak shoulder at 455 nm ($\varepsilon_{max} = 50$ dm^3 mol^{-1} cm^{-1}) for *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})](ClO_4)_2$, have been attributed to the larger spin–orbit coupling

constant for the heavier osmium atom. The X-ray structure of $[Os^{VI}(O)_2(14\text{-TMC})](PF_6)_2$ has been determined. The dominant isomer present in the crystal is the RSSR isomer in which one pair of *N*-methyl groups is "up" and the other is "down." The average Os—O and Os—N distances are 1.735 Å and 2.126 Å, respectively.[253]

(ii) Electrochemistry

The electrochemistry of dioxoruthenium(VI) and dioxoosmium(VI) complexes with polypyridyl and macrocyclic tertiary amine ligands has been extensively studied by cyclic voltammetric techniques.[7] In general, *cis*-dioxo species have higher reduction potentials than the corresponding *trans*-dioxo species.[237,248,254] For the *trans*-dioxo species, the d_π orbital ordering is $d_{xy} < d_{xz},d_{yz}$ (the O═M═O bond axis is taken as the *z*-axis). Reduction of M^{VI} ($(d_{xy})^2$) to M^{V} ($(d_{xy})^1(d_\pi{*})^1$) would involve adding an electron to d_{xz},d_{yz} ($d_\pi{*}$) which have considerable antibonding character arising from $d_\pi{*}$(M)–p_π (O) mixing. The d_π orbital ordering in the *cis* isomer is $d_{\pi1} < d_{\pi2} \ll d_{xy}$ with the ground state electronic configuration $(d_{\pi1})^2$, where $d_{\pi1}$ and $d_{\pi2}$ are taken as if constructed from linear combinations of d_{xz} and d_{yz}, including spin–orbit coupling. Electronic destabilization effects in the reduction of M^{VI} to M^{V} are smaller since the $d_{\pi1}$–$d_{\pi2}$ energy separation is relatively small.

trans-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$, *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$, and related complexes display similar cyclic voltammograms in aqueous solutions.[254,255] At low pH (usually <7) three reversible/quasi-reversible redox couples corresponding to the redox reactions shown in Equations (18)–(20) are observed (Figure 5). At higher pH (usually >8) the two-electron $Ru^{VI/IV}$ couple splits into two reversible one-electron couples $Ru^{VI/V}$ and $Ru^{V/IV}$ (Equations (20) and (21)). The observation of a two-electron $Ru^{VI/IV}$ couple at low pH indicates that *trans*-dioxoruthenium(V) undergoes rapid acid-catalyzed disproportionation (Equation (23)).[256]

$$trans\text{-}[Ru^{VI}(O)_2]^{2+} + 2e^- + 2H^+ \longrightarrow trans\text{-}[Ru^{IV}(O)(OH_2)]^{2+} \quad (18)$$

$$trans\text{-}[Ru^{IV}(O)(OH_2)]^{2+} + e^- + H^+ \longrightarrow trans\text{-}[Ru^{III}(OH)(OH_2)]^{2+} \quad (19)$$

$$trans\text{-}[Ru^{III}(OH)(OH_2)]^{2+} + e^- + H^+ \longrightarrow trans\text{-}[Ru^{II}(OH_2)_2]^{2+} \quad (20)$$

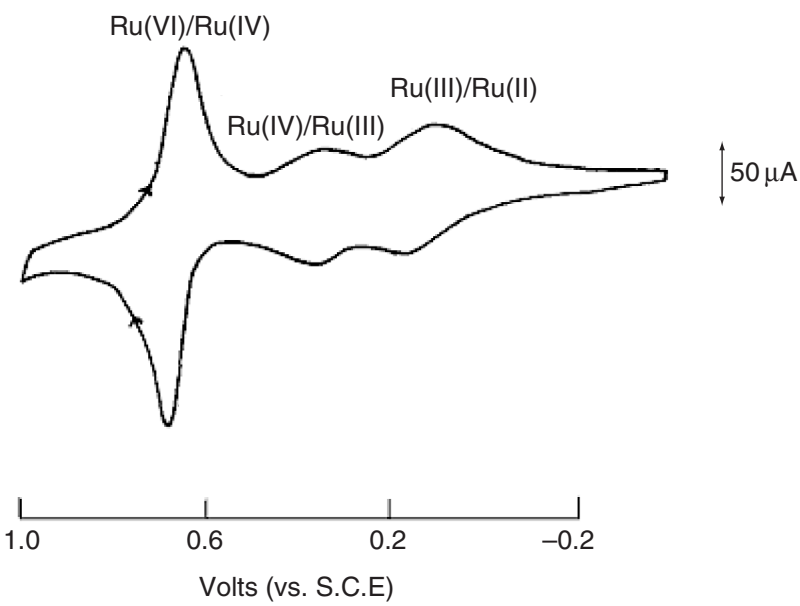


Figure 5 Cyclic voltammograms for *trans*-$[Ru^{VI}(16\text{-TMC})O_2](ClO_4)_2$ (~1 mM) in 0.1 M $HClO_4$ in MeCN. Conditions: working electrode, pyrolytic graphite; scan rate, 50 mV s^{-1}.

$$trans\text{-}[Ru^{VI}(O)_2]^{2+} + e^- \longrightarrow trans\text{-}[Ru^{V}(O)_2]^{+} \quad (21)$$

$$trans\text{-}[Ru^{V}(O)_2]^{+} + e^- + H^+ \longrightarrow trans\text{-}[Ru^{IV}(O)(OH)]^{+} \quad (22)$$

$$2[Ru^{V}(O)_2]^{+} + 2H^+ \longrightarrow [Ru^{IV}(O)(OH_2)]^{2+} + [Ru^{VI}(O)_2]^{2+} \quad (23)$$

The kinetics of the disproportionation of $[Ru^{V}(O)_2(TMC)]^{+}$ is described in Section 5.6.5.4.1(ii). As expected, the E° values of these proton-coupled redox couples shift cathodically with increase in pH in a manner predicted by the Nernst equation. The reversibilities of these redox couples are strongly affected by the pretreatment of the electrode (see Section 5.6.6.6.1(ii)). The Pourbaix diagrams for *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$ and *trans*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$ are shown in Figures 6 and 7, respectively. The electrochemical data of *trans*-dioxoruthenium(VI) complexes are summarized in Table 6. The change in ring size on going from 14-TMC to 16-TMC has little effect on the redox potentials. However, replacing amine nitrogens with weaker σ-donor atoms such as pyridine nitrogen or ether oxygen leads to an increase in redox potential. For example, E° for the $Ru^{VI/IV}$ couple follows the order L = 14-TMC < $CRMe_3$ < N_2O_2 < quaterpy (quaterpy=3″,5,5′,5‴-tetramethy1-2,2′:6′,2″:6″,2‴-quaterpyridine). *trans*-$[Ru^{VI}(O)_2(quaterpy)]^{2+}$ is by far the most strongly oxidizing *trans*-dioxoruthenium(VI) complex known.[257] Similar ligand effects on the reduction potentials of Ru^{IV}=O complexes have also been observed.

The electrochemistry of *cis*-dioxoruthenium(VI) complexes also shows pH-dependent redox couples. In the cyclic voltammogram of *cis*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$ four couples are observed (Equations (24)–(27)) even at pH 1: $Ru^{VI/V}$, $Ru^{V/IV}$, $Ru^{IV/III}$, and $Ru^{III/II}$.[254,392]

$$cis\text{-}[Ru^{VI}(O)_2(bpy)_2]^{2+} + H^+ + e^- \longrightarrow cis\text{-}[Ru^{V}(O)(bpy)_2(OH)]^{2+} \quad (24)$$

$$cis\text{-}[Ru^{V}(O)(bpy)_2(OH)]^{2+} + H^+ + e^- \longrightarrow cis\text{-}[Ru^{IV}(O)(bpy)_2(OH_2)]^{2+} \quad (25)$$

$$cis\text{-}[Ru^{IV}(O)(bpy)_2\,(OH_2)]^{2+} + 2H^+ + e^- \longrightarrow cis\text{-}[Ru^{III}(bpy)_2(OH_2)_2]^{3+} \quad (26)$$

$$cis\text{-}[Ru^{III}(bpy)_2(OH_2)_2]^{3+} + e^- \longrightarrow cis\text{-}[Ru^{II}(bpy)_2(OH_2)_2]^{2+} \quad (27)$$

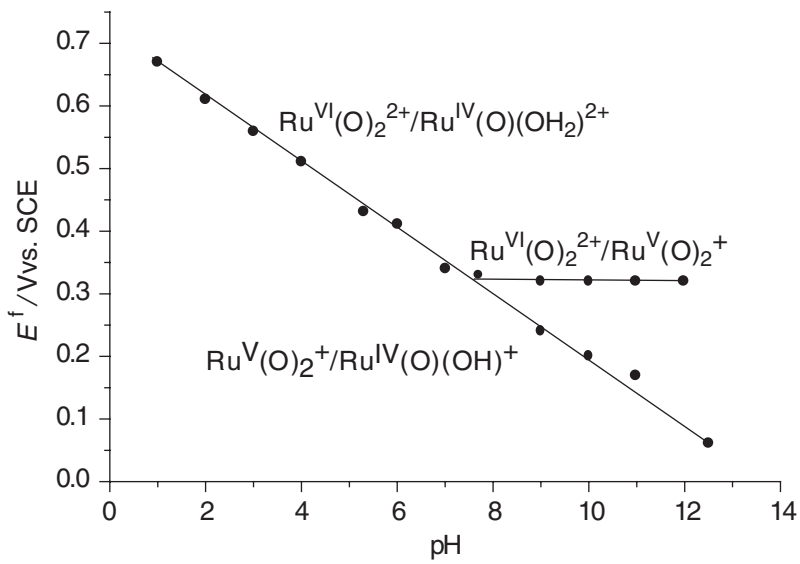


Figure 6 Pourbaix diagram for *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$.

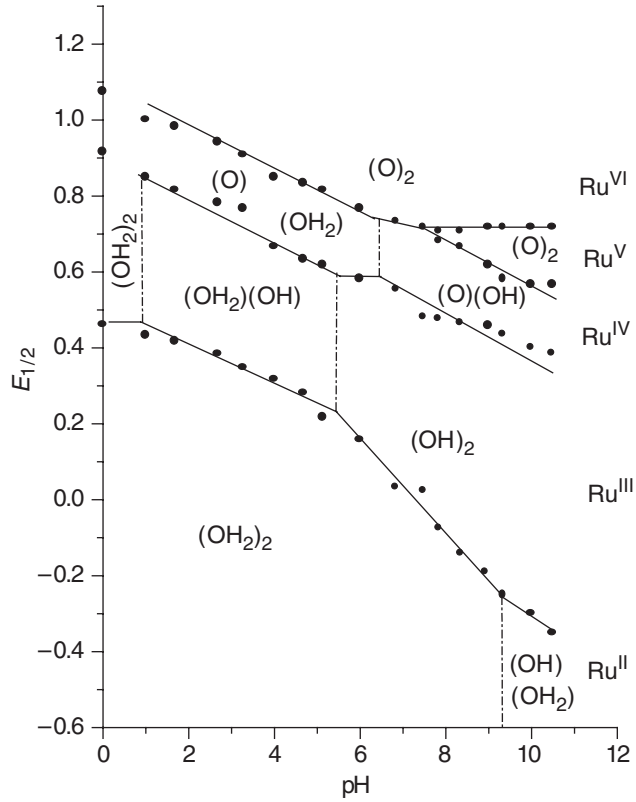


Figure 7 Pourbaix diagram for *trans*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$.

Table 6 Summary of formal potentials for selected ruthenium and osmium oxo complexes.

Complex	E°(V vs. SCE)	*References*
Ruthenium(VI)		
Electrode reaction (at pH 1.0): $[Ru^{VI}(O)_2]^{2+} + 2H^+ + 2e^- \rightarrow [Ru^{IV}(O)(OH_2)]^{2+}$		
trans-$[Ru^{VI}(O)_2(14\text{-TMC})](ClO_4)_2$	0.66	240
trans-$[Ru^{VI}(O)_2(15\text{-TMC})](ClO_4)_2$	0.65	240
trans-$[Ru^{VI}(O)_2(16\text{-TMC})](ClO_4)_2$	0.66	240
trans-$[Ru^{VI}(O)_2(TMEA)_2](ClO_4)_2$	0.67	240
trans-$[Ru^{VI}(O)_2(CRMe_3)](ClO_4)_2$	0.76	243
trans-$[Ru^{VI}(O)_2(pytn)](ClO_4)_2$	0.89	244
trans-$[Ru^{VI}(O)_2(N_2O_2)](ClO_4)_2$	0.92	247
trans-$[Ru^{VI}(O)_2(bpy)_2](ClO_4)_2$	1.01	227
trans-$[Ru^{VI}(O)_2(5,5'\text{-}Me_2bpy)](ClO_4)_2$	1.00	226
trans-$[Ru^{VI}(O)_2(quaterpy)](ClO_4)_2$	1.12	257
cis-$[Ru^{VI}(O)_2(6,6'\text{-}Cl_2bpy)_2](ClO_4)_2$	1.17	234
Ruthenium(VI)		
Electrode reaction (at pH 1.0): $[Ru^{VI}(O)_2]^{2+} + H^+ + e^- \rightarrow [Ru^{V}(O)(OH)]^{2+}$		
cis-$[Ru^{VI}(O)_2(bpy)_2](ClO_4)_2$	1.23	254,392
cis-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)](ClO_4)_2$	0.80	260
Ruthenium(V)		
Electrode reaction: $[Ru^{V}(O)X]^{2+} + e^- \rightarrow [Ru^{IV}(O)X]^{+}$		
$[Ru^{V}(O)(N_4O)](ClO_4)_2$	0.98 (pH 4.0)	492
$[Ru^{V}(O)(pyen)Cl]^{2+}$	1.29 (pH 1.0) (V vs. $Cp_2Fe^{+/0}$)	385
trans-$[Ru^{V}(O)(14\text{-TMC})(NCO)]^{2+}$	0.89 (MeCN)	240
trans-$[Ru^{V}(O)(14\text{-TMC})(Cl)]^{2+}$	1.10 (MeCN)	240

Table 6 continued

Complex	*E*°(V vs. SCE)	*References*
trans-$[Ru^{V}(O)(14\text{-TMC})(N_3)]^{2+}$	0.72 (MeCN)	240
trans-$[Ru^{V}(O)(15\text{-TMC})Cl]^{2+}$	1.10 (MeCN)	240
trans-$[Ru^{V}(O)(CRMe_3)(NCO)]^{2+}$	0.96 (MeCN)	243
trans-$[Ru^{V}(O)(TMEA)_2Cl]^{2+}$	1.06 (MeCN)	240
	(V vs. $Ag/AgNO_3$)	
trans-$[Ru^{V}(O)(py)_4Cl]^{2+}$	1.39 (MeCN)	486
Ruthenium(IV)		
Electrode reaction: $[Ru^{IV}(O)]^{2+} + H^+ + e^- \rightarrow [Ru^{III}(OH)]^{2+}$		
	(V vs. SCE)	
$[Ru^{IV}(O)(tpy)(bpy)](ClO_4)_2$	0.62 (pH7.0)	481
$[Ru^{IV}(O)(tpy)(4,4'\text{-}Me_2bpy)](ClO_4)_2$	0.55 (pH 7.0)	481
cis-$[Ru^{IV}(O)(tpy)(pic)](ClO_4)_2$	0.56 (pH 7.0)	483
trans-$[Ru^{IV}(O)(tpy)(pic)](ClO_4)_2$	0.45 (pH 7.0)	483
$[Ru^{IV}(O)(tpy)(TMEA)](ClO_4)_2$	0.93 (pH 1.0)	476
$[Ru^{IV}(O)(tpy)(6,6'\text{-}Cl_2bpy)](ClO_4)_2$	1.13 (pH 1.0)	269
$[Ru^{IV}(O)(bpy)_2(PEt_3)]^{2+}$	0.97 (pH 2.0)	489
$[Ru^{IV}(O)(bpy)_2(SbPh_3)]^{2+}$	1.10 (pH 2.0)	489
$[Ru^{IV}(O)(bpy)_2(PMe_3)]^{2+}$	1.10 (pH 2.0)	489
$[Ru^{IV}(O)(bpy)_2(P^iPr_3)]^{2+}$	0.98 (pH 2.0)	489
$[Ru^{IV}(O)(bpy)_2(PPh_3)]^{2+}$	1.06 (pH 2.0)	489
$[Ru^{IV}(O)(bpy)_2(AsPh_3)]^{2+}$	0.97 (pH 2.0)	489
$[Ru^{IV}(O)(bpy)_2(PCy_3)]^{2+}$	0.99 (pH 2.0)	489
$[Ru^{IV}(O)(bpy)_2(P(p\text{-}CF_3C_6H_4)_3)]^{2+}$	1.23 (pH 2.0)	489
$[Ru^{IV}(O)(bpy)(biq)(PEt_3)]^{2+}$	0.91 (pH 1.97)	475
$[Ru^{IV}(O)(biq)_2(PEt_3)]^{2+}$	0.91 (pH 1.97)	475
$[Ru^{IV}(O)(bpy)(biq)(PPh_3)]^{2+}$	1.0 (pH 2.0)	475
$[Ru^{IV}(O)(tpm)(bpy)](ClO_4)_2$	0.71 (pH 7.0)	483
$[Ru^{IV}(O)(tpm)(4,4'\text{-}Me_2bpy)](ClO_4)_2$	0.66 (pH 7.0)	483
$[Ru^{IV}(O)(tpm)(phen)](ClO_4)_2$	0.71 (pH 7.0)	483
$[Ru^{IV}(O)(OH_2)(14\text{-TMC})]^{2+}$	0.36 (pH 1.0)	240
$[Ru^{IV}(O)(OH_2)(15\text{-TMC})]^{2+}$	0.34 (pH 1.0)	240
$[Ru^{IV}(O)(OH_2)(16\text{-TMC})]^{2+}$	0.33 (pH 1.0)	240
$[Ru^{IV}(O)(OH_2)(CRMe_3)]^{2+}$	0.52 (pH 1.1)	243
$[Ru^{IV}(O)(OH_2)(N_2O_2)](ClO_4)_2$	0.62 (pH 1.0)	247
$[Ru^{IV}(O)(Me_3tacn)(bpy)]^{2+}$	0.53 (pH 7.0)	498
Osmium(VI)		
Electrode reaction: $[Os^{VI}(O)_2]^{2+} + e^- \rightarrow [Os^{V}(O)_2]^{+}$		
	(V vs. $Cp_2Fe^{+/0}$, CH_2Cl_2)	
cis-$[Os^{VI}(O)_2(S_2O_3)_2]Na_2$	−1.10	300
	(V vs. $Cp_2Fe^{+/0}$, CH_3CN)	
trans-$[Os^{VI}(O)_2(CN)_4](Ph_4As)_2$	−1.52	217
	(V vs. $Ag/AgNO_3$, CH_3CN)	
trans-$[Os^{VI}(O)_2(3\text{-}Bu^t\text{-saltmen})]$	−1.38	311
trans-$[Os^{VI}(O)_2(tmen)(CN)_2]$	−1.02	218
	(V vs. $Ag/AgNO_3$, CH_3CN)	
trans-$[Os^{VI}(O)_2(4,4'\text{-}Me_2bpy)(CN)_2]$	−0.88	218
	(V vs. $Ag/AgNO_3$, CH_3CN)	
Electrode reaction: $[Os^{VI}(O)_2]^{2+} + H^+ + e^- \rightarrow [Os^{V}(O)_2(OH)]^{2+}$		
cis-$[Os^{VI}(O)_2(bpy)_2]^{2+}$	0.81 (pH 1.0)	237
Electrode reaction: $[Os^{VI}(O)_2]^{2+} + 3H^+ + 3e^- \rightarrow [Os^{III}(OH)(OH_2)]^{2+}$		
trans-$[Os^{VI}(O)_2(bpy)_2]^{2+}$	0.51 (pH 1.0)	237
trans-$[Os^{VI}(O)_2(14\text{-TMC})](ClO_4)_2$	0.04 (pH 1.0)	251
trans-$[Os^{VI}(O)_2(15\text{-TMC})](ClO_4)_2$	0.05 (pH 1.0)	251
trans-$[Os^{VI}(O)_2(16\text{-TMC})](ClO_4)_2$	0.05 (pH 1.0)	251
trans-$[Os^{VI}(O)_2(CRMe_3)](ClO_4)_2$	0.14 (pH 1.0)	251
Electrode reaction: $[Os^{VI}(O)(OH)(OH_2)]^{3+} + 3H^+ + 3e^- \rightarrow [Os^{III}(OH_2)_3]^{3+}$		
trans-$[Os^{VI}(O)(OH)(OH_2)]^{3+}$	0.44 (pH 1.0)	262

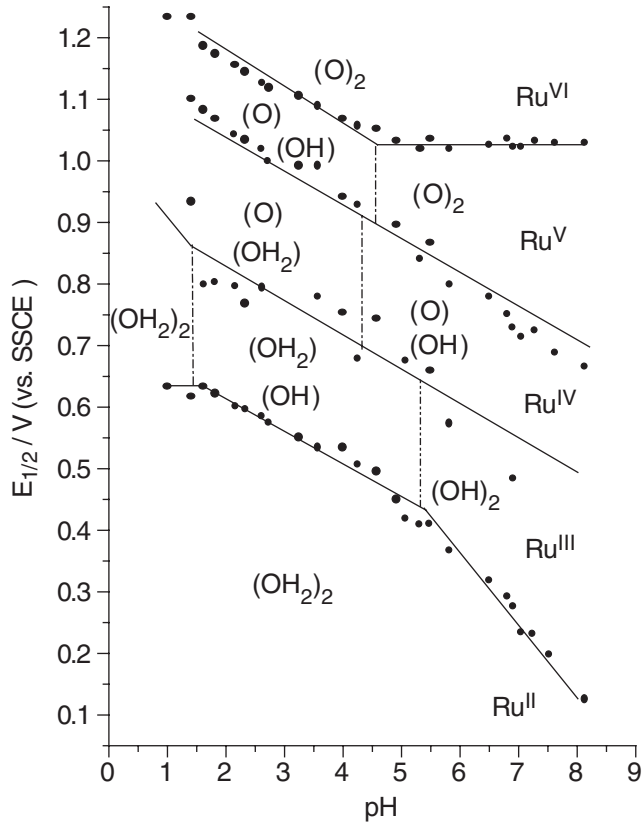


Figure 8 Pourbaix diagram for *cis*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$.

The Pourbaix diagram for *cis*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$ is shown in Figure 8. Similar electrochemical behavior is observed for *cis*-$[Ru^{VI}(O)_2(L)_2]^{2+}$ (L = 6,6′-Me_2bpy, 2,9-Me_2phen).[258] The cyclic voltammogram in acidic medium shows all four couples, though not all of them are reversible. The electrochemical steps have not been easily observed individually, the difficulties being attributed to absorption phenomena or precipitations on the electrodes, and slow electrochemical kinetics.

Electrodes coated with thin polymeric films of poly-*cis*-$[Ru(vbpy)_2(H_2O)_2]^{2+}$ (vbpy = 4-methyl-4′-vinyl-2,2′-bipyridine) or poly-*cis*-$[Ru(pyr\text{-}bpy)_2(H_2O)_2]^{2+}$ (pyr-bpy = 4-(2-pyrrol-1-yl-ethyl)-4′-methyl-2,2′-bipyridine) have been prepared, and cyclic voltammograms of these films are similar to that of *cis*-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$ in solution.[259]

The cyclic voltammogram of *cis*-$[Ru^{VI}(O)_2(6,6'\text{-}Cl_2bpy)_2]^{2+}$ at pH 1–3 shows only two couples assigned to $Ru^{VI/IV}$ and $Ru^{IV/II}$ (Equations (28) and (29)). For *cis*-$[Ru^{VI}(Tet\text{-}Me_6)(O)_2]^{2+}$(**95**) three couples are observed at pH 1 due to $Ru^{VI/IV}$, $Ru^{IV/III}$, and $Ru^{III/II}$ (Equations (30)–(32)).[260]

$$cis\text{-}[Ru^{VI}(O)_2(6,6'\text{-}Cl_2bpy)_2]^{2+} + 2e^- + 2H^+ \longrightarrow cis\text{-}[Ru^{IV}(O)(6,6'\text{-}Cl_2bpy)_2(OH_2)]^{2+} \quad (28)$$

$$cis\text{-}[Ru^{IV}(O)(6,6'\text{-}Cl_2bpy)_2(OH_2)]^{2+} + 2e^- + 2H^+ \longrightarrow cis\text{-}[Ru^{II}(6,6'\text{-}Cl_2bpy)_2(OH_2)_2]^{2+} \quad (29)$$

$$cis\text{-}[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+} + 2e^- + 2H^+ \longrightarrow cis\text{-}[Ru^{IV}(O)(OH_2)(Tet\text{-}Me_6)]^{2+} \quad (30)$$

$$cis\text{-}[Ru^{IV}(O)(OH_2)(Tet\text{-}Me_6)]^{2+} + e^- + H^+ \longrightarrow cis\text{-}[Ru^{III}(Tet\text{-}Me_6)(OH)(OH_2)]^{2+} \quad (31)$$

$$cis\text{-}[Ru^{III}(Tet\text{-}Me_6)(OH)(OH_2)]^{2+} + e^- + H^+ \longrightarrow cis\text{-}[Ru^{II}(Tet\text{-}Me_6)(OH_2)_2]^{2+} \quad (32)$$

At pH 2 the $Ru^{VI/IV}$ couple begins to split into two quasi-reversible one-electron waves, corresponding to the $Ru^{VI/V}$ and $Ru^{V/IV}$ couples (Equations (33) and (34). At pH 4.5 the $Ru^{V/IV}$ and $Ru^{IV/III}$ couples merge to form a new two-electron $Ru^{V/III}$ couple (Equation (35)).

$$cis\text{-}[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+} + e^- \longrightarrow cis\text{-}[Ru^{V}(O)_2(Tet\text{-}Me_6)]^{+} \quad (33)$$

$$cis\text{-}[Ru^{V}(O)_2(Tet\text{-}Me_6)]^{+} + e^- + 2H^+ \longrightarrow cis\text{-}[Ru^{IV}(O)(OH_2)(Tet\text{-}Me_6)]^{2+} \quad (34)$$

$$cis\text{-}[Ru^{V}(O)_2(Tet\text{-}Me_6)]^{+} + 2e^- + 3H^+ \longrightarrow cis\text{-}[Ru^{III}(Tet\text{-}Me_6)(OH)(OH_2)]^{2+} \quad (35)$$

The Pourbaix diagram for $cis\text{-}[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$ is shown in Figure 9. These electrochemical data show that for this system Ru^{V} is unstable with respect to disproportionation at pH 1, while Ru^{IV} is unstable at pH.4.5. The Ru^{V} complex $cis\text{-}[Ru^{V}(O)_2(Tet\text{-}Me_6)]^{+}$ has been isolated and is found to disproportionate in strongly acidic medium (Equation (36)).

$$2\ cis\text{-}[Ru^{V}(O)_2(Tet\text{-}Me_6)]^{+} + 2H^+ \longrightarrow cis\text{-}[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+} + cis\text{-}[Ru^{IV}(O)(OH_2)(Tet\text{-}Me_6)]^{2+} \quad (36)$$

$cis\text{-}[Ru^{VI}(O)_2(OH_2)(Me_3tacn)]^{2+}$, which contains a facially coordinated Me_3tacn ligand,[249] shows three reversible couples at pH 1 (Equations (37)–(39)). As the pH increases the $Ru^{V/III}$ couple splits into $Ru^{V/IV}$ and $Ru^{IV/III}$ couples.

$$cis\text{-}[Ru^{VI}(O)_2(OH_2)(Me_3tacn)]^{2+} + H^+ + e^- \longrightarrow cis\text{-}[Ru^{V}(O)(OH)(OH_2)(Me_3tacn)]^{2+} \quad (37)$$

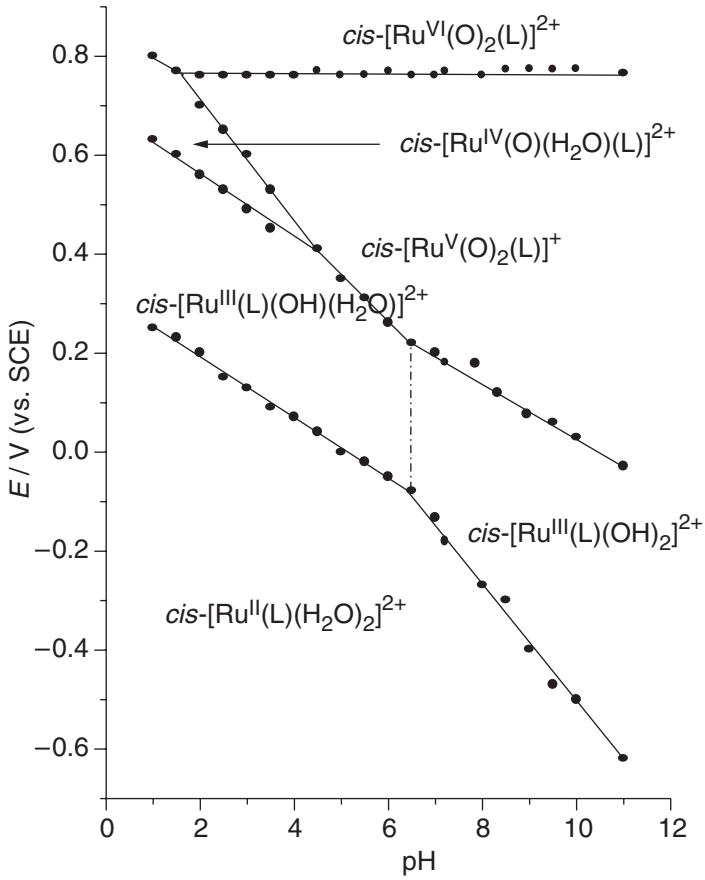


Figure 9 Pourbaix diagram for $cis\text{-}[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$.

$$cis\text{-}[Ru^{V}(O)(OH)(OH_2)(Me_3tacn)]^{2+} + 3H^{+} + 2e^{-} \longrightarrow cis\text{-}[Ru^{III}(Me_3tacn)(OH_2)_3]^{3+} \quad (38)$$

$$cis\text{-}[Ru^{III}(Me_3tacn)(OH_2)_3]^{3+} + e^{-} \longrightarrow cis\text{-}[Ru^{II}(Me_3tacn)(OH_2)_3]^{2+} \quad (39)$$

In acetonitrile, a reversible $Ru^{VI/V}$ couple is observed (Equation (40)) for *trans*-$[Ru^{VI}(O)_2(L)]^{2+}$ (L = 14-TMC, 15-TMC, 16-TMC, $(TMEA)_2$)[240] (Table 6). *cis*-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$ (**95**) also exhibits a reversible $Ru^{VI/V}$ couple in acetonitrile.[260] The electrochemistry of *cis*-$[Ru^{VI}(O)_2(b)_2]^{2+}$ (b = bpy and its derivatives) has not been explored due to its instability in organic solvents.

$$trans\text{-}[Ru^{VI}(O)_2(L)]^{2+} + e^{-} \longrightarrow trans\text{-}[Ru^{V}(O)_2(L)]^{+} \quad (40)$$

The electrochemistry of dioxoosmium(VI) complexes has also been extensively studied. The *trans*-dioxoosmium(VI) complexes of polypyridyl and macrocyclic tertiary amine ligands display very similar proton-coupled electron transfer couples. In aqueous solutions at pH < ~5–7 the cyclic voltammograms of *trans*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$ show a remarkable reversible three-electron $Os^{VI/III}$ couple and a one-electron $Os^{III/II}$ couple.[237] In the Pourbaix diagram two break points are observed in the pH dependence of the $Os^{VI/III}$ couple, which correspond to the pK_a values of Os^{III}—OH_2 and Os^{III}—$(OH)(OH_2)$ (Figure 10). The redox reactions are shown in Equations (41)–(43). At pH >8 the 3e $Os^{VI/III}$ wave splits into a pH-independent 1e $Os^{VI/V}$ wave and a $2e/2H^{+}$ $Os^{V/III}$ wave (Equations (44) and (45)).

$$trans\text{-}[Os^{VI}(O)_2(bpy)_2]^{2+} + 3e^{-} + 4H^{+} \longrightarrow trans\text{-}[Os^{III}(bpy)_2(OH_2)_2]^{3+} \quad (41)$$

$$trans\text{-}[Os^{VI}(O)_2(bpy)_2]^{2+} + 3e^{-} + 3H^{+} \longrightarrow trans\text{-}[Os^{III}(bpy)_2(OH)(OH_2)]^{2+} \quad (42)$$

$$trans\text{-}[Os^{VI}(O)_2(bpy)_2]^{2+} + 3e^{-} + 2H^{+} \longrightarrow trans\text{-}[Os^{III}(bpy)_2(OH)_2]^{+} \quad (43)$$

$$trans\text{-}[Os^{VI}(O)_2(bpy)_2]^{2+} + e^{-} \longrightarrow trans\text{-}[Os^{V}(O)_2(bpy)_2]^{+} \quad (44)$$

$$trans\text{-}[Os^{V}(O)_2(bpy)_2]^{+} + 2e^{-} + 2H^{+} \longrightarrow trans\text{-}[Os^{III}(bpy)_2(OH)_2]^{+} \quad (45)$$

A reversible three-electron $Os^{VI/III}$ couple is also observed with $[Os^{VI}(O)_2(tpy)(OH)]^{+}$.[262] The electrochemical behavior of *trans*-$[Os^{VI}(O)_2(14\text{-}TMC)]^{2+}$ is also similar to that of *trans*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$ and the Pourbaix diagram is shown in Figure 11(a).[252] Only one break point is observed in the pH dependence of the $Os^{VI/III}$ couple, with slopes of −60 and −42 mV/pH, which correspond to the reactions shown in Equations (46) and (47).

$$trans\text{-}[Os^{VI}(O)_2(14\text{-}TMC)]^{2+} + 3e^{-} + 3H^{+} \longrightarrow trans\text{-}[Os^{III}(14\text{-}TMC)(OH)(OH_2)]^{2+} \quad (46)$$

$$trans\text{-}[Os^{VI}(O)_2(14\text{-}TMC)]^{2+} + 3e^{-} + 2H^{+} \longrightarrow trans\text{-}[Os^{III}(14\text{-}TMC)(OH)_2]^{+} \quad (47)$$

It appears that the observation of a reversible $Os^{VI/III}$ couple is a general feature of *trans*-dioxoosmium(VI) complexes in acidic media, indicating that the intermediates Os^{V} and Os^{IV} species undergo rapid acid-catalyzed disproportionation.

For *cis*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$ three couples are observed at pH 1, namely the $Os^{VI/V}$, $Os^{V/III}$, and $Os^{III/II}$ couples.[237] The $Os^{V/III}$ couple splits into two one-electron waves at pH 4, corresponding to the $Os^{V/IV}$ and the $Os^{IV/III}$ couples. The Pourbaix diagram for *cis*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$ is shown in Figure 11(b).

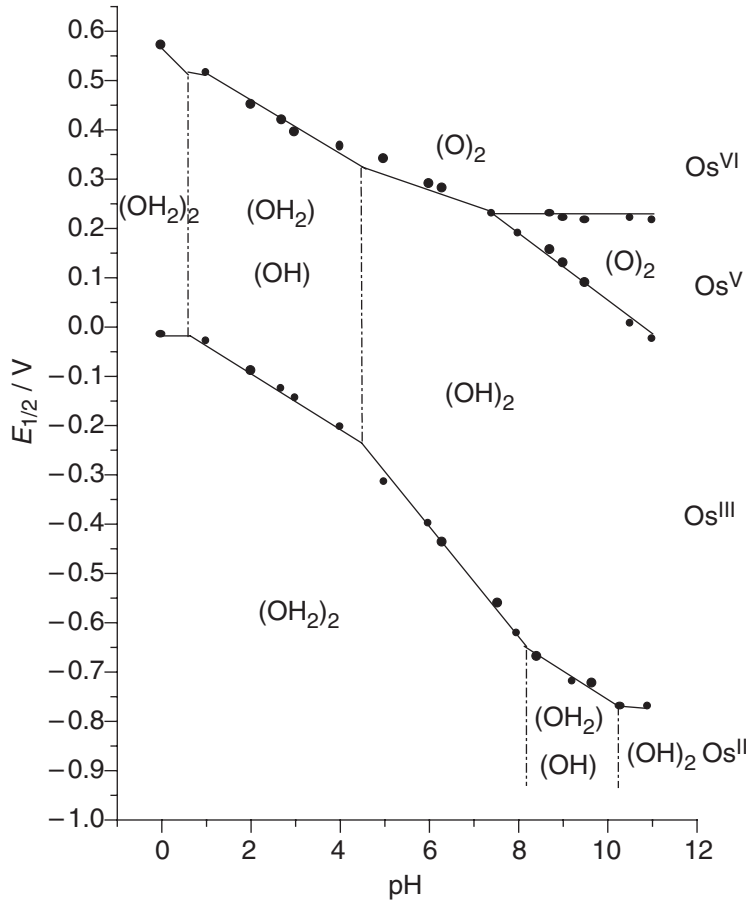


Figure 10 Pourbaix diagram for *trans*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$.

In acetonitrile, the cyclic voltammogram of *trans*-$[Os^{VI}(O)_2(L)]^{2+}$ (L = 14-TMC, 15-TMC, 16-TMC, $CRMe_3$) displays two reversible/quasi-reversible one-electron redox couples (Equations (48) and (49)).[251]

$$trans\text{-}[Os^{VI}(O)_2(L)]^{2+} + e^- \longrightarrow trans\text{-}[Os^{V}(O)_2(L)]^{+} \tag{48}$$

$$trans\text{-}[Os^{V}(O)_2(L)]^{+} + e^- \longrightarrow trans\text{-}[Os^{IV}(O)_2(L)] \tag{49}$$

The $Os^{VI/V}$ couples occur at −0.67 V to −0.73 V vs. $Cp_2Fe^{+/0}$ (Table 6),[214,251] while the $Os^{V/IV}$ couples occur at −1.48 V to −1.74 V. The change in the macrocyclic ring size of L has little effect on the E° values. However, a shift to more positive redox potential has been observed upon substitution of a tertiary amine nitrogen by a pyridyl group as in $CRMe_3$. This is attributed to greater σ-donating properties of tertiary amines than pyridines.

(iii) Reactivities

trans-Dioxoruthenium(VI) complexes with polypyridyl and macrocyclic tertiary amine ligands are active oxidants for a variety of organic and inorganic substrates. In general, the rates of oxidation increase with the redox potentials of the ruthenium complexes. The redox potentials ($Ru^{VI/V}$ and $Ru^{VI/IV}$) and the rates of oxidation of substrates by *trans*-$[Ru^{VI}(O)_2(L)]^{2+}$ follow the same order L = $(bpy)_2 > N_2O_2 > CRMe_3 >$ pytn > TMC. Replacing an amine nitrogen with a pyridine nitrogen in L will cause an increase in redox potentials and rates of reaction. *cis*-Dioxoruthenium(VI)

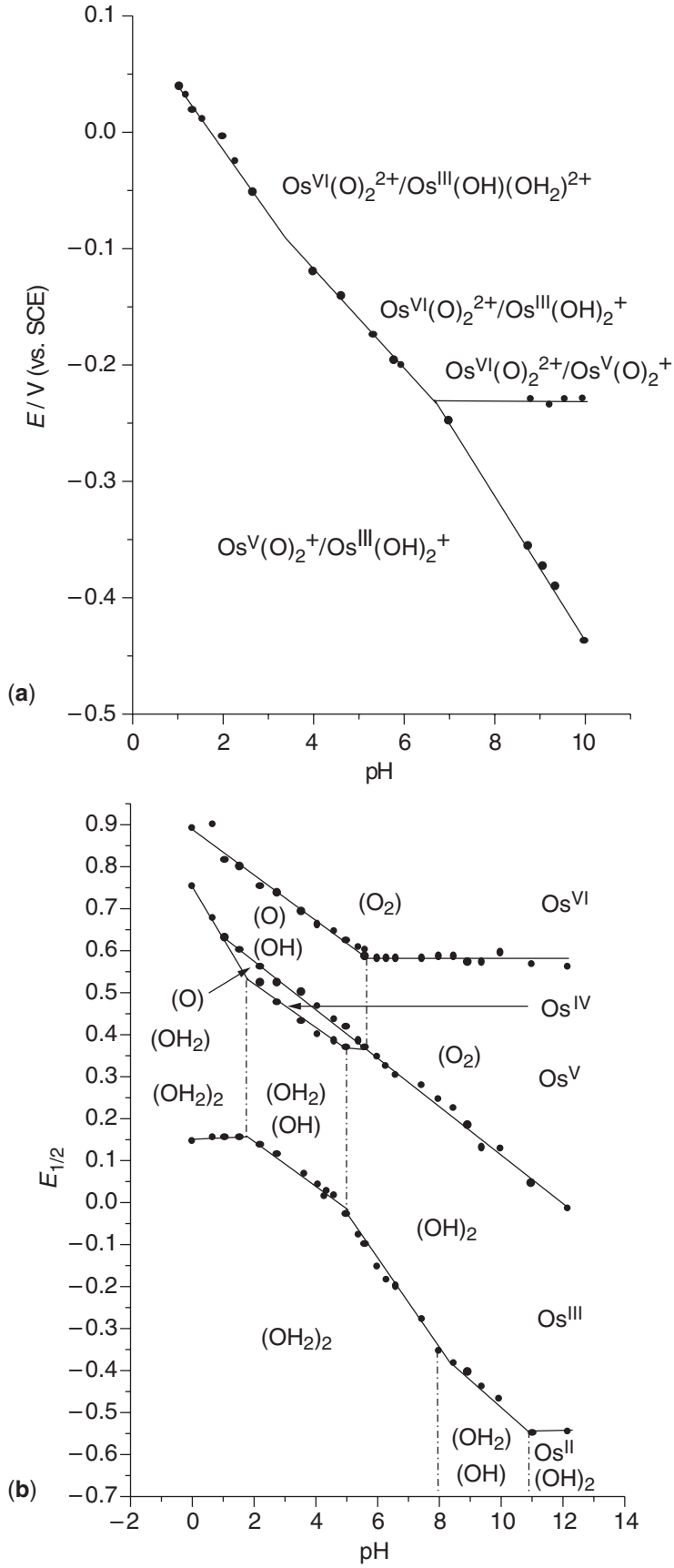


Figure 11 Pourbaix diagram: (a) *trans*-$[Os^{VI}(O)_2(14\text{-TMC})]^{2+}$; (b) *cis*-$[Os^{VI}(O)_2(bpy)_2]^{2+}$.

complexes have higher redox potentials than the corresponding *trans* complex and they react faster with reducing agents. *trans*-Dioxoosmium(VI) complexes are much more stable than their ruthenium counterparts, and in general they react only with strong reducing agents such as phosphines. However, *trans*-dioxoosmium(VI) complexes of macrocyclic tertiary amine ligands have strongly oxidizing and emissive excited states that are capable of oxidizing a wide variety of organic and inorganic substrates.

(a) Oxidation of organic substrates. The *trans*-dioxoruthenium(VI) complexes readily oxidize alcohols and ethers at ambient conditions. Tables 7–9 summarize the second-order rate constants for the oxidation of benzyl alcohol to benzaldehyde,[263] propan-2-ol to acetone,[263] and tetrahydrofuran to γ-butyrolactone,[264] respectively, by different *trans*-dioxoruthenium(VI) species. In general, the rates of oxidation increase with an increase in the redox potential of the $Ru^{VI/IV}$ couple. A linear free energy plot with a slope close to the theoretical value for a two-electron transfer (i.e., $16.8\,V^{-1}$) has been obtained for the oxidation of alcohols and THF. For the oxidation of benzyl alcohol, the kinetic isotope effects range from 15 to 19, and do not appear to have any correlation with the E° values of the $Ru^{VI/IV}$ couple.[263] A mechanism involving hydride abstraction or an initial hydrogen atom abstraction followed by rapid in-cage electron transfer has been suggested for the oxidation of these substrates. A [2 + 2] (C—H + Ru═O) addition mechanism has been proposed for the oxidation of benzhydrols by $[Ru(O)_2(14\text{-TMC})]^{2+}$.[265]

Oxidation of various alkylaromatics, including toluene, ethylbenzene, and cumene, by *trans*-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$ in MeCN also has large kinetic isotope effects ($k_H/k_D = 16$ for ethylbenzene), indicating C—H bond cleavage in the transition state. The second-order rate constants for ethylbenzene and cumene are similar but are substantially higher than that for toluene.[264] Representative kinetic data for the oxidation of ethylbenzene, cumene, and toluene are collected in Table 10.

Table 7 Representative kinetic data for the oxidation of benzyl alcohol by ruthenium oxo complexes.

Complex	k_2 *at 298 K*($M^{-1}\,s^{-1}$)	k_H/k_D	$\Delta H^{\ddagger}$ ($\Delta S^{\ddagger}$) (kcal mol^{-1} (eu))	*References*
trans-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$	1.98×10^{-4} (H_2O)			263
trans-$[Ru^{VI}(O)_2(TMEA)_2]^{2+}$	4.99×10^{-4} (H_2O)			263
trans-$[Ru^{VI}(O)_2(CRMe_3)]^{2+}$	3.25×10^{-3} (H_2O)	18 ± 2		263
trans-$[Ru^{VI}(O)_2(pytn)]^{2+}$	9.30×10^{-1} (H_2O)	15 ± 2		263
trans-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$	6.85×10^{-1} (H_2O)	19 ± 2	10 (−26)	263
trans-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$	2.08×10^{-1} (H_2O)	17 ± 2		263
trans-$[Ru^{VI}(O)_2(dmbpy)_2]^{2+}$	3.60 (H_2O)	19	8.3 (−23)	226
$[Ru^{V}(O)(N_4O)]^{2+}$	1.17×10^{2} (0.1 M $HClO_4$)	5.9	9.1 (−18)	387
trans-$[Ru^{V}(O)(14\text{-TMC})(NCO)]^{2+}$	1.40×10^{2} (CH_3CN)	4.1		383
trans-$[Ru^{V}(O)(14\text{-TMC})Cl]^{2+}$	2.1×10^{2} (CH_3CN)			383
cis-$[Ru^{V}(O)(pyen)(Cl)]^{2+}$	8.4×10^{4} (0.1 M HOTf)			385
$[Ru^{IV}(O)(bpy)_2(py)]^{2+}$	2.43 (0.1 M $HClO_4$)	50	5.7 (−38)	410,411
	1.54 (CH_3CN)		5.8 (−38)	410,411
$[Ru^{IV}(O)(tpy)(6,6'\text{-}Cl_2bpy)]^{2+}$	2.23 (0.1 M $HClO_4$)	39		269
$[Ru^{IV}(O)(tpy)(TMEA)]^{2+}$	2.4×10^{-2} (0.1 M $HClO_4$)			476
$[Ru^{IV}(O)(bpy)(PEt_3)]^{2+}$	9.2×10^{-2} (H_2O)			509
	2.8×10^{-1} (CH_3CN)			509
$[Ru^{IV}(O)(bpy)_2(PPh_3)]^{2+}$	1.05 (H_2O)			509
	8.3×10^{-1} (MeCN)			509
	5.5×10^{-1} (CH_2Cl_2)			509
$[Ru^{IV}(O)(bpy)_2(AsPh_3)]^{2+}$	6.8×10^{-1} (CH_3CN)			509
	5.8×10^{-1} (CH_2Cl_2)			509
$[Ru^{IV}(O)(bpy)(biq)(PEt_3)]^{2+}$	4.07×10^{-2} (H_2O)			475
	3.22×10^{-1} (CH_2Cl_2)			475
$[Ru^{IV}(O)(bpy)(biq)(PMe_3)]^{2+}$	6.62×10^{-1} (H_2O)			475
	5.35×10^{-1} (CH_2Cl_2)			475
$[Ru^{IV}(O)(bpy)(biq)(PPh_3)]^{2+}$	2.23 (H_2O)			475
	6.44×10^{-1} (CH_2Cl_2)			475

Table 8 Representative kinetic data for the oxidation of propan-2-ol by ruthenium oxo complexes.

Complex	k_2 *at 298 K* (M^{-1} s^{-1})	k_H/k_D	$\Delta H^{\ddagger}(\Delta S^{\ddagger})$ (kcal mol^{-1} (eu))	*References*
trans-$[Ru^{V}(O)_2(bpy)_2]^{2+}$	2.0 (H_2O)			263
trans-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$	5.6×10^{-2} (H_2O)	11	12 (−28)	263
	1.5×10^{-2} (MeCN)			263
trans-$[Ru^{VI}(O)_2(pytn)]^{2+}$	1.9×10^{-2} (H_2O)			263
$[Ru^{V}(O)(N_4O)]^{2+}$	13.5×10^{1} (0.1 M $HClO_4$)	5.3	9.2 (−22)	387
$[Ru^{IV}(O)(tpy)(bpy)]^{2+}$	6.7×10^{-2} (H_2O)	18	9 (−34)	411
$[Ru^{IV}(O)(bpy)_2(py)]^{2+}$	8.7×10^{-3} (MeCN)		8 (−42)	411
$[Ru^{IV}(O)(bpy)_2(PEt_3)]^{2+}$	1.35×10^{-3} (MeCN)			509
	2.3×10^{-3} (CH_2Cl_2)			509
$[Ru^{IV}(O)(bpy)_2(PPh_3)]^{2+}$	2.3×10^{-3} (H_2O)			509
$[Ru^{IV}(O)(tpy)(6,6'\text{-}Cl_2bpy)]^{2+}$	7.7×10^{-3} (MeCN)			269
$[Ru^{IV}(O)(tpy)(TMEA)]^{2+}$	4.3×10^{-3} (MeCN)			476

Table 9 Representative kinetic data for the oxidation of tetrahydrofuran by ruthenium oxo complexes.

Complex	k_2 *at 298 K*(M^{-1} s^{-1})	k_H/k_D	$\Delta H^{\ddagger}(\Delta S^{\ddagger})$ (kcal mol^{-1} (eu))	*References*
trans-$[Ru^{VI}(O)_2(CRMe_3)]^{2+}$	4.2×10^{-3} (0.1 M CF_3SO_3H)		14 (−28)	264
trans-$[Ru^{VI}(O)_2(pyen)]^{2+}$	1.2×10^{-2} (0.1 M CF_3SO_3H)			264
trans-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$	0.17 (0.1 M CF_3SO_3H)	20	10 (−28)	264
trans-$[Ru^{VI}(O)_2(bpy)_2]^{2+}$	3.5 (0.1 M CF_3SO_3H)			264
trans-$[Ru^{V}(O)(N_4O)]^{2+}$	31 (0.1 M $HClO_4$)	6	11.4 (−14)	387
RuO_4	4.3×10^{-2} (1.49 M $HClO_4$)	1.5	14 (−18)	607

Table 10 Representative kinetic data for the oxidation of ethylbenzene, cumene, and toluene by ruthenium oxo complexes.

Complex	k_2 *at 298 K*(M^{-1} s^{-1})	k_H/k_D	$\Delta H^{\ddagger}(\Delta S^{\ddagger})$ (kcal mol^{-1} (eu))	*References*
Ethylbenzene				
trans-$[Ru^{VI}(O)_2(pytn)]^{2+}$	1.32×10^{-3} (MeCN)	12	13 (−24)	264
trans-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$	1.98×10^{-3} (MeCN)	16	14 (−22)	264
trans-$[Ru^{VI}(O)_2(TPP)]$	2.2×10^{-4} (CH_2Cl_2/MeOH 19:1)			319
Cumene				
trans-$[Ru^{VI}(O)_2(pytn)]^{2+}$	1.96×10^{-3} (MeCN)		14 (−25)	264
trans-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$	2.9×10^{-3} (MeCN)		11 (−31)	264
trans-$[Ru^{VI}(O)_2(TPP)]$	3.16×10^{-4} (CH_2Cl_2/MeOH 19:1)			319
$[Ru^{IV}(O)(bpy)_2(py)]^{2+}$	2.6×10^{-2} (MeCN)			398b
Toluene				
trans-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$	1.8×10^{-5} (MeCN)			264
$[Ru^{IV}(O)(bpy)_2(py)]^{2+}$	5×10^{-5} (MeCN)			398b

The kinetics of the oxidation of alkenes by *trans*-$[Ru^{VI}(O)_2(14\text{-}TMC)]^{2+}$, *trans*-$[Ru^{VI}(O)_2(CRMe_3)]^{2+}$, *trans*-$[Ru^{VI}(O)_2(pytn)]^{2+}$, and *trans*-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$ with $E^{\circ}(Ru^{VI/V})$ ranging from 0.23 V to 0.70 V vs. SCE have been investigated in acetonitrile.[266] The rate constants depend on the redox potential of the ruthenium oxidant as well as on the oxidation potentials and

Table 11 Representative kinetic data for the oxidation of styrene by ruthenium oxo complexes.

Complex	k_2 *at 298 K*(M^{-1} s^{-1})	$\Delta H^{\ddagger}(\Delta S^{\ddagger})$ (kcal mol^{-1} (eu))	*References*
trans-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$	1×10^{-6} (MeCN)		217
trans-$[Ru^{VI}(O)_2(CRMe_3)]^{2+}$	1.5×10^{-5} (MeCN)	15 (−24)	217
trans-$[Ru^{VI}(O)_2(pytn)]^{2+}$	9.2×10^{-2} (MeCN)	12 (−24)	217
trans-$[Ru^{VI}(O)_2(N_2O_2)]^{2+}$	2.1×10^{-1} (MeCN)	11 (−22)	217
trans-$[Ru^{VI}(O)_2(TPP)]$	4.3×10^{-3} (CH_2Cl_2/MeOH 19:1)	10 (−35)	319
trans-$[Ru^{VI}(O)_2(OEP)]$	1.55×10^{-3} ($ClCH_2CH_2Cl$)	16 (−18)	319
$[Ru^{IV}(O)(bpy)_2(py)]^{2+}$	1.48×10^{-2} (MeCN)	7.2 (−43)	513
$[Ru^{IV}(O)(tpy)(6,6'\text{-}Cl_2bpy)]^{2+}$	2.8×10^{-2} (MeCN)	11.1 (−28.2)	269
$[Ru^{IV}(O)(tpy)(TMEA)]^{2+}$	2.0×10^{-2} (0.1 M $HClO_4$)		476
$[Ru^{IV}(O)(bpy)_2(PEt_3)]^{2+}$	3.7×10^{-3} (MeCN)	15.6 (−15.9)	490
	4.3×10^{-3} (CH_2Cl_2)	9.7 (−36.7)	490
$[Ru^{IV}(O)(bpy)_2(PPh_3)]^{2+}$	8.9×10^{-3} (MeCN)	13.1 (−22.5)	490
	9.1×10^{-3} (CH_2Cl_2)	13.3 (−23.4)	490

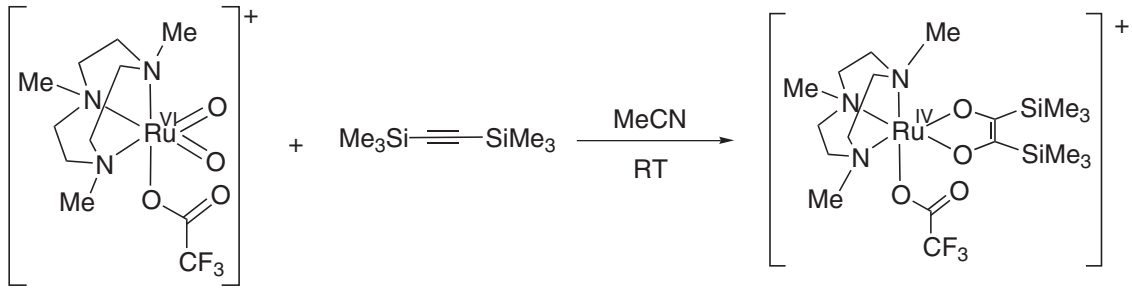
structures of the alkenes. Representative kinetic data for the oxidation of styrene are summarized in Table 11. For the oxidation of *para*-substituted styrenes a linear Hammett plot of log k_X/k_H vs. σ^+ of *para*-substituents with a ρ value of −2.1 has been obtained. A linear correlation between log k_X/k_H and $E^{\circ}(Ru^{VI/V})$ has been observed in the oxidation of styrene and norbornene, suggesting the importance of charge transfer in the transition state.

In general the reactivities of *cis*-dioxoruthenium(VI) complexes toward organic substrates are similar to that of the *trans* complexes. *cis*-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$ is also able to oxidize a variety of organic substrates at room temperature.[260] Alcohols are oxidized to aldehydes and ketones, and large α-CH deuterium isotope effects are observed ($k_H/k_D = 10$, 21, and 8 for 2-propanol, benzyl alcohol, and methanol, respectively). A linear Hammett plot for the oxidation of *para*-substituted benzyl alcohols with a slope of −1.0 is obtained. A hydride abstraction mechanism has been proposed. In general the rates of oxidation of alcohols by dioxoruthenium(VI) complexes appear to depend only on the $Ru^{VI/IV}$ redox potential, irrespective of whether the complex is *cis* or *trans*. Aromatic hydrocarbons are also readily oxidized by *cis*-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$. The oxidation of toluene, ethylbenzene, and cumene gives benzaldehyde, acetophenone and *s*-phenethyl alcohol, and 2-phenylisopropyl alcohol, respectively. The oxidation of alkenes such as styrene, *cis*- and *trans*-stilbene, and cyclooctene are again similar to that of the *trans* complexes; both epoxidation and oxidative cleavage of the C=C bond are observed. No diol products were reported. Oxidation of adamantane occurs predominantly at the tertiary C—H position. The complex *cis*-$[Ru^{VI}(O)_2(6,6'\text{-}Cl_2bpy)_2]^{2+}$ is among the most active and robust ruthenium oxidants.[229,233,267–269] It is able to oxidize stoichiometrically, among other substrates, unactivated C—H bonds such as cyclohexane and *n*-hexane at room temperature.

The complex *cis*-$[Ru^{VI}(O)_2(Me_3tacn)(CF_3CO_2)]^{+}$ is an active oxidant for alcohols and alkenes.[249] The oxidation of alkynes by this complex has also been investigated.[270] In MeCN in the presence of CF_3CO_2H, disubstituted alkynes are oxidized to 1,2-diketones in good to excellent yields under ambient conditions. The reaction proceeds via the formation of a dark blue ruthenium(IV) dioxolene intermediate, which is formally a [3 + 2] cycloadduct, as revealed by an X-ray structure determination of the adduct with bis(trimethylsilyl)acetylene (Scheme 14) (see Section 5.6.6.7.3). The kinetics of the cycloaddition with various substituted trimethylsilylacetylenes have been investigated. The rate constants are within an order of magnitude despite the large difference of ionization potentials (2.3 eV) of the substrates. A mechanism involving rate-limiting formation of a vinyl radical intermediate followed by subsequent collapse with the adjacent Ru=O moiety to form the ruthenium(IV) dioxolene product has been proposed.[270]

(b) Oxidation of inorganic substrates. The kinetics of the reduction of *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$ with the outer-sphere ruthenium(II) reductants *cis*-$[Ru(NH_3)_4(bpy)]^{2+}$, *cis*-$[Ru(NH_3)_4(isn)]^{2+}$ (isn = isonicotinamide), and $[Ru(NH_3)_5(py)]^{2+}$ have been investigated. From the rate data a self-exchange rate constant of 1.5×10^5 M^{-1} s^{-1} (25.0 °C and 0.1 M ionic strength) for the $[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}/[Ru^{V}(O)_2(14\text{-TMC})]^{+}$ couple has been obtained.[256] The rates and equilibrium constants for the reaction *trans*-$[Os^{VI}(O)_2(14\text{-TMC})]^{2+} + Q^{-} \rightleftharpoons$ *trans*-$[Os^{V}(O)_2\text{-}(14\text{-TMC})]^{+} + Q$

(Q = quinones) have been measured by pulse radiolysis methods.[253] From the results a self-exchange rate constant of $1.1 \times 10^6\ M^{-1}\ s^{-1}$ and a reduction potential of +0.048 V vs. NHE for Os^{VI}/Os^{V} have been obtained. The relatively fast self-exchange rates of the $Ru^{VI/V}$ and $Os^{VI/V}$ couples are consistent with the reactions being adiabatic, with relatively small inner-sphere reorganization barriers. The small barriers are due to small bond distance changes when the oxidation states differ only in their d_π orbital populations.[253]



Scheme 14

The reduction of *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$ by Fe^{2+} has an enthalpy of activation that is close to zero and a large negative entropy of activation, $\Delta H^{\ddagger} = 1.3 \pm 0.3\ kJ\ mol^{-1}$ and $\Delta S^{\ddagger} = -(210 \pm 20)\ J\ K^{-1}\ mol^{-1}$ at 1.0 M ionic strength, consistent with an inner-sphere mechanism.[271]

The oxidation of I^- by *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$ in aqueous acidic solution has the following stoichiometry: *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+} + 3I^- + 2H^+ \rightarrow$ *trans*-$[Ru^{IV}(O)(OH_2)(14\text{-TMC})]^{2+} + I_3^-$. The rate law is $-d[Ru(VI)]/dt = (k_a + k_b[H^+])[Ru^{VI}][I^-]$ with $k_a = 0.041\ M^{-1}\ s^{-1}$ and $k_b = 18.5\ M^{-2}\ s^{-2}$ at 25.0 °C and 0.1 M ionic strength. A mechanism involving oxygen atom transfer from $O{=}Ru^{VI}{=}O$ to I^- is consistent with the data.[272]

The oxidation of SO_3^{2-} by *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+}$ has the following stoichiometry in aqueous solution: *trans*-$[Ru^{VI}(O)_2(14\text{-TMC})]^{2+} + SO_3^{2-} + H_2O \rightarrow$ *trans*-$[Ru^{IV}(O)(OH_2)(14\text{-TMC})]^{2+} + SO_4^{2-}$. The rate law is $-d[Ru^{VI}]/dt = k/(1 + [H^+]/K)[Ru^{VI}][S^{IV}]$ with $k = 7.0 \times 10^4\ M^{-1}\ s^{-1}$ and $K = 3.4 \times 10^{-7}$ M at 1.0 M ionic strength. A simple outer-sphere mechanism can be ruled out since k is more than two orders of magnitude greater than predicted by the Marcus cross-relation, and an oxygen atom transfer mechanism has been proposed.[273]

The oxidation of hypophosphite and phosphite by *trans*-$[Ru(O)_2(N_2O_2)]^{2+}$ in aqueous acidic solutions has the following stoichiometry ($x = 2$ or 3): *trans*-$[Ru^{VI}(O)_2(N_2O_2)]^{2+} + H_2PO_x^- + H_2O \rightarrow$ *trans*-$[Ru^{IV}(O)(OH_2)(N_2O_2)]^{2+} + H_2PO_{x+1}^-$. The two reactions have the same rate law ($P = P^{I}$ or P^{III}): $-d[Ru^{VI}]/dt = k/(1 + [H^+]/K)[Ru^{VI}][P]$. For P^{I}, $k = 1.3\ M^{-1}\ s^{-1}$ and $K = 9.7 \times 10^{-2}$ M at 298 K and 1.0 M ionic strength. For P^{III}, $k = 4.8 \times 10^{-2}\ M^{-1}\ s^{-1}$ and $K = 1.2 \times 10^{-2}$ M at 298 K and 0.2 M ionic strength. For hypophosphite, the kinetic isotope effect, $k(H_2PO_2^-)/k(D_2PO_2^-)$, is 4.1 at pH = 1.07. For phosphite, the kinetic isotopic effect, $k(HDPO_3^-)/k(D_2PO_3^-)$, is 4.0 at pH = 2.30. A mechanism involving hydride transfer from P—H to Ru=O is proposed for these two reactions.[274]

The kinetics of the reduction of *cis*-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$ by $[Ni(tacn)_2]^{2+}$ (tacn = 1,4,7-triazacyclononane) and $[Fe(H_2O)_6]^{2+}$ in aqueous acidic solutions have the following stoichiometry: $2M^{II} +$ *cis*-$[Ru^{VI}(O)_2(L)]^{2+} + 2H^+ \rightarrow 2M^{III} +$ *cis*-$[Ru^{IV}(O)(OH)_2(L)]^{2+}$ (M = Ni or Fe). Two distinct steps are observed for both reactions and these are assigned to $Ru^{VI} \rightarrow Ru^{V}$ and $Ru^{V} \rightarrow Ru^{IV}$. For reduction by $[Ni(tacn)_2]^{2+}$ an outer-sphere mechanism is proposed for the $Ru^{VI} \rightarrow Ru^{V}$ step and a self-exchange rate of $2 \times 10^4\ M^{-1}\ s^{-1}$ for the *cis*-$[Ru^{VI}(O)_2(L)]^{2+}$/*cis*-$[Ru^{V}(O)_2(L)]^{+}$ couple has been estimated; a mechanism involving a pre-equilibrium protonation of *cis*-$[Ru^{V}(O)_2(L)]^{+}$ followed by outer-sphere electron transfer is proposed for the $Ru^{V} \rightarrow Ru^{IV}$ step. For reduction by $[Fe(H_2O)_6]^{2+}$, an outer-sphere mechanism is proposed for the first step and an inner-sphere mechanism is proposed for the second step.[275]

(c) Photophysical and photochemical properties of trans-dioxoosmium(VI) complexes. The complexes *trans*-$[Os^{VI}(O)_2(L)]^{2+}$ (L = 14-TMC, 15-TMC, 16-TMC, $(TMEA)_2$, $CRMe_3$) exhibit room temperature photoluminescence both in the solid state and in fluid solution.[214–216] Excitation of *trans*-$[Os^{VI}(O)_2(L)]^{2+}$ at $\lambda > 350$ nm results in phosphorescence in the 600–700 nm region. The emitting state has been assigned to the $[(d_{xy})^1(d_\pi{*})^1]$ triplet state ($d_\pi{*} = d_{xz}$, d_{yz}). The photophysical properties are summarized in Table 3. The phosphorescence of

trans-$[Os^{VI}(O)_2(14\text{-TMC})]^{2+*}$ is found to display large excited state lifetime dependence on the concentration of *trans*-$[Os^{VI}(O)_2(14\text{-TMC})]^{2+}$, indicating a self-quenching process; and an inherent life time of 3.3 μs has been estimated by extrapolating the lifetime to infinite dilution. An excited state redox potential of 2.2 V vs. NHE has been determined for *trans*-$[Os^{VI}(O)_2\text{-}(14\text{-TMC})]^{2+}$ using spectroscopic and electrochemical data. The excited state $\nu_{sym}(OsO_2)$ stretch has been estimated to be 740–750 cm^{-1}, which is substantially lower than the ground state value of 917 cm^{-1}, indicating a weakening of the Os=O bond upon light excitation. Because of the high excited state redox potential and the weakening of Os=O bond upon light excitation, *trans*-$[Os^{VI}(O)_2(14\text{-TMC})]^{2+*}$ is both a strong one-electron oxidant and an oxygen atom transfer reagent. Photooxidation of aromatic hydrocarbons to the corresponding cation radicals has been observed. Steady-state photolysis of *trans*-$[Os^{VI}(O)_2(14\text{-TMC})]^{2+}$ in the presence of phosphines, sulfides, and alkenes results in the formation of phosphine oxides, sulfoxides, and epoxides, respectively. The primary step in these photoinduced oxygen atom transfer reactions is probably charge transfer in nature (Equation (50)). This is supported by a linear correlation between the logarithm of the quenching rate constant and the vertical ionization potential of alkenes, suggesting an electron transfer mechanism in the initial step of the quenching reactions:

$$[Os^{VI}(O)_2]^* + S \longrightarrow [Os^{V}(O)_2, S^+] \tag{50}$$

The reductive quenching of $[Os^{VI}(O)_2(TMC)]^{2+*}$ by various inorganic anions and cations has also been investigated in water at 25 °C.[276] The rate constants for the quenching by a number of anions are NO_2^-, 2.0×10^9 M^{-1} s^{-1}; N_3^-, 4.0×10^9 M^{-1} s^{-1}; and I^-, 6.5×10^9 M^{-1} s^{-1}. The rate constants for the quenching of the aqua ions $[Fe(H_2O)_6]^{2+}$ (1.0×10^9 M^{-1} s^{-1}), $[Co(H_2O)_6]^{2+}$ (1.0×10^6 M^{-1} s^{-1}), and Ce^{III} (1.0×10^5 M^{-1} s^{-1}) are in fair agreement with values calculated from the Marcus cross-relation and the self-exchange rates for the $[Os^{VI}(O)_2(TMC)]^{2+*}$/$[Os^{V}(O)_2(TMC)]^{+}$ couple (1.0×10^5 M^{-1} s^{-1}).[276]

5.6.4.4.3 Phosphorus and arsenic ligands

It appears that there are no examples for ruthenium. *trans*-$[Os(O)_2(Cl)_2(PPh_3)_2]$ and *trans*-$[Os(O)_2(Br)_2(PPh_3)_2]$ can be made in a pure form by reaction of OsO_4 with PPh_3 in ethanolic HCl or HBr.[277] A number of other $[Os(O)_2(Cl)_2(PR_3)_2]$ species ($PR_3 = PMePh_2$, $PEtPh_2$, PEt_2Ph),[277] as well as complexes with diphosphines, diarsines, and diamines, $[Os(O)_2(X)_2\text{-}(L\text{–}L)]$,[278] have also been made using similar procedures.

5.6.4.4.4 Oxygen ligands

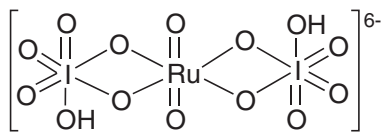
Many ruthenyl and osmyl complexes with O donor ligands are known. The ruthenium compounds are usually prepared from $[RuO_4]$, which can be generated by the oxidation of $RuCl_3 \cdot xH_2O$ or $[RuO_2]$ with $[IO_4]^-$. The osmium compounds are usually prepared from $[OsO_4]$ or $K_2[Os(O)_2(OH)_4]$.

The ruthenate ion has been known for a long time and was thought to have a tetrahedral structure with the formula $[RuO_4]^{2-}$. X-ray studies of the potassium and barium salts show the presence of the trigonal bipyramidal *trans*-$[Ru(O)_3(OH)_2]^{2-}$ anion instead.[279–281] However, it is possible that the $[RuO_4]^{2-}$ ion may exist in solution. The ruthenate ion functions as a two-electron oxidant for alcohols in aqueous solutions at high pH. The oxidation can be made catalytic by using persulfate as co-oxidant; however, competing C=C cleavage occurs in the oxidation of allylic alcohols.[100] The insoluble barium salt can be used as a stoichiometric oxidant in nonaqueous solvents for the conversion of benzyl alcohols to aldehydes and ketones.[100] Catalytic oxidation of activated primary alkyl halides to alkanoic acids, secondary halides to ketones, and nitro compounds to alkanoic acids by ruthenate/persulfate has also been reported.[103] The kinetics and mechanisms of the oxidation of alcohols by $[RuO_4]^{2-}$ have been investigated.[99,109] In the oxidation of substituted mandelic acids a concave Hammett plot is obtained, suggesting a free radical-like transition state. The oxidation of 2-propanol has an α-CH deuterium isotope effect of 2.4. The oxidation of sulfides to sulfoxides and sulfones by $[Ru(O)_3(OH)_2]^{2-}$ (also $[RuO_4]^-$ and $[RuO_4]$)

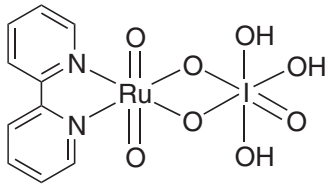
appears to occur by an oxygen atom transfer mechanism.[37] The corresponding osmate(VI) ion, *trans*-$[Os(O)_2(OH)_4]^{2-}$, is octahedral. The purple diamagnetic potassium osmate, $K_2[Os(O)_2(OH)_4]$, is a useful starting material for the preparation of other osmyl or osmium complexes. It is best prepared from the reaction of $[OsO_4]$ with excess KOH. A closely related species is the olive green $K_2[Os(O)_2(OMe)_4]$, made from KOH and $[OsO_4]$ in methanol.[282]

There are a number of complexes that contain the periodato ligand; both the metal center and the ligand have oxidation capacity. The species *trans*-$[Ru(O)_2(HIO_6)_2]^{6-}$ has been prepared from $RuCl_3 \cdot nH_2O$ and IO_4^-.[283] The X-ray structure of *trans*-$NaK_5[Ru(O)_2(HIO_6)_2] \cdot 8H_2O$ (**98**) shows *trans*-dioxo ligands (d(Ru=O) = 1.732 Å) and bidentate monoprotonated periodato ligands (Ru—O = 2.012 Å).[283] This complex is unusual in that both the metal center and the ligand function as oxidants. It functions as an overall six-electron oxidant, two electrons going to each $[I^{VII}(O)_5(OH)]^{4-}$ ligand, which is reduced to $[I^{V}(O)_3]^-$, and two to the Ru^{VI}, which is reduced to $[RuO_2]$. Primary alcohols are oxidized to carboxylic acids and secondary alcohols to ketones. Double bonds are cleaved, as are diol linkages. The oxidation can be made catalytic by using excess $[IO_4]^-$ as co-oxidant. *trans*-$[Ru(O)_2(H_2TeO_6)_2]^{6-}$ has also been prepared similarly. It functions only as a two-electron oxidant; the tellurato ligand does not function as an oxidizing moiety.[283]

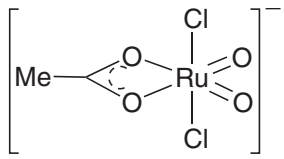
The complex *trans*-$[Ru(O)_2(bpy)\{IO_3(OH)_3\}]$ (**99**), prepared by the reaction of $[RuO_4]$ with IO_4^- and bpy, is the first example of a complex that contains the triply protonated periodate ligand, $[I(O)_3(OH)_3]^{2-}$. The Ru=O and Ru—O distances are 1.727 Å and 1.99 Å, respectively. The complex (**99**) is an efficient catalyst for the oxidation of alkenes using IO_4^- as the co-oxidant. It also oxidizes primary alcohols to aldehydes and secondary alcohols to ketones. In the stoichiometric oxidation of alkenes, IO_3^- and a Ru^{II}bpy complex can be identified as the products, indicating that the complex functions as a six-electron oxidant.[284,285] (**99**) is also an effective catalyst for the oxidation of alkanes using TBHP or IO_4^- as the terminal oxidant.[285] The osmium analog of this complex can be made from $K_2[Os^{VI}(O)_2(OH)_4]$, bpy, and $Na[IO_4]$, and a number of complexes of the type $[Os(O)_2(L)\{I(O)_3(OH)_3\}]$ (L = bpy, phen, 2,2′-dipyridylamine) have been isolated. $[Ru(O)_2(bpy)\{Te(O)_2(OH)_4\}]$ has also be made: it is a four-electron oxidant that can catalyze the epoxidation of alkenes using IO_4^-.[285]



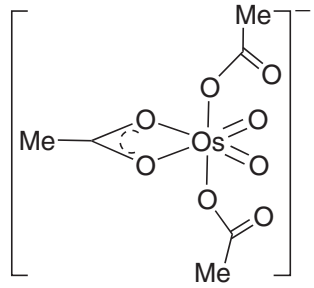
(**98**)



(**99**)



(**100**)



(**101**)

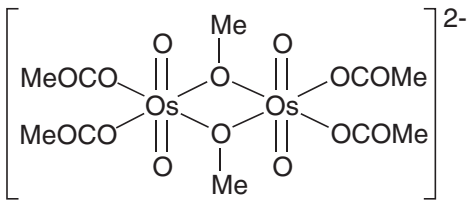
Carboxylato complexes of ruthenium(VI) and osmium(VI) are known. Reaction of $[RuO_4]$ with PPh_4Cl in glacial acetic acid yields $(PPh_4)[Ru(O)_2(OAc)(Cl)_2] \cdot 2AcOH$ (**100**).[286] The measured Ru=O distances and O=Ru=O angle are 1.64–1.71 Å and 120.2°, respectively. Complexes of other carboxylate ligands, $[Ru(O)_2(OCOR)(Cl)_2]^-$ (R = Et, Pr, CHF_2), have also been prepared.[287] These complexes are good two-electron oxidants at room temperature, both stoichiometrically and catalytically using NMO. Primary halides are oxidized to aldehydes, secondary halides to ketones, alcohols to aldehydes and ketones, and sulfides to sulfoxides and sulfones.[286,287]

A dark green solid, formulated as $Ba[Ru(O)_2(OCOMe)_4] \cdot 3H_2O$, has been obtained by dissolving $Ba[Ru(O)_3(OH)_2]$ in $MeCO_2H/CH_2Cl_2$.[288] This compound is able to stoichiometrically

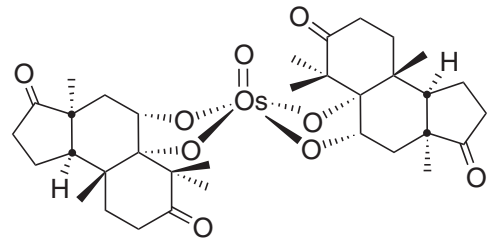
oxidize alkanes at room temperature. The reaction can be made catalytic by using $(NBu^t_4)(IO_4)$ as the terminal oxidant. The stoichiometric oxidation of alkanes is greatly increased by the addition of a few equivalents of metal chlorides such as $ZnCl_2$, $FeCl_3$, and $AlCl_3$. It was proposed that the metal chlorides function as Lewis acids by withdrawing electron density from the oxo group.[288] Dissolving $Ba[Ru(O)_3(OH)_2]$ in trifluoroacetic acid/CH_2Cl_2 generates an unstable solution that can oxidize alkanes at room temperature, presumably the active species being a *trans*-dioxoruthenium(VI) species with trifluoroacetate ligands.[289] In the presence of bpy, a more stable solution that can oxidize ethane (to ethanoic acid) and propane (to 2-propanone) is obtained. The active species is proposed to be *trans*-$[Ru^{VI}(O)_2(bpy)(CF_3CO_2)_2]$.[289]

The blue $K[Os(O)_2(OAc)_3]\cdot 2AcOH$ (**101**) can be prepared from $K_2[Os(O)_2(OMe)_4]$ and acetic acid, the structure of which has been established by X-ray crystallography;[290] the O═Os═O angle is 125.2° and the Os═O distances are 1.700 Å and 1.722 Å. The species $(PPh_4)[Os(O)_2(OCOR)(Cl)_2]$ (R = Me, Et) is prepared by adding $[OsO_4]$ to PPh_4Cl in RCO_2H. $(PPh_4)[Os(O)_2(OCOMe)(Cl)_2]$ is unable to oxidize alcohols under stoichiometric conditions. However, it can perform catalytic oxidation of alcohols using NMO as the terminal oxidant, the active species being most probably $[OsO_4\cdot NMO]$.$(PPh_4)[Os(O)_2(OCOMe)(Cl)_2]$ is a good starting material for the preparation of a variety of osmium compounds.[290]

An osmyl acetate complex has been produced by an unusual CO insertion reaction: interaction of CO (1.4 atm) with $[Os(O)_2(OMe)_4]^{2-}$ in MeOH gives the methoxy-bridged dimer $[\{Os(O)_2(OCOMe)_2(\mu\text{-}OMe)\}_2]^{2-}$ (**102**).[291] The X-ray structure of the $(NBu^n_4)^+$ salt has been determined (average Os═O bond length is 1.725 Å).[291]



(**102**)

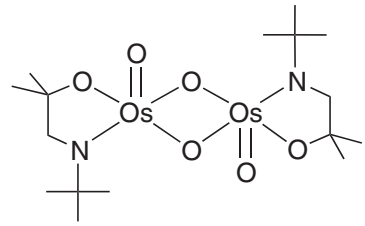


(**103**)

A number of hydroxycarboxylato complexes of osmium(VI) have been prepared as models for glycols and aldonic acid forms of sugars. These include $[Os(O)_2(L)(py)_2]$ (L = glycolate, oxoisobutyrate, mandelate, salicylate),[292] $[Os(O)_2(L')(py)_2]$ (L′ = oxalate, lactate, atrolactate, citrate, quinate),[293] $[Os(O)_2(pic)_2(L)]$ (pic = 3-methylpyridine, L = oxalate, oxoisobutyrate), $[Os(O)_2(py)_2]_2$(tartrate), $K_2[Os(O)_2(L)_2]$ (L = glycolate, quinate), and $K_4[\{Os(O)_2\}_2$ (tartrate)$_3]$.[293] IR, Raman, and NMR studies suggest that these complexes contain the *trans*-OsO_2 osmyl linkages. The X-ray structures of $[Os(O)_2(py)_2$(glycolate)$]$[294] and $[Os(O)_2(py)_2$(salicylate)$]$[295] have been determined.

A large number of osmium(VI) oxo esters are known, generally made by the reaction of $[OsO_4]$ and an alkene R. These have been described in detail in *CCC* (1987). The X-ray structure of an osmium(VI) bisglycolate species (**103**) produced by reaction of a sterically hindered chiral alkene with $[OsO_4]$ has been determined.[296] These kinds of bisglycolate species may be key intermediates in catalytic osmylation processes. There are also a few osmium(VI) oxo esters prepared from photochemical or thermal reactions of $[OsO_4]$ with arenes (see Section 5.6.2.3.1(ii)).[70,71] Analogous osmium(VI) esters are obtained from the reaction of $[Os(O)_3(NR)]$ and $[Os(O)_3(NR)(L)]$ with alkenes.[297,298] Reaction of $[Os(O)_3(NBu^t)]$ with isobutylene produces $[Os_2(O)_4(OCMe_2CH_2NBu^t)_2]$ (**104**).[297] The Os—O(terminal) and Os—O(bridging) distances are 1.67 Å and 1.92 Å, respectively. The structure is comparable to $[Os_2(O)_4(O_2C_2Me_4)_2]$ which is made from $[OsO_4]$. The adducts $[Os(O)_3(NR)(L)]$ (R = Bu^t, *t*-pentyl, C_8H_{17}; L = quinuclidine) and $[\{Os(O)_3(NR)\}_2(L')]$ (R = Bu^t or C_8H_{17}, L′ = 1,4-diazabicyclo[2.2.2]octane (dabco) or 1,3,5,7-tetraazatricyclo-[3.3.1.1]decane; R = *t*-pentyl, L′ = dabco) react with alkenes R′ to give $[Os(O)_2(OR'NR)(L)]$ and $[\{Os(O)_2(OR'NR)\}_2(L)']$, respectively.[298]

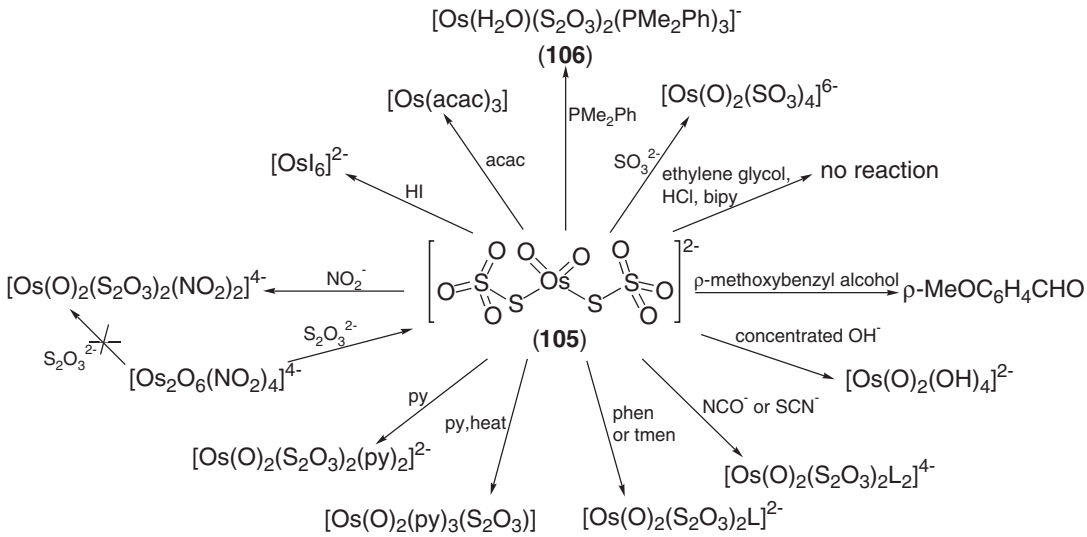
Other osmyl complexes with O donor ligands include $(PPh_4)_2[Os(O)_2(OSiMe_3)_4]$, prepared from $(PPh_4)_2[Os(O)_2(Cl)_4]$ and $NaOSiMe_3$; and *trans*-$[Os(O)_2(trop)_2]$ (trop = tropolonato $C_7H_5O_2^-$), prepared from $K_2[Os(O)_2(OH)_4]$ and the ligand.[299]



(**104**)

5.6.4.4.5 Sulfur and selenium ligands

An unusual tetrahedral osmyl thiosulfato complex, $[Os(O)_2(S_2O_3)_2]^{2-}$ (**105**), has been prepared by reaction of $[OsO_4]$ with $Na_2S_2O_3$ in water. The X-ray structure of the $(NBu^n_4)^+$ salt reveals a distorted tetrahedral structure; the O—Os—O angle is significantly enlarged at 127.2° and the S—Os—S angle is appreciably contracted at 89.2°. The Os—S and Os—O distances are 2.218 Å and 1.692 Å respectively.[300,301] The IR and Raman spectra in the solid state are similar to those in CH_2Cl_2, suggesting that the tetrahedral geometry is retained in solution. Cyclic voltammetry of the complex in dichloroethane shows a reversible $Os^{VI/V}$ couple at −1.10 V vs. $Cp_2Fe^{+/0}$ and an irreversible oxidative wave. $[Os(O)_2(S_2O_3)_2]^{2-}$ is found to be very reactive; it reacts with a variety of organic and inorganic substrates to produce a number of new thiosufato complexes (Scheme 15).[301] The X-ray structure of one of these products, $(NBu_4^t)[Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$ (**106**), has been determined.



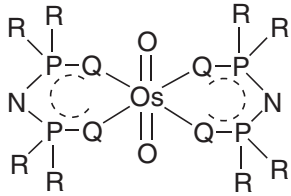
Scheme 15

The osmyl thioether and selenoether complexes $[Os(O)_2(X)_2(SR_2)_2]$ ($(SR_2)_2 = (SMe_2)_2$, $MeS(CH_2)_2SMe$, *o*-$C_6H_4(SMe)_2$, *o*-$C_6H_4(PPh_2)(SMe)$ or $MeSe(CH_2)_2SeMe$; X = Cl, Br) have been prepared by reaction of the ligand with $[OsO_4]$ in a mixture of ethanol and concentrated HX.[302]

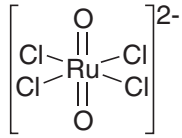
Reaction of $K_2[Os(O)_2(OH)_4]$ with the imidodiphosphinochalcogenide ligands $HN(QPR_2)_2$ yields the dioxoosmium(VI) complexes *trans*-$[Os(O)_2\{N(QPR_2)_2\}_2]$ (**107**) (Q = S, R = Ph, Pr^i; Q = Se, R = Ph).[303]

5.6.4.4.6 Halogen ligands

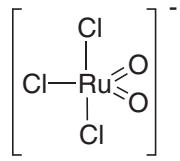
A clear-cut method for the preparation of $[Ru(O)(F)_4]$ was reported, which involves reaction of $[RuO_4]$ with KrF_2 in HF.[610] Its IR spectrum shows a strong ν(Ru═O) stretch at 900 cm^{-1}.



(**107**)



(**108a**)



(**108b**)

Chloro complexes of dioxoruthenium(VI) exist as six-coordinate $[Ru(O)_2(Cl)_4]^{2-}$ (**108a**) as well as five-coordinate $[Ru(O)_2(Cl)_3]^-$ (**108b**) forms.[100] The six-coordinate form rapidly converts to the five-coordinate form, with a dissociation constant $K = 5.3 \times 10^{-3}$ M for chloride loss in CH_2Cl_2.[304] The structure of $(PPN)_2[Ru(O)_2(Cl)_4]$ has been established by X-ray crystallography. It has an octahedral geometry and consists of *trans*-dioxo ligands with d(Ru=O) = 1.709 Å. The $\nu_{as}(RuO_2)$ stretch occurs at 830 cm^{-1} [304] (Table 4). The solid-state structure of $[Ru(O)_2(Cl)_3]^-$ is dependent on the counterion. In the $(PPN)^+$ salt the $[Ru(O)_2(Cl)_3]^-$ ion has a trigonal bipyramidal structure with *cis*-dioxo ligands. The Ru=O distances are 1.658 Å and 1.694 Å and the O—Ru—O angle is 127°.[304] The $\nu_{as}(RuO_2)$ stretch occurs at 881 cm^{-1}. However, the $[Ru(O)_2(Cl)_3]^-$ ion in the $(PPh_4)^+$ salt is disordered between trigonal bipyramidal and square pyramidal geometries, which can be refined by using an occupancy ratio of 6:4. The square pyramidal component of $[Ru(O)_2(Cl)_3]^-$ is assigned with *trans*-dioxo ligands that accounts for the appearance of the unusual IR band at 891 cm^{-1} (together with the band at 878 cm^{-1} in crystalline $(PPh_4)[Ru(O)_2(Cl)_3]$.

The oxidation of alcohols and various organic substrates by $(PPh_4)[Ru(O)_2(Cl)_3]$ has been described.[100,304] Salts of the form *trans*-$(R\text{-}pyH)_2[Ru(O)_2(Cl)_4]$ (R-py = pyridine, substituted pyridines), *trans*-$(R)_2[Ru(O)_2(X)_4]$ (X = Cl, Br; R = $Me_2NH(CH_2)_2NHMe_2$, $Me_2N(C_2H_4)_2NMe_2$), $(PPh_4)[Ru(O)_2Br_3]$, *trans*-$(PPh_4)_2[Ru(O)_2(Br)_4]$, and *trans*-$(AsPh_4)[Ru(O)_2(Cl)_3(OPPh_3)]$ have been shown to function as catalysts for the oxidation of primary alcohols to aldehydes and of secondary alcohols to ketones, without competing olefinic bond cleavage, using NMO as the terminal oxidant.[305]

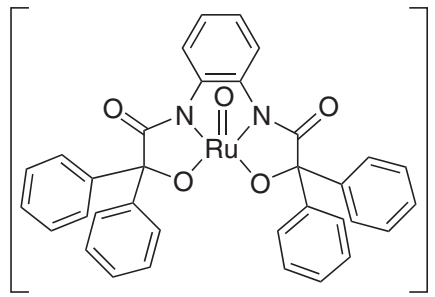
$[Os(O)(Cl)_4]$ and $[Os(O)(F)_4]$ have been described in *CCC* (1987). The matrix IR spectrum of $[Os(O)(F)_4]$ has been measured, and shows absorptions at 1,079 cm^{-1} (Os=O) and 685 cm^{-1}(Os—F), consistent with C_{4v} geometry.[89] The molecular structure of $[Os(O)(Cl)_4]$ has been studied by gas-phase electron diffraction.[306] The X-ray structure of *trans*-(H_2TMEA)-$[Os(O)_2(Cl)_4]$ has been determined (Os—O = 1.718–1.728 Å, Os—Cl = 2.381–2.397 Å).[307] The bromo analog, $(PPh_4)_2[Os(O)_2(Br)_4]$, has been prepared by the addition of PPh_4Br in HBr to $K_2[Os(O)_2(OMe)_4]$ in MeOH.[287]

5.6.4.4.7 Mixed donor atom ligands

There are a number of osmium(VI) oxo complexes of this type; however, there appears to be only one example for ruthenium (see Figure 12 for structures of ligands).

Oxidation of $(NPr^n_4)[Ru^V(O)(PHAB)]$ (**109**) by Ce^{IV} yields the diamagnetic monooxoruthenium(VI) complex $[Ru^{VI}(O)(PHAB)]$. As expected, the ν(Ru=O) stretch (935 cm^{-1}) occurs at a higher frequency than that of the corresponding Ru^V complex (887 cm^{-1}). X-ray diffraction studies reveal that it has a square pyramidal structure with a Ru=O distance of 1.661 Å, which is shorter than that in Ru^V (1.702 Å).

A *trans*-dioxoosmium(VI) complex of the tetradentate pyridine-amido ligand bpb has been isolated.[308] Reaction of $K_2[Os^{VI}(O)_2(OH)_4]$ with H_2bpb in MeOH/HCl (2 M) produces *trans*-$[Os^{VI}(O)_2(H_2bpb)]Cl_2$, which can be deprotonated with Et_3N in MeOH to give *trans*-$[Os^{VI}(O)_2(bpb)]$. As expected for a d^2 *trans*-dioxoosmium(VI) complex, this compound is diamagnetic and exhibits an intense IR band at 850 cm^{-1} characteristic of the $\nu_{asym}(OsO_2)$ stretch. It reacts with excess PPh_3 in MeCN at 50–60 °C to produce *trans*-$[Os(bpb)(PPh_3)(Cl)]$. A chiral version of *trans*-$[Os^{VI}(O)_2(bpb)]$ has also been reported.[309] Stirring the *R*(−) or *S*(+) form of the amide ligand L (**148**) (Figure 12) with $K_2[Os(O)_2(OH)_4]$ in methanol at 40 °C gives the respective *R* or *S* form of the orange $[Os^{VI}(O)_2(L)]$. The *R* form has been established by X-ray crystallography.[309] The osmium atom is six-coordinate with the two oxo groups *trans* to each other.



(**109**)

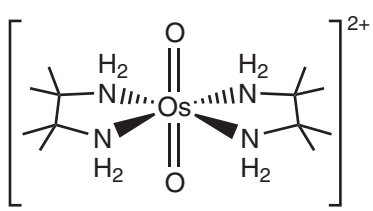
However, the measured O—Os—O angle of 166.7° significantly deviates from 180°. The measured Os=O distances of 1.726 Å and 1.727 Å are in the normal range expected for *trans*-dioxo-osmium(VI) complexes.

A series of *trans*-dioxoosmium(VI) complexes with Schiff base ligands (salen, 5-Pr^{i}-salen, 5-Bu^{t}-salen, 3-Bu^{t}-saltmen, 5-{(3-Me)-Bu}-saltmen, 5-Bu^{t}-saltmen) have also been prepared by the reaction of $K_2[Os(O)_2(OH)_4]$ with the ligand in methanol.[310,311] Surprisingly the corresponding ruthenium complexes have yet to be reported. The X-ray crystal structure of *trans*-[Os^{VI}(O)$_2$-(3-Bu^{t}-saltmen)] has been determined (d(Os=O) = 1.760 Å and 1.722 Å, O—Os—O = 176.6°). These complexes undergo irreversible electrochemical oxidation and reduction in acetonitrile. A related species, [Os^{VI}(O)$_2$(phenba)], is able to oxidize benzyl alcohol in the presence of one equivalent of PPh_3, the active oxidant being probably a Os^{IV}=O species.[312] *trans*-Dioxoosmium(VI) complexes of Schiff base ligands obtained from the condensation of β-diketones and 1,2-diaminoethane are also known.[313] The X-ray structure of *trans*-[Os^{VI}(O)$_2${(BA)$_2$en}] has been determined. The Os=O distances are 1.753 Å and 1.736 Å (average) for the two crystallographically independent molecules.

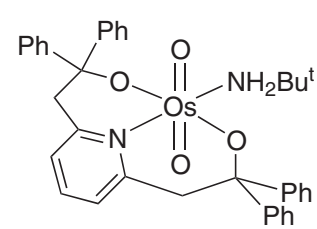
trans-Dioxoosmium(VI) complexes with tetraanionic ligands are also known. The complexes $K_2[Os(O)_2(CHBA\text{-}Et)]$ and $K_2[Os(O)_2(CHBA\text{-}DCB)]$ are prepared from $K_2[Os(O)_2(OH)_4]$ ($\nu_{as}(OsO_2) = 820\ cm^{-1}$).[314] In the presence of pyridine these complexes react with PPh_3 to give bis(pyridine)osmium(IV) derivatives. There are also complexes of the form *trans*-$[Os(O)_2(H_2L)]^{2-}$ (L = (**149**), (**150**), (**151**)) (Figure 12) where H_2L are tetraamidato ligands with appendages containing hydrogen bond donors.[315]

A rare example of a *cis*-dioxoosmium(VI) complex is *cis*-[Os(O)$_2$(L)], L = 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridinato(2-), which is prepared from $K_2[Os(O)_2(OH)_4]$ and H_2L.[149] The assignment of *cis* configuration is based on IR spectroscopy. This complex reacts readily with nitrogen bases to form six-coordinate *trans*-dioxoosmiun(VI) complexes. The crystal structure of $[Os(O)_2(L)\text{-}(Bu^tNH_2)]\cdot 0.5C_6H_{14}$ (**110**) has been determined; the average Os=O distance is 1.741 Å.[149]

An unusual osmium(VI) monooxo species stabilized by amido ligands, [Os^{VI}(O)(tmen-2H)(tmen-H)]$^{+}$, has been prepared by treatment of [Os^{VI}(O)$_2$(tmen)$_2$]$^{2+}$ (**97b**) with a base such as collidine in acetonitrile.[250] The crystal structure of the perchlorate salt has been determined: the osmium atom is displaced 0.67 Å from the plane of the four N atoms. The Os=O distance is 1.72 Å, and the Os—N distances of 1.85 Å and 1.99 Å indicate double bond character.[250]

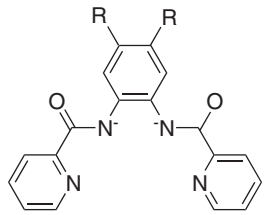


(**97b**)

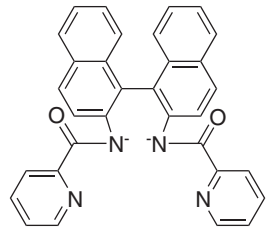


(**110**)

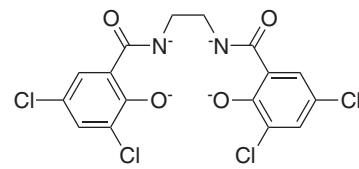
trans-Dioxoruthenium(VI) complexes containing bidentate cysteinate-*S*,*O* or 3-mercapto-propionate-*S*,*O* ligands have been prepared as models for the active site of isopenicillin *N*-synthetase.[316]



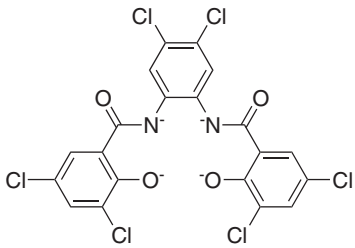
bpb, R = H
bpc, R = Cl



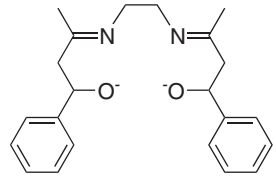
(**148**)



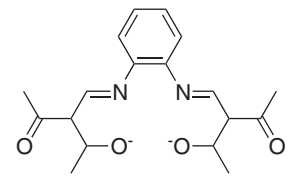
CHBA-Et



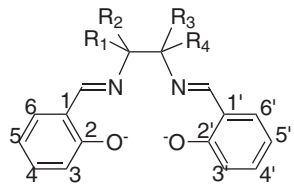
CHBA-DCB



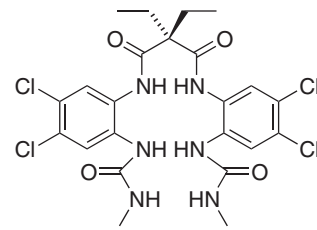
$(Ba)_2$en



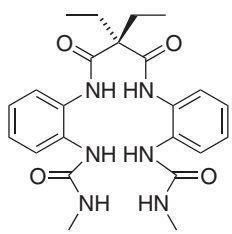
phenba



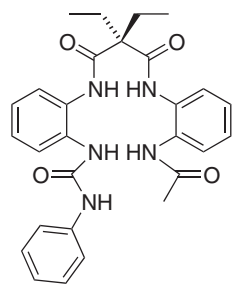
salen, R_1, R_2, R_3, R_4 = H
5-*i*-Pr-salen, R_1, R_2, R_3, R_4 = H, 5,5' = -$CHMe_2$
5-*t*-Bu-salen, R_1, R_2, R_3, R_4 = H, 5,5' = -CMe_3
3-*t*-Bu-saltmen, R_1, R_2, R_3, R_4 = CH_3, 3,3' = -CMe_3
5-(3-Me)-Bu-saltmen, R_1, R_2, R_3, R_4 = CH_3, 5,5' = -$CH_2CH_2CHMe_2$
5-t-Bu-saltmen, R_1, R_2, R_3, R_4 = CH_3, 5,5' = -CMe_3



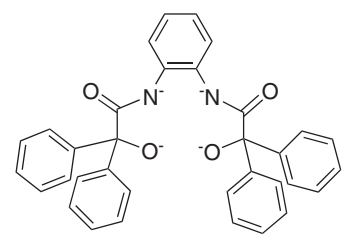
(**149**)



(**150**)



(**151**)



PHAB

Figure 12 Structures of some tetradentate ligands.

Reaction of $[Ru(O)_2(OH)_2(py)_2]$ or $[Ru(O)_2(bpy)(Cl)_2]$ with H_2L (H_2L = *N*-acetylcysteine, *N*-formylcysteine, or 3-mercaptopropionic acid) produces the complexes $[Ru(O)_2(py)_2(L)]$ or $[Ru(O)_2(bpy)(L)]$.[316] The IR spectra show a single and strong $\nu_{as}(RuO_2)$ stretch at 800–835 cm^{-1}, consistent with the *trans* configurations of these species.

5.6.4.4.8 Macrocyclic tertiary amine ligands

These are described in Section 5.6.4.4.2.

5.6.4.4.9 Porphyrins and related complexes

(i) Syntheses

There is an extensive series of dioxoruthenium(VI) complexes with porphyrinato ligands, *trans*-[$Ru^{VI}(O)_2$(por)].[317] These include the nonsterically bulky porphyrins 4-X-TPP and OEP;[318,319] sterically encumbered porphyrins such as TMP,[320] DPP,[321,322] 2,6-Cl-TPP,[322] and 2,4,6-MeO-TPP;[322] chiral porphyrins such as chiral picket-fence porphyrin (Pf-por),[323] D_2-porphyrins (D_2-por1 and D_2-por2)[324,325,338] (Figure 13), and D_4-porphyrin (D_4-por) (**35**);[326,327] and dentritic porphyrins.[328] These complexes are much more stable than oxoiron porphyrins, and have been used as models for cytochrome P450 and related enzymes. They are also an important class of oxidants for organic substrates. Initial attempts to oxidize ruthenium(II) porphyrins to generate high-valent terminal oxo species resulted only in μ-oxo ruthenium(IV) dimers (see Section 5.6.6.6.2(i) in Ru(IV)) The first dioxoruthenium(VI) porphyrin complex, *trans*-[$Ru^{VI}(O)_2$(TMP)], was obtained by oxidation of [Ru(TMP)CO] with *m*-CPBA (*m*-chloroperbenzoic acid) in CH_2Cl_2.[320] Evidently the sterically bulky TMP ligand prevents dimerization. Later, it was found that *trans*-[$Ru^{VI}(O)_2$(por)] complexes of nonsterically bulky porphyrin ligands such as TPP and OEP can also be prepared if an EtOH/CH_2Cl_2 solvent is used.[318] Presumably the alcohol coordinates to the putative Ru^{IV} intermediate and prevents dimerization. Dioxoruthenium(VI) complexes with other sterically encumbered prophyrins such as H_2DPP, H_2(2,6-Cl-TPP), and H_2(2,4,6-MeO-TPP) can be obtained by simply carrying out the oxidation of the ruthenium(II) carbonyl complex with PhIO in CH_2Cl_2. The X-ray structure of the chiral complex [$Ru^{VI}(O)_2$(D_4-por)*] has been determined; the Ru=O distances are 1.73 Å and 1.75 Å.[327]

All the Ru^{VI} complexes are diamagnetic and display well-revolved ^{1}H NMR spectra. The pyrrolic proton signals are shifted about 0.4 ppm downfield from those of the carbonylruthenium(II) precursors.

All [$Ru^{VI}(O)_2$(por)] complexes show a strong $\nu_{asym}(RuO_2)$ stretch at around 820 cm^{-1} (Table 4) in the IR, and for [$Ru^{VI}(O)_2$(4-X-TPP)] the frequency is insensitive to the nature of the *para*-substitutent on the *meso*-phenyl groups. There is also a strong band near 1,000 cm^{-1} in the IR spectra of ruthenium porphyrin complexes, which is assigned as the rocking vibrations of the porphyrin ring. The position of this band (here referred as the oxidation marker band) is sensitive to the strength of the metal–nitrogen bond and is related to the oxidation state of ruthenium.

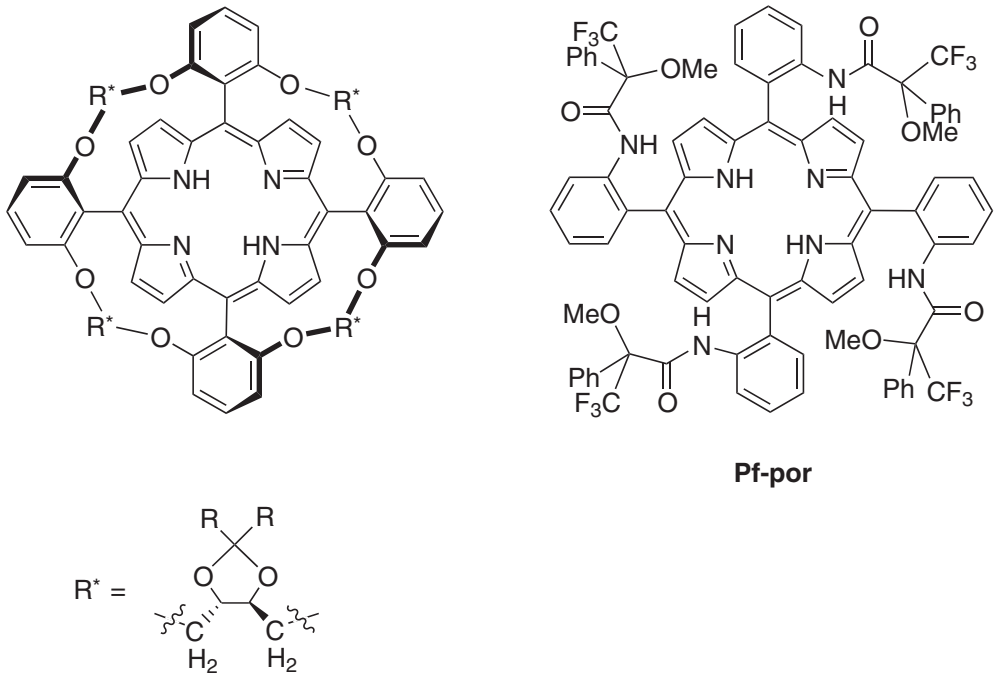


Figure 13 Structures of chiral porphyrins.

The oxidation state marker band for $[Ru^{II}(por)(CO)(MeOH)]$ occurs at 1,007–1,009 cm^{-1}, while for $[Ru^{VI}(O)_2(por)]$ the band is located at 1017–1020 cm^{-1}.[317]

The UV–vis spectra of $[Ru^{VI}(O)_2(por)]$ (Table 12) feature mainly the B band (Soret band) and a less intense Q band typical of a normal porphyrin. The Q band is split into α and β in the OEP complexes.

The cyclic voltammogram of $[Ru^{VI}(O)_2(por)]$ shows a reversible oxidation wave and an irreversible reduction wave (Table 13). The oxidation wave is probably due to ligand-centered oxidation (Equation (51)).

$$[Ru^{VI}(O)_2(por)] - e^- \longrightarrow [Ru^{VI}(O)_2(por^{\cdot+})] \tag{51}$$

$[Ru^{VI}(O)_2(por^{\cdot+})]$ (for por = TMP and OEP) have been generated by oxidation of $[Ru^{VI}(O)_2(por)]$ with phenoxathiin hexachloroantimonate.[329] The products show a broad Q band and a less intense and blue-shifted Soret band, consistent with the formation of the porphyrin cation radical. The ESR spectra show a signal at $g = 2.002$ at 77 K. $[Ru^{VI}(O)_2(por^{\cdot+})]$ reacts with PPh_3 to produce two equivalents of PPh_3O.

(ii) Reactivities

The *trans*-$[Ru^{VI}(O)_2(por)]$ complexes are active stoichiometric oxidants of alkenes and alkylaromatics under ambient conditions. Unlike cationic macrocyclic dioxoruthenium(VI) complexes that give substantial C=C bond cleavage products, the oxidation of alkenes by $[Ru^{VI}(O)_2(por)]$ affords epoxides in good yields.[319,321,322,326] Stereoretentive epoxidation of *trans*- and *cis*-stilbenes by $[Ru^{VI}(O)_2(L)]$ (L = TPP and sterically bulky porphyrins) has been observed, whereas the reaction between $[Ru^{VI}(O)_2(OEP)]$ and *cis*-stilbene gives a mixture of *cis*- and *trans*-stilbene oxides.[318,319] Adamantane and methylcyclohexane are hydroxylated at the tertiary C—H positions.[318,319] Using $[Ru^{VI}(O)_2(D_4\text{-por})]$, enantioselective epoxidation of alkenes can be achieved with ee up to 77%.[326] In the oxidation of aromatic hydrocarbons such as ethylbenzenes, 2-ethylnaphthalene, indane, and tetrahydronaphthalene by $[Ru^{VI}(O)_2(D_4\text{-por*})]$, enantioselective hydroxylation of benzylic C—H bonds occurs resulting in enantioenriched alcohols with ee up to 76%.[330]

Table 12 UV–visible spectral data of selected dioxoruthenium(VI) porphyrins in CH_2Cl_2.

Complex	λ_{max} *(*log ε*)*(nm (dm^3 mol^{-1} cm^{-1}))
$[Ru^{VI}(O)_2(TPP)]$	545 sh (3.89), 518 (4.24), 418 (5.29), 340 sh (4.19)
$[Ru^{VI}(O)_2(OEP)]$	540 (4.40), 508 (4.28), 396 (5.44), 335 sh (4.45)
$[Ru^{VI}(O)_2(DPP)]$	586 (3.59), 550 (3.85), 448 (4.78), 358 sh (3.98)
$[Ru^{VI}(O)_2(2,6\text{-Cl-TPP})]$	420 (5.49), 510 (4.16), 566 sh (3.60)
$[Ru^{VI}(O)_2(2,4,6\text{-MeO-TPP})]$	4.23 (5.38), 512 (4.40)
$[Ru^{VI}(O)_2(TMP)]$	4.22(5.44), 526 (4.18)
$[Ru^{VI}(TPP)(NTs)_2]$	416 (5.14), 536 (4.18), 568 (3.77)
$[Ru^{VI}(OEP)(NTs)_2]$	406 (5.07), 520 (4.21), 551 (4.16)

Table 13 E° values (V vs. $Cp_2Fe^{+/0}$) for selected dioxoruthenium(VI) porphyrins.[a]

Complex	*Oxidation*	*Reduction*[b]
$[Ru^{VI}O_2(OEP)]$	0.60	−0.90
$[Ru^{VI}O_2(TPP)]$	0.79	−0.83
$[Ru^{VI}O_2(4\text{-Me-TPP})]$	0.72	−0.85
$[Ru^{VI}O_2(4\text{-MeO-TPP})]$	0.64	−0.88
$[Ru^{VI}O_2(4\text{-Cl-TPP})]$	0.86	−0.76
$[Ru^{VI}O_2(DPP)]$	0.90[b], 0.55	−1.00

Source: Che and Yu.[317]

[a] Conditions: 0.1 mol dm^{-3} NBu_4PF_6 CH_2Cl_2, $Ag/AgNO_3$ in MeCN as the reference electrode and glassy carbon working electrode; scan rate = 100 mV s^{-1}. [b] Irreversible.

The nature of the ruthenium product depends on the porphyrin and the solvent used. For sterically nonbulky ligands such as TPP and OEP in noncoordinating solvents such as benzene, the product is the μ-oxo species $[Ru^{IV}(por)(OH)]_2(\mu\text{-}O)$.[318] For sterically bulky porphyrins, the product is a ruthenium(II) species that arises from disproportionation of the intermediate $[Ru^{IV}(O)(por)]$.[331] In CH_2Cl_2/ROH, a monomeric Ru^{IV} product is formed for all porphyrins, which can be formulated either as $[Ru^{IV}(por)(OR)_2]$ or $[Ru^{IV}(O)(por)(ROH)]$.[318,319] In CH_2Cl_2/pyrazole (Hpz), the product for all porphyrins is $[Ru^{IV}(por)(pz)_2]$.[321,322,326]

The kinetics of the reaction of $[Ru^{VI}(O)_2(por)]$ with various alkenes have been investigated either in CH_2Cl_2/MeOH or CH_2Cl_2/Hpz.[319,321,322,326] In the absence of MeOH or Hpz, clean kinetics are not always observed, presumably because dimerization or disproportionation of the intermediate $Ru^{IV}{=}O$ species occurs at comparable rates as epoxidation. The reactions have the following rate law: rate $= k[Ru^{VI}(O)_2(por)][alkene]$. The rate constants for the oxidation of styrene are in the range 6×10^{-4}–4.8×10^{-3} M^{-1} s^{-1}. The oxidation of norbornene occurs at similar rates (9×10^{-4}–1.3×10^{-2} M^{-1} s^{-1}).[317]

Remarkably $[Ru^{VI}(O)_2(por)]$ with sterically bulky ligands can catalyze the aerobic epoxidation of alkenes[317,321,327,332,333] and the first example was demonstrated by $[Ru^{VI}(O)_2(TMP)]$.[333,334] With the chiral $[Ru^{VI}(O)_2(D_4\text{-por*})]$, enantioselective aerobic epoxidation of alkenes can also be achieved.[327] These catalysts usually become deactivated after 1–2 days, probably due to the formation of [Ru(por)(CO)].[335]

Apart from O_2, $[Ru^{VI}(O)_2(por)]$ can also catalyze the oxidation of hydrocarbons using other terminal oxidants such as N_2O[336] and pyridine *N*-oxides.[328,330,337,338] Notably $[Ru^{VI}(O)_2(D_2\text{-por1})]$[325] and $[Ru^{VI}(O)_2(D_2\text{-por2})]$[339] are selective catalysts for asymmetric epoxidation of terminal and *trans*-substituted alkenes with 2,6-dichloropyridine *N*-oxide. In the catalytic oxidation with pyridine *N*-oxides, the most important intermediate appears to be a *N*-oxide coordinated $Ru^{IV}{=}O$ species.[338] The precursor $[Ru^{II}(por)(CO)]$ is often used as the catalyst. The electrocatalytic oxidation of styrene by $[Ru^{VI}(O)_2(TMP^{\cdot+})]$ has also been reported.[340]

The ruthenium catalysts have also been attached to various solid supports, including polyethyleneglycol (PEG),[341] mesoporous molecular sieves,[342–344] and Merrifield's peptide resin.[345]

Apart from alkenes, the oxidation of phosphines by the chiral $[Ru^{VI}(O)_2(Pf\text{-}por)]$[346] and $[Ru^{VI}(O)_2(TMP)]$,[347] as well as the aerobic oxidation of sulfides by $[Ru^{VI}(O)_2(TMP)]$[348] have also been investigated.

A number of *trans*-dioxoosmium(VI) complexes with porphyrins are also known. $[Os^{VI}(O)_2(por)]$ (por = 4-X-TPP, OEP, TMP, DPP) are synthesized by the oxidation of $[Os^{II}(por)(CO)]$ with *m*-CPBA.[321,349,350] The X-ray structure of $[Os(O)_2(4\text{-Me-TPP})]$ has been determined; the Os=O distance is 1.743 Å.[349] $[Os^{VI}(O)_2(por)]$ are in general much weaker oxidants than their ruthenium counterparts; they do not react with alkenes even at 50 °C. However, they catalyze the reaction of alkenes with iodosylarenes.[351] The main reaction pathway is oxidative double bond cleavage, presumably through a seven-coordinate osmium intermediate. Both $[Os^{VI}(O)_2(OEP)]$ and $[Os^{VI}(O)_2(TPP)]$ react with PPh_3 to give $[Os^{II}(por)(OPPh_3)_2]$ (por = TPP, OEP), and their X-ray structures have been determined.[352] $[Os^{VI}(O)_2(OEP)]$ is reduced by ascorbic acid to give $[Os^{IV}(OEP)(OH)_2]$.[349] The photophysics and photochemistry of $[Os(O)_2(OEP)]$ have also been reported.[353] The complex $[Os(O)_2(OEP)]$ shows emission at 729 nm [$\tau_0 < 6$ μs and $\phi_p = 5 \times 10^{-3}$ at 300 K in deoxygenated acetone]. An extended Hückel calculation has been performed on $[Os^{VI}(O)_2(por)]$.[207a]

5.6.4.5 Sulfur Complexes

Apparently, soft sulfur ligands alone cannot stabilize Ru^{VI} or Os^{VI}. The existing thioether, thiolato, and sulfide complexes of ruthenium(VI) and osmium(VI) are associated with either the oxo or the nitrido ligand and they have been discussed in the previous sections.

5.6.4.6 Halide Complexes

5.6.4.6.1 Fluoro complexes

The hexafluorides $[RuF_6]$ and $[OsF_6]$ are known. The rather unstable RuF_6 can be obtained as a brown solid in high yield by the interaction of $[RuF_5]$ with F_2 at 220 °C and 30 atm. The IR spectrum is consistent with an octahedral geometry.[354] The metal K-edge EXAFS data for RuF_6 have been obtained and a Ru—F distance of 1.83 Å was found.[355]

The bright yellow $[OsF_6]$ has been described in *CCC* (1987). It can be prepared by the direct fluorination of osmium.[356] The molecular structure has been studied by EXAFS (Os—F = 1.816 Å)[357] and neutron diffraction (Os—F = 1.831 Å).[358] The gas-phase molecular structure of $[OsF_6]$ has also been studied by electron diffraction and *ab initio* calculations.[359] The experimental Os—F distance is 1.828 Å. The electronic spectral study of $[OsF_6]$ has been reported.[360] The compound $(NO)[Os(F)_7]$ has also been mentioned in *CCC* (1987).

The reaction of $[OsF_6]$ with ZnS or B_2S_3 at elevated temperature yields $[OsF_5{\cdot}SF_4]$ instead of an osmium thiofluoride.[361]

5.6.4.6.2 Chloro, bromo, and iodo complexes

Apparently there are no M^{VI} binary complexes of these three halides. These halides are found in oxo (Section 5.6.4.4.6), nitrido (Section 5.6.4.2.5), and imido (Section 5.6.4.1) complexes.

5.6.4.7 Hydride Complexes

A number of hexahydridoosmium(VI) species $[Os(H)_6(PR_3)_2]$ (PR_3 = tertiary phosphine) are known.[362–366] These can be prepared by treatment of $[Os(Cl)_4(PR_3)_2]$ ($PR_3 = PMe_2Ph$)[362] or $[Os(O)_2(Cl)_2(PR_3)_2]$ ($PR_3 = PPhPr^i_2$)[365] with $LiAlH_4$, or by reaction of $[Os(H)_2(Cl)_2(PR_3)_2]$ ($PR_3 = PPr^i_3$, $PMeBu^t_2$) with $NaBH_4$;[366] they are characterized by ^1H NMR. A single-crystal neutron diffraction study of $[Os(H)_6(PPhPr^i_2)_2]$ has established the eight-coordinate core geometry about the osmium atom to be that of an irregular dodecahedron.[367] The Os—H distances range from 1.637 Å to 1.668 Å with a very short H···H interaction (1.650 Å) between the two most closely bound hydrides. The two phosphine ligands are essentially equivalent, Os—P = 2.338 Å and 2.347 Å, P—Os—P = 155.2°. $[Os(H)_6(PPh^iPr_2)_2]$ reacts with $HgCl_2$ to give $[Hg(Cl)_2\{Os(H)_6(PPh^iPr_2)_2\}_2]$, which is characterized by ^1H NMR.[365]

5.6.4.8 Miscellaneous

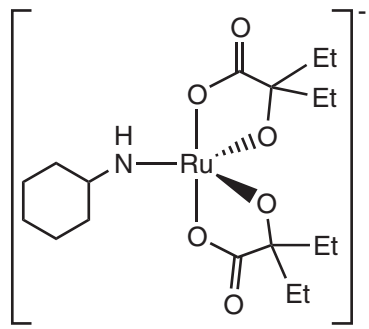
$[Os\{(HN)SC_6H_4\}_3]$ has been synthesized by interaction of aminothiol with $[OsO_4]$.[368]

5.6.5 RUTHENIUM(V) AND OSMIUM(V)

5.6.5.1 Imido Complexes

There are only a few examples, and the ruthenium complexes are all unstable.

A paramagnetic imidoruthenium(V) complex, $[Ru^V\{N(C_6H_{11})\}(OCEt_2CO_2)_2]^-$, has been obtained via interaction of the corresponding amidoruthenium(IV) species $[Ru^{IV}\{NH(C_6H_{11})\}(OCEt_2CO_2)_2]^-$ (**116**) with O_2.[369] The formulation of the complex is supported by EPR.



(**116**)

An unstable imidoruthenium(V) species, formulated as *cis*-$[Ru^{V}(bpy)_2(NC(Me)_2C(Me)_2NH)]^{2+}$, has been generated by electrochemical oxidation of *cis*-$[Ru^{II}(bpy)_2(tmen)]^{2+}$.[370] This species undergoes C—C bond cleavage in acidic solutions to give $[Ru(bpy)_2(NH{=}CMe_2)_2]^{2+}$.

The unstable species $[Ru^{V}(4\text{-}Bu^{t}\text{-}TPP)(NR)]^{+}$ is prepared by the oxidation of $[Ru^{IV}(4\text{-}Bu^{t}\text{-}TPP)(NR)]$ (Section 5.6.6.2) using Ag^{+} or Ce^{IV}.[371] This complex can transfer the imido group to PMe_2Ph at a rate 60 times faster than that its Ru^{IV} analog.

Reaction of $[Ru_2(O)_2(CH_2SiMe_3)_6]$ with PhNCO and $Me_3P{=}NSiMe_3$ gives the dimeric $[Ru_2(NPh)_2(CH_2SiMe_3)_6]$ ($\nu(Ru{\equiv}N) = 1132\,cm^{-1}$) and $[Ru_2(NSiMe_3)_2(CH_2SiMe_3)_6]$ ($\nu(Ru{\equiv}N) = 1{,}160\,cm^{-1}$), respectively.[372]

A novel osmium(V) imido complex, $[Os^{V}(NH)(Tp)(Cl)_2]$ (**151**), has been obtained by one-electron electrochemical reduction of $[Os^{VI}(N)(Tp)(Cl)_2]$ in dry CH_3CN containing 3.5 M HPF_6 (see Scheme 8 in Section 5.6.4.2.2(ii)).[373] The Os—N(H) distance of 1.749 Å[373] is the longest reported for transition metal M=NH complexes, which fall in the range 1.638–1.749 Å. There is evidence for an imido structural *trans* effect: the Os—N(Tp) bond of 2.291 Å *trans* to the NH^{2-} ligand is much longer than those *cis* to NH^{2-} (2.053 Å and 2.063 Å). The complex is also characterized by IR spectroscopy ($\nu(^{14}N{-}H) = 3257\,cm^{-1}$ and $\nu(^{15}N{-}H) = 3{,}250\,cm^{-1}$). $[Os^{V}\text{-}(bpy)(Cl)_3\text{-}(NH)]$ is also prepared in the same manner. (**151**) readily disproportionate in aqueous solution to give $[Os^{VI}(N)(Tp)(Cl)_2]$ and $[Os^{III}(Tp)(Cl)_2(NH_3)]$ (Equation (52)).

$$3[Os^{V}(NH)(Tp)(Cl)_2] \longrightarrow 2[Os^{VI}(N)(Tp)(Cl)_2] + [Os^{III}(Tp)(Cl)_2(NH_3)] \tag{52}$$

5.6.5.2 Nitrido Complexes

The only example of ruthenium(V) nitrido species would appear to be $[Ru^{V}(N)(L)]^{2-}$ ($\mu_{eff} = 1.84\mu_B$ at 293 K), where L is the tetraanionic macrocyclic ligand *meso*-octamethylporphyrinogen, which is prepared by the reduction of $[Ru^{VI}(N)(L)]^{-}$ with Na in THF (Scheme 12).[209] In the X-ray structure of this compound, the Ru≡N is disordered. The bond lengths for the two different sites are 1.74 Å and 1.78 Å.

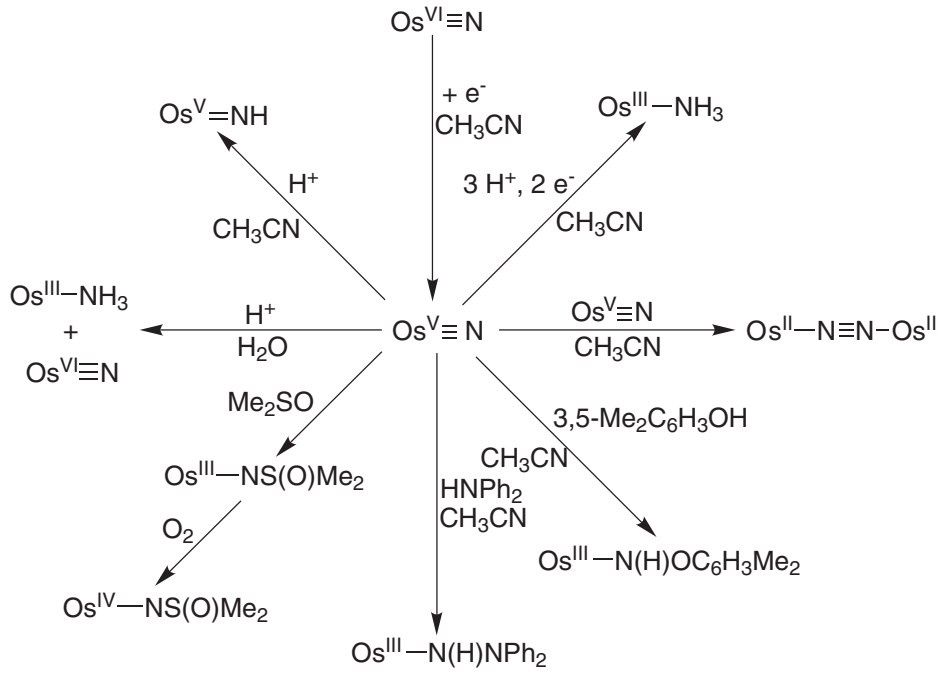
An osmium(V) nitrido complex $[Os^{V}(N)(CO)(NH_3)_4]^{2+}$ has been invoked as an intermediate involved in the formation of $[Os_2(N_2)(NH_3)_8(CO)_2]^{4+}$ by oxidation of $[Os(NH_3)_5(CO)]^{2+}$.[374] The complex $[Os^{V}(N)(NH_3)_4]^{2+}$ has been generated by reductive quenching of the ^3E_g state of $[Os^{VI}(N)(NH_3)_4]^{3+}$.[179,375] This species, once formed, undergoes rapid coupling with $[Os^{VI}(N)(NH_3)_4]^{3+}$ to form the mixed-valence $[Os_2(NH_3)_8(CH_3CN)_2(\mu\text{-}N_2)]^{5+}$ species (see also Section 5.6.4.2). Similarly, one-electron reduction of $[Os^{VI}(N)(tpy)(Cl)_2]^{+}$ generates $[Os^{V}(N)(tpy)(Cl)_2]$ which rapidly couples with another $Os^{V}{\equiv}N$ unit to form a μ-dinitrogen osmium(II) complex, $[(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)]$.[376] Dimerization can be prevented by adding appropriate reductants at high concentrations as trapping agents, such as Me_2SO, 3,5-$Me_2C_6H_3OH$, and $HNPh_2$.[373] A generalized reaction scheme for $Os^{V}{\equiv}N$ species is shown in Scheme 16.

5.6.5.3 Miscellaneous Nitrogen Ligands

5.6.5.3.1 Hydrazido complexes

Electrochemical oxidation of $[Os^{II}(tpy)(bpy)(NH_3)]^{2+}$ in aqueous solutions in the presence of a secondary aliphatic amine produces the formally osmium(V) hydrazido(2-) complex $[Os^{V}(tpy)(bpy)(NNR_2)]^{3+}$, which can be reduced electrochemically to $[Os^{IV}(tpy)(bpy)(NNR_2)]^{2+}$.[377] A series of osmium(V) hydrazido complexes, $[Os^{V}(L)(Cl)_2(NNR_2)]^{+}$ (L = tpy, tpm; $NNR_2 = NN(CH_2)_4CH_2$, $NN(CH_2)_4O$, $NNEt_2$), can be obtained by reaction between the corresponding osmium(VI) nitrido complex and HNR_2 (Equation (53)):[177,178,378]

$$2\text{trans-}[Os^{VI}(N)(tpy)(Cl)_2]^{+} + 2HNR_2 \longrightarrow \textit{trans}\text{-}[Os^{V}(tpy)(Cl)_2(NNR_2)]^{+} + \tfrac{1}{2}\textit{trans,trans}\text{-}[(tpy)(Cl)_2Os^{II}(N_2)Os^{II}(Cl)_2(tpy)] + H_2NR_2^{+} \tag{53}$$



Scheme 16

A number of these complexes have been structurally characterized (Table 14). The Os—N(N) bond lengths (1.846–1.915 Å) are significantly shorter than Os—N single bonds (2.039–2.123 Å). The N—N bond lengths (1.231–1.321 Å) are relatively short, consistent with a N=N double bond. The Os^{V} complexes exhibit reversible $Os^{VI/V}$, $Os^{V/IV}$, $Os^{IV/III}$ in cyclic voltammetry, and the $E_{1/2}$ values are shown in Table 15.

5.6.5.3.2 *Phosphoraniminato complexes*

Although a number of stable osmium(IV) phosphoraniminato complexes are known, the corresponding osmium(V) complexes are unstable. The net reaction for one-electron oxidation of $[Os^{IV}(NPPh_3)(tpy)(Cl)_2]^{+}$ to Os^{V} is shown in Equation (54).[379] The reaction presumably occurs by initial disproportionation of Os^{V} to Os^{VI} and Os^{IV} followed by PPh_3 transfer. Similarly,

Table 14 Summary of bond distances, angles, and stretching frequencies for osmium hydrazido complexes.

Complex	*d(Os—N)* (Å)	*∠Os—N—N*(°)	*ν(N—N)* (cm^{-1})	*References*
$[Os^{IV}(NNEt_2)(tpy)(bpy)](PF_6)_2$	1.89(1)	137(1)	1259	377
$[Os^{IV}\{NN(CH_2)_4O\}(tpy)(bpy)](PF_6)_2$	1.849(16)	137.1(12)	1219	377
cis-$[Os^{IV}\{NN(CH_2)_4O\}(tpy)(MeCN)_2](PF_6)_2$	1.971(7),	130.9(5),	1384	177,211
$[Os^{IV}(N(H)N(CH_2)_4O)(tpm)(Cl)_2](PF_6)$	1.904(8)	136.0(6)	1218	178
cis-$[Os^{IV}\{NN(CH_2)_4O\}(tpy)(MeCN)(Cl)](PF_6)_2$	1.984(10)	129.3(7)		177
$[Os^{V}(NNEt_2)(tpy)(bpy)](PF_6)_3$			1332	377
$[Os^{V}\{NN(CH_2)_4O\}(tpy)(bpy)](PF_6)_3$			1340	377
cis-$[Os^{V}\{NN(CH_2)_4O\}(tpy)(Cl)(MeCN)](PF_6)_2$	1.915(7) 1.846(8)	148.9(8) 148.9(7)		178
trans-$[Os^{V}\{NN(CH_2)_4CH_2\}(tpy)(Cl)_2](PF_6)$	1.855(9)	157.2(9)	1352	177,178
$[Os^{V}(NN(C_2H_5)_2)(tpm)(Cl)_2](BF_4)$	1.855(4)	148.5(4)	1227	177,178
trans-$[Os^{VI}\{NN(CH_2)_4O\}(tpy)(Cl)_2](PF_6)_2$	1.778(8)	170.3(7)		177,178
trans-$[Os^{VI}\{NN(CH_2)_4O\}(4\text{-}O(CH_2)_4Ntpy)(Cl)_2](PF_6)_2$	1.778	172.5(4)		212

Table 15 Summary of formal potentials for osmium hydrazido complexes.

	Vs. SSCE (MeCN) (V)			
Complex	*($Os^{VI/V}$)*	*($Os^{V/VI}$)*	*($Os^{IV/III}$)*	*References*
$[Os^{IV}(NNEt_2)(tpy)(bpy)]^{2+}$	1.425 1.18[a] (H_2O)	0.586 0.360 (H_2O)		377
$[Os^{IV}\{NN(CH_2)_4CH_2\}(py)(bpy)]^{2+}$	1.415 1.16[a] (H_2O)	0.625 0.397 (H_2O)		377
$[Os^{IV}\{NN(CH_2)_4O\}(tpy)(bpy)]^{2+}$	1.489 1.22[a] (H_2O)	0.669 0.464 (H_2O)		377
cis-$[Os^{IV}\{NN(CH_2)_4O\}(tpy)(MeCN)_2]^{2+}$	1.52	0.95	−0.36	211
$[Os^{IV}(N(H)N(CH_2)_4O)(tpy)(Cl)_2]^{+}$	0.98	0.84[d]	−0.08	178
trans-$[Os^{V}\{NN(CH_2)_4CH_2\}(tpy)(Cl)_2]^{+}$	0.90	−0.05	−0.75	178
cis-$[Os^{V}\{NN(CH_2)_4O\}(tpy)(MeCN)(Cl)]^{+2}$	1.30	0.42	−0.22	178
$[Os^{V}\{NN(CH_2)_4O\}(tpm)(Cl)_2]^{+}$	1.05	0.27	−0.62[b]	178
$[Os^{V}\{NN(CH_2)_4CH_2\}(tpm)(Cl)_2]^{+}$	0.95	0.05	−0.77[b], −0.05[c]	178
$[Os^{V}\{NN(C_2H_5)_2\}(tpm)(Cl)_2]^{+}$	0.92	0.03	−0.77[b]	178
trans-$[Os^{VI}\{NN(CH_2)_4O\}(tpy)(Cl)_2]^{+}$	0.98	0.00	−0.79	178
trans-$[Os^{VI}\{NN(CH_2)_4O\}(4'\text{-}O(CH_2)_4Ntpy)(Cl)_2]^{+}$	0.780	0.15	0.48	212
trans-$[Os^{VI}\{NN(CH_2)_4O\}(Bu^tN(H)tpy)(Cl)_2]^{2+}$	0.775	0.113	−0.586	212
trans-$[Os^{VI}\{NN(CH_2)_4O\}(Et_2Ntpy)(Cl)_2]^{2+}$	0.761	0.144	−0.533	212
trans-$[Os^{VI}\{NN(CH_2)_4O\}((CH_2)_5Ntpy)(Cl)_2]^{2+}$	0.759	0.156	−0.580	212

[a] Irreversible oxidation. *E*pa value is given. [b] *E*pc (Os(IV) → Os(III)). [c] *E*pa (Os(III) → Os(IV)). [d] $Os^{V/IV}$–N(H)N$(CH_2)_4$O.

$[Os^{V}(tpm)Cl_2(NPEt_3)]^{2+}$, generated by oxidation of $[Os^{IV}(tpm)Cl_2(NPEt_3)]^{+}$, undergoes a group transfer reaction with 3,5-dimethylbenzenethiol in MeCN (Equation (55)).[380]

$$2[Os^{V}(NPPh_3)(tpy)(Cl)_2]^{2+} \longrightarrow [Os^{VI}(N)(tpy)(Cl)_2]^{+} + [Os^{III}(tpy)(Cl)_2(MeCN)]^{+} + [PPN]^{+} \quad (54)$$

$$[Os^{V}(NPEt_3)(tpm)(Cl)_2]^{2+} + Me_2C_6H_3SH + MeCN \longrightarrow [Os^{III}(tpm)(Cl)_2(MeCN)]^{+} + Et_3P{=}N{-}SC_6H_3Me_2 + H^{+} \quad (55)$$

5.6.5.3.3 Sulfilimido complexes

Osmium(V) sulfilimido complexes can be generated by electrochemical or chemical oxidation of the corresponding osmium(IV) complexes (see Section 5.6.6.4.5).

5.6.5.4 Oxo Complexes

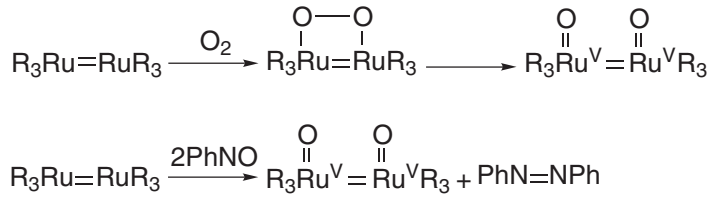
The compound $Ba_5[Ru_2(O)_{11}]$ has been synthesized by solid-state reactions of barium carbonate with ruthenium oxide. The X-ray structure shows that it contains peroxide ions and the ruthenium is in the +5 oxidation state, i.e., $Ba_5[Ru_2(O_2)O_9]$.[381] The novel mixed-valence Ru^{V}—Ru^{VI} triple perovskites, $Ba_3M[Ru_2(O)_9]$ (M = Li, Na), have been grown from reactive hydroxide fluxes.[382]

5.6.5.4.1 Terminal oxo complexes

(i) Carbon ligands

Reaction of $[Ru_2(CH_2SiMe_3)_6]$ in hexane at −30 °C with O_2 produces the unusual metal–metal bridged oxoruthenium(V) species, $[Ru_2O_2(CH_2SiMe_3)_6]$, as a red crystalline solid.[372] This

compound is also formed by reaction of $[Ru_2(CH_2SiMe_3)_6]$ with PhNO at −80 °C in toluene (Scheme 17).



Scheme 17

The IR absorption band at 908 cm^{-1} is assigned as the Ru=O stretch. The X-ray structure of $[Ru(O)(CH_2SiMe_3)_3]_2$ has been obtained.[372] The molecule can be considered to comprise two $[Ru(O)_2C_3]$ trigonal bipyramids, in which the equator is formed from one oxo oxygen atom and two alkyl carbons, linked via asymmetric oxygen bridges between one axial and one equatorial site (Ru—O = 1.733 Å, Ru···O = 2.208 Å, Ru—Ru = 2.738 Å). The diamagnetism of the complex has been suggested to result from the single Ru—Ru link. $[Ru_2(O)_2(CH_2CMe_3)_6]$ can also be obtained by treatment of $[Ru_2(CH_2CMe_3)_6]$ with PhNO.

(ii) Nitrogen ligands

A series of monooxo complexes of ruthenium(V), *trans*-$[Ru^V(O)(14\text{-TMC})(X)]^{2+}$ (X = Cl, NCO, N_3), have been generated electrochemically from the parent Ru^{IV} oxo complexes in acetonitrile.[241,242,383] These complexes have high one-electron reduction potentials with $E^\circ(Ru^{V/IV})$ ranging from 1.10 V to 0.70 V vs. $Cp_2Fe^{+/0}$. They are active electrocatalysts for the oxidation of benzyl alcohol to benzaldehyde. The second-order rate constants for the reaction between *trans*-$[Ru^V(O)(L)(X)]^{2+}$ and benzyl alcohol have been evaluated by rotating disk voltammetry. The values obtained are $2.1 \times 10^2\ M^{-1}\ s^{-1}$ and $1.4 \times 10^2\ M^{-1}\ s^{-1}$ for $X = Cl^-$ and NCO^-, respectively. In the oxidation of substituted benzyl alcohols by *trans*-$[Ru^V(O)$-$(14\text{-TMC})(NCO)]^{2+}$, a linear Hammett plot with a slope of −2.0 is obtained, consistent with the buildup of positive charge at the alcohol in the transition state. These results suggest a hydrogen atom abstraction mechanism.[384]

In aqueous solution, *cis*-$[Ru^V(O)(pyen)Cl]^{2+}$ has also been generated electrochemically from *cis*-$[Ru^{III}(pyen)Cl(OH_2)]^{2+}$[385] (see Figure 3 for structure of ligand). This Ru^V oxo complex has an $E^\circ(Ru^{V/IV})$ value of 1.29 V vs. SCE and it is an active catalyst for the electrochemical oxidation of alcohols and THF. The rate constants for the oxidation of $PhCH_2OH$, CH_3OH, CH_3OD, and CD_3OH evaluated by rotating disk voltammetry are $8.4 \times 10^4\ M^{-1}\ s^{-1}$, $6.6 \times 10^2\ M^{-1}\ s^{-1}$, $5.5 \times 10^2\ M^{-1}\ s^{-1}$, and $6.6 \times 10\ M^{-1}\ s^{-1}$, respectively, at 25 °C.[385,386] The large deuterium isotope effect for methanol indicates the importance of α-CH bond cleavage in the transition state. A chemically modified electrode prepared by immobilization of the complex inside a Nafion film on a pyrolytic graphite electrode surface is capable of catalyzing the electrooxidation of methanol.[386]

A monooxoruthenium(V) complex containing a pentadentate N_4O^- ligand, $[Ru^V(O)(N_4O)]$-$(ClO_4)_2$ (N_4OH = bis(2-(2-pyridyl)ethyl)(2-hydroxy-2-(2-pyridyl)ethyl)amine) (Figure 14), has been obtained by oxidation of $[Ru^{III}(N_4O)(OH_2)](ClO_4)_2$ with Ce^{IV}.[492] The complex has a measured μ_{eff} of 2.2 μ_B, higher than in *trans*-$[Ru^V(O)_2(14\text{-TMC})]^+$.[240] The expected ground state for $[Ru^V(N_4O)(O)]^{2+}$ is $(d_{xy})^2(d_\pi{*})^1$ ($d_\pi{*} = d_{xz}$, d_{yz}). The measured higher μ_{eff} than the spin only value for one unpaired electron suggests orbital contribution to the magnetic moment. The IR

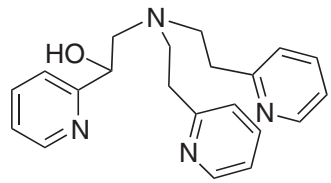


Figure 14 Structure of N_4OH.

spectrum of $[Ru^{V}(O)(N_4O)](ClO_4)_2$ shows an intense Ru=O stretch at 872 cm^{-1}, which is higher than the values of 790–840 cm^{-1} in monooxo ruthenium(IV) complexes (Table 4). The complex exhibits reversible redox couples. At pH 1, a two-electron two-proton couple at 1.02 V vs. SCE is observed (Equation (56)):[492]

$$[Ru^{V}(O)(N_4O)]^{2+} + 2H^{+} + 2e^{-} \longrightarrow [Ru^{III}(N_4O)(OH_2)]^{2+} \quad (56)$$

At $5.5 > pH > 3.5$ the wave for the $Ru^{V/III}$ couple splits into two waves, a pH-independent one-electron wave for the $[Ru^{V}(O)(N_4O)]^{2+}/[Ru^{IV}(O)(N_4O)]^{+}$ couple (slope = 0 mV/pH unit) and a two-proton one-electron $[Ru^{IV}(O)(N_4O)]^{+}/[Ru^{III}(N_4O)(OH_2)]^{2+}$ couple (Figure 15).[492]

$[Ru^{V}(O)(N_4O)]^{2+}$ oxidizes a variety of organic substrates such as alcohols, alkenes, THF, and saturated hydrocarbons.[387] In all cases $[Ru^{V}(O)(N_4O)]^{2+}$ is reduced to $[Ru^{III}(N_4O)(OH_2)]^{2+}$. The C—H deuterium isotope effects for the oxidation of cyclohexane, tetrahydrofuran, 2-propanol, and benzyl alcohol are 5.3, 6.0, 5.3, and 5.9 respectively, indicating the importance of C—H cleavage in the transitions state. For the oxidation of alcohols, a linear correlation is observed between log(rate constant) and the ionization potential of the alcohols. $[Ru^{V}(O)(N_4O)]^{2+}$ is also able to function as an electrocatalyst for the oxidation of alcohols.[388] Using rotating disk voltammetry, the rate constant for the oxidation of benzyl alcohol by $[Ru^{V}(O)(N_4O)]^{2+}$ is found to be 1.7×10^{2} M^{-1} s^{-1}. The Ru^{V} electrocatalyst remains active when immobilized inside Nafion films.

Reaction of $[RuO_4]^{-}$ with H_4[PHAB] gives the paramagnetic monoxoruthenium(V) complex (NPr^{n}_4)[Ru(O)PHAB] (**109**).[389] It has a ν(Ru=O) stretch at 887 cm^{-1}. X-ray diffraction studies reveal that it has a distorted trigonal bipyramidal geometry, with a Ru=O distance of 1.702 Å.

Monooxoruthenium(V) complexes [Ru(O)(salophen)X]$^{n+}$ [salophen = *N*,*N*′-bis(salicylidene)-*o*-phenylenediaminato; X = Cl, Im(Imidazole), 2-Me-Im(2-methyl-imdazole)][390] and [Ru(O)(edta)][391] have also been claimed, but further characterization of these species is desirable.

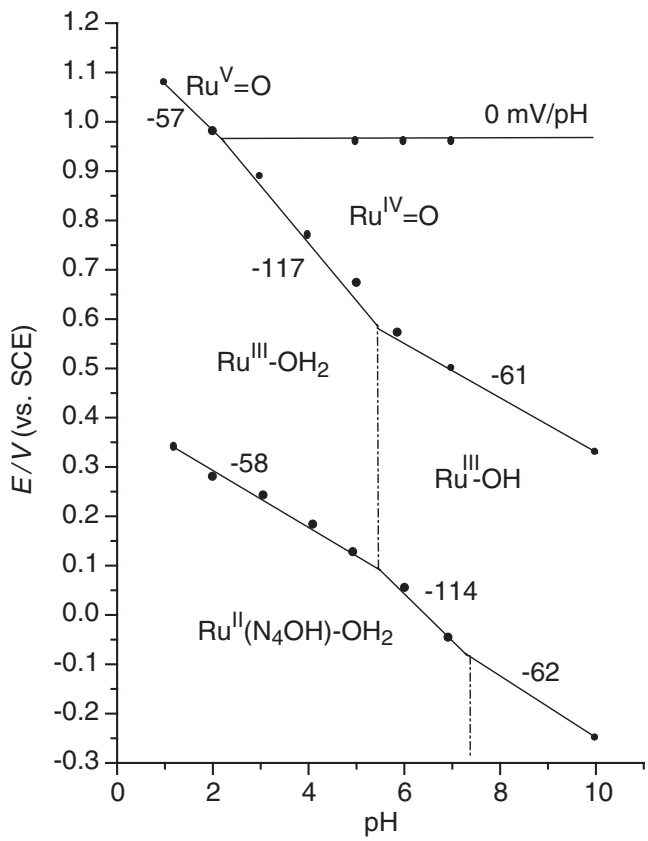


Figure 15 Pourbaix diagram for $[Ru^{V}(O)(N_4O)]^{2+}$.

Dioxoruthenium(V) and dioxoosmium(V) species containing polypyridyl ligands, *cis*- and *trans*-$[M^{V}(O)_2(bpy)_2]^{+}$, are intermediates in the sequential electrochemical oxidation of the corresponding M^{II} diaquo species *cis*- and *trans*-$[M^{II}(bpy)_2(OH_2)_2]^{2+}$; as well as in the sequential electrochemical reduction of the corresponding M^{VI} dioxo species *cis*- and *trans*-$[M^{VI}(O)_2(bpy)_2]^{2+}$.[237,254,392] These species are stable within the timescale of cyclic voltammetry; however, no isolation of these complexes has been reported.

A series of *trans*-$[Ru^{V}(O)_2(L)]^{+}$ complexes (L = 14-TMC, 15-TMC, 16-TMC, $(TMEA)_2$, $CRMe_3$, pyen (see Figure 3 for structures of ligand) have been prepared by electrochemical reduction of the corresponding *trans*-$[Ru^{VI}(O)_2(L)]^{2+}$ species in acetonitrile under argon atmosphere. *trans*-$[Ru^{V}(O)_2(14\text{-TMC})]ClO_4$ has a measured μ_{eff} value of 1.94 μ_B, consistent with a $(d_{xy})^2(d_\pi^*)^1$ ground state electronic configuration ($d_\pi^* = d_{xz}$, d_{yz}).[240,393] The UV–vis spectral data for *trans*-$[Ru^{V}(O)_2(L)]^{+}$ in acetonitrile are collected in Table 5. The low-energy vibronic structured absorption band at 420–450 nm is assigned as the ligand field $d_{xy} \rightarrow d_\pi^*$ transition[240] (Table 5; see also Section 5.6.4.4.2(iii)(c)). The complex *trans*-$[Ru^{V}(O)_2(N_2O_2)]ClO_4$ has also been isolated and is stable in aqueous solution at pH $\leq$ 7.[394]

trans-$[Ru^{V}(O)_2(L)]^{+}$ is unstable with respect to disproportionation in acidic solutions (Equation (57)).[256]

$$2\textit{trans}\text{-}[Ru^{V}(O)_2(L)]^{+} + 2H^{+} \longrightarrow \textit{trans}\text{-}[Ru^{VI}(O)_2(L)]^{2+} + \textit{trans}\text{-}[Ru^{IV}(O)(OH_2)(L)]^{2+} \quad (57)$$

For *trans*-$[Ru^{V}(O)_2(14\text{-TMC})]^{+}$, E° for the disproportionation is 0.86 V at 25 °C. The kinetics of the disproportionation have been studied.[256] The rate law is: rate = $k_{disp}[Ru^{V}]^2$, where $k_{disp} = 2k_eK_p[H^+]/(1 + K_p[H^+])^2$. This is consistent with the mechanism shown in Equations (58) and (59). At 299 K and 0.1 M ionic strength, K_p and k_e are 615 M^{-1} and 2.72×10^6 M^{-1} s^{-1}, respectively. The self-exchange rate constant of the *trans*-$[Ru^{V}(O)(OH)(14\text{-TMC})]^{2+}$/*trans*-$[Ru^{IV}(O)(OH)(14\text{-TMC})]^{+}$ couple has also been estimated to be 5×10^3 M^{-1} s^{-1} at 298 K and 0.1 M ionic strength from the kinetics data.

$$\textit{trans}\text{-}[Ru^{V}(O)_2(14\text{-TMC})]^{+} + H^{+} \underset{}{\overset{K_p}{\rightleftharpoons}} \textit{trans}\text{-}[Ru^{V}(O)(OH)(14\text{-TMC})]^{2+} \quad (58)$$

$$\textit{trans}\text{-}[Ru^{V}(O)(OH)(14\text{-TMC})]^{2+} + \textit{trans}\text{-}[Ru^{V}(O)_2(14\text{-TMC})]^{+} \xrightarrow{k_e} \textit{trans}\text{-}[Ru^{IV}(O)(OH)(14\text{-TMC})]^{+} + \textit{trans}\text{-}[Ru^{VI}(O)_2(14\text{-TMC})]^{2+} \quad (59)$$

A *cis*-dioxoruthenium(V) complex, *cis*-$[Ru^{V}(O)_2(Tet\text{-}Me_6)]ClO_4$, has also been isolated by electrochemical or chemical reduction of *cis*-$[Ru^{VI}(O)_2(Tet\text{-}Me_6)]^{2+}$ (**95**) in MeCN. Its structure has been characterized by X-ray crystallography. The O—Ru—O angle is 115.1° and the two Ru=O distances are the same (1.751 Å). It has a measured μ_{eff} of 1.9μ_B at 25 °C. Only one ν(Ru=O) band has been located at 850 cm^{-1}; the other one probably overlaps with the ligand peaks.[260]

A series of *trans*-dioxoosmium(V) complexes analogous to that of ruthenium, *trans*-$[Os^{V}(O)_2(L)]ClO_4$ (L = 14-TMC, 15-TMC, 16-TMC, $CRMe_3$), have been prepared by electrochemical reduction of the corresponding *trans*-dioxoosmium(VI) complexes in MeCN.[251] *trans*-$[Os(O)_2(14\text{-TMC})]ClO_4$ has a μ_{eff} value of 1.89 μ_B. The IR spectrum shows two intense absorption bands at 879 and 873 cm^{-1}, tentatively assigned as the $\nu_{asym}(OsO_2)$ stretch. The UV–vis absorption spectra of *trans*-$[Os^{V}(O)_2(L)]^{+}$ in MeCN exhibit two vibronic structured bands, centered at ~335 nm and 410 nm (Figure 16, Table 5). These bands are also red shifted from that of the corresponding Os^{VI} complexes. This is attributed to the splitting of the doubly degenerate d_π^* orbitals of d^3 Os^{V} and lowering of their energy level by occupancy of an electron in the d_π^* orbitals. Similar red shifts have been observed for the corresponding Ru^{VI} and Ru^{V} systems.[240] In the presence of acids, *trans*-$[Os^{V}(O)_2(L)]^{+}$ disproportionates according to Equation (60):[251]

$$3\textit{trans}\text{-}[Os^{V}(O)_2(L)]^{+} + 3H^{+} \longrightarrow 2\textit{trans}\text{-}[Os^{VI}(O)_2(L)]^{2+} + \textit{trans}\text{-}[Os^{III}(L)(OH)(OH_2)]^{2+} \quad (60)$$

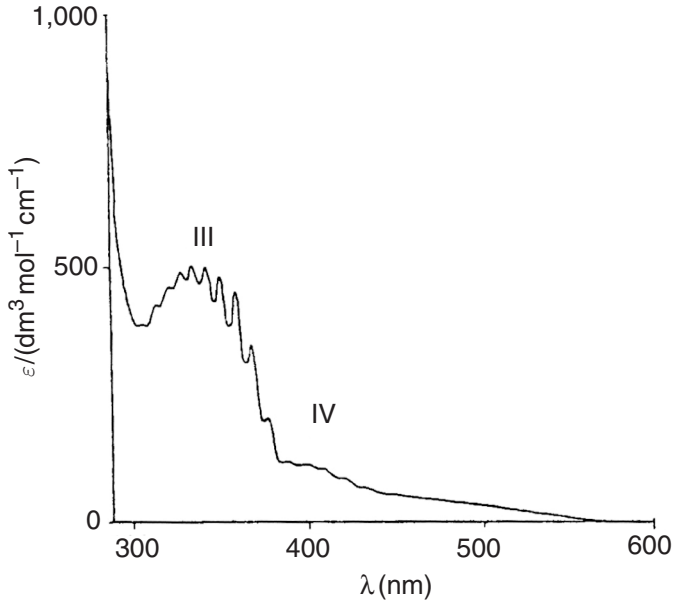
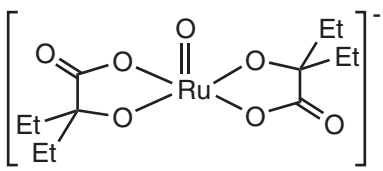


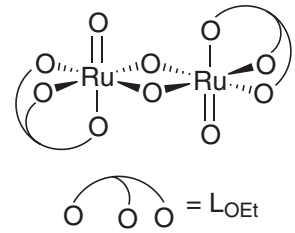
Figure 16 UV–vis spectrum of *trans*-$[Os(O)_2(14\text{-TMC})]^+$ in acetonitrile.

(iii) Oxygen ligands

Reaction of $(NPr^n_4)[RuO_4]$ in acetone with 2-hydroxy-2-ethylbutyric acid gives the brown $Ru^V{=}O$ species $(NPr^n_4)[Ru(O)(O_2COCEt_2)_2]$ (**113**), the structure of which has been established by X-ray crystallography.[395] There are two crystallographically independent molecules with Ru=O distances of 1.697 Å and 1.676 Å. The complex is paramagnetic ($\mu_{eff} = 1.70\mu_B$ at 25 °C). In CH_2Cl_2/MeOH glass at ~100 K it gives an anisotropic EPR spectrum typical of a $S = 1/2$ system with $g_x = 2.076$, $g_y = 1.977$, $g_z = 1.911$. This indicates that the complex has a single unpaired electron in the ground state, consistent with a penta-coordinate Ru(V) configuration.[395,396] The IR spectrum shows a strong band at 900 cm^{-1} assigned to the Ru=O stretch. The complex functions as a mild oxidant in MeCN, capable of slowly oxidizing alcohols to aldehydes or ketones and PPh_3 to $OPPh_3$. These reactions can be made catalytic using NMO as the terminal oxidant.[395]



(**113**)



(**114**)

A series of related ruthenium(V) oxo complexes with α-hydroxycarboxylate ligands, $(NPr^n_4)[Ru(O)(O_2COCR^1R^2)_2]$ ($R^1R^2 = Me_2$, EtMe, PhMe), and α-amino carboxylate ligands, $(NPr^n_4)[Ru(O)(O_2C(NH)CHEt)_2]$, have also been prepared by the same method.[396] An osmium analog, $(PPh_4)[Os(O)(O_2COCEt_2)_2]$, is similarly prepared from $(PPh_4)[OsO_4]$ and 2-hydroxy-2-ethylbutyric acid in acetone. It has a ν(Os=O) stretch at 958 cm^{-1}.[396] A $Ru^V{=}O$ species has been generated by electrochemical oxidation of the polyoxometalate $Ru^{III}{-}OH_2$ species $[(P)W_{11}(O)_{39}Ru^{III}(H_2O)]^{4-}$. This species is able to oxidize DMSO to the sulfone.[397]

5.6.5.4.2 Oxo-bridged species

The oxo-bridged ruthenium(V) dimer $[(bpy)_2(O)Ru^V(\mu\text{-}O)Ru^V(O)(bpy)_2]^{4+}$ has been suggested as the active intermediate in the catalytic oxidation of H_2O to O_2 by $[(bpy)_2(H_2O)Ru^{III}$

$(\mu\text{-O})Ru^{III}(OH_2)(bpy)_2]^{4+}$.[398–404] This species can be generated in solution from $[(bpy)_2(H_2O)Ru^{III}(\mu\text{-O})Ru^{III}(OH_2)(bpy)_2]^{4+}$ either electrochemically or by oxidation with Ce^{IV} or Co^{3+}. It oxidizes water with a rate constant $>1\,s^{-1}$.[400] It is characterized by resonance Raman bands at $357\,cm^{-1}$ (ν_{sym}(Ru—O—Ru)) and $816\,cm^{-1}$ (ν(Ru=O)). The perchlorate salt of this species has also been isolated as an unstable black solid.[400] The Ru^V—O—Ru^V species is a strong oxidant. The redox potential as a function of pH for this species and its lower oxidation states are summarized in the Pourbaix diagram for $[(bpy)_2(H_2O)Ru^{III}(\mu\text{-O})Ru^{III}(OH_2)(bpy)_2]^{4+}$ (Figure 17). A Ru^V—O—Ru^V active intermediate is also proposed for the catalytic water oxidation by $[(L)_2(H_2O)Ru^{III}$—O—$Ru^{III}(OH_2)(L)_2]$ (L = 5,5′-$(COOH)_2$-bpy)[405] and $[(tpy)(H_2O)_2Ru^{III}(\mu\text{-O})\text{-}Ru^{III}(H_2O)_2(tpy)]^{4+}$.[406] The Ru^{IV}—O—Ru^V dimer seems to be the active catalyst in the chemical or electrochemical oxidation of water by $[(L)_2(H_2O)Ru^{III}(\mu\text{-O})Ru^{III}(OH_2)(L)_2]^{4+}$ (L = 4,4′-Cl_2bpy or 5,5′-Cl_2bpy).[407] This difference may be due to the fact that the chloro-substituted dimers have more positive redox potentials than the unsubstituted dimers.

The mixed-valence μ-oxo ions $[(bpy)_2(O)Ru^{IV}(\mu\text{-O})Ru^V(O)(bpy)_2]^{3+}$[408] and $[(bpy)_2(py)Ru^{III}\text{-}(\mu\text{-O})Ru^V(O)(bpy)_2]^{4+}$[408,409] have been generated in solution by electrochemical or chemical oxidation of $[(bpy)_2(HO)Ru^{III}(\mu\text{-O})Ru^{IV}(OH)(bpy)_2]^{3+}$ and $[(bpy)_2(py)Ru^{III}(\mu\text{-O})Ru^{IV}$ $(OH)(bpy)_2]^{4+}$, respectively. Both complexes are facile oxidants toward a variety of organic functional groups. The rate constants for the oxidation of 2-propanol are $2.5\,M^{-1}s^{-1}$ and $6.9\,M^{-1}s^{-1}$, respectively, at 25 °C and pH = 5.8,[408,409] which are substantially higher than the value of $8.7\times10^{-3}\,M^{-1}\,s^{-1}$ for oxidation by $[Ru^{IV}(O)(bpy)_2(py)]^{2+}$ (see Section 5.6.6.6.1).[410,411] The complex $[(bpy)_2(O)Ru^{IV}$ $(\mu\text{-O})Ru^V(O)(bpy)_2]^{3+}$ can also oxidize H_2O to O_2 by a pH-independent reaction that is first order in the oxidant. The rate constant at 298 K and 0.1 M ionic strength is $3.0\times10^{-4}\,s^{-1}$.[408]

The species $(PPh_4)_2[Ru_2(O)(\mu\text{-OCOEt})_2Cl_6]$ has been prepared by ozonolysis of a solution of $RuCl_3$ and PPh_4Cl in propanoic acid.[412] The ozonolysis method can also be used to prepare $[RuO_4]$, $[RuO_4]^-$, $[Ru(O)_3(OH)_2]^{2-}$, and $[OsO_4]$. Reaction of $[L_{OEt}(HO)Ru\ (\mu\text{-O})_2Ru(OH)L_{OEt}]$ (see Section 5.6.6.6.2(ii)) with $[RuO_4]$ in CCl_4 produces the Ru^V–Ru^V dioxo species $[L_{OEt}(O)Ru\text{-}(\mu\text{-O})_2Ru(O)L_{OEt}]$ (**114**).[413] This complex, although diamagnetic, has a Ru—Ru separation of 2.912 Å, indicating a relatively weak metal–metal interaction. The Ru=O and Ru—O(bridging)

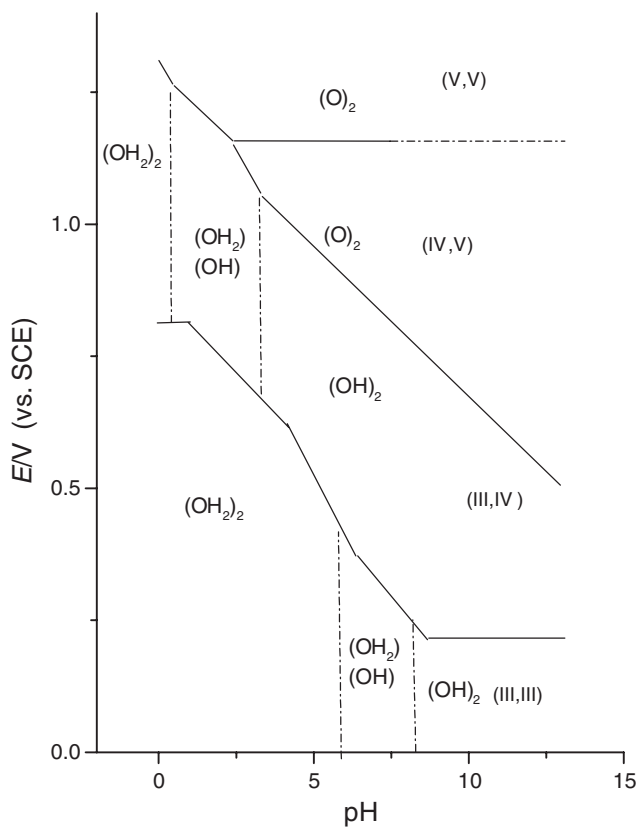


Figure 17 Pourbaix diagram for $[(bpy)_2(OH_2)Ru^{III}(\mu\text{-O})Ru^{III}(OH_2)(bpy)_2]^{4+}$.

distances are 1.725 Å and 1.887 Å, respectively. The IR spectrum shows a strong peak at 848 cm^{-1}, which is assigned to the ν(Ru=O) stretch. This complex oxidizes primary and secondary alcohols to the corresponding aldehydes and ketones.

5.6.5.5 Alkoxo Complexes

The osmium(V) porphyrin complexes $[Os^{V}(por)(OR)_2]^+$ (por = OEP, TPP; R = Et) have been generated by electrochemical oxidation of the corresponding $[Os^{IV}(por)(OR)_2]$ and were characterized by UV–vis spectroscopy.[414] $[Os^{V}(L)(OR)_2]^+$ (L = salen, bpb, bpc; R = Me, Et, Pr^i) (see Figure 12 for structures of ligands complexes) have also been prepared and characterized in a similar manner.[415]

5.6.5.6 Sulfur Ligands

No M^{V} complexes seem to have been reported.

5.6.5.7 Halide Ligands

The only binary ruthenium(V) halides are those containing fluoride, which are of some interest to the nuclear industry. The species $[RuF_5]$, $[RuF_5]_4$, $[RuF_6]^-$ (with a wide range of cations), and $(X)[Ru_2F_{11}]$ (X = XeF, KrF) have been described in *CCC* (1987). The salt $(ClO_2)[RuF_6]$ is also known. The Ru—F distance of 1.845(2) Å in $K[RuF_6]$ has been determined by EXAFS.[355] The molecular structure of gaseous RuF_5 and OsF_5 have been studied by electron diffraction. For both compounds the main constituents are trimeric molecules together with smaller amounts of dimeric species. The tetrameric structure of $[RuF_5]_4$ has been determined by X-ray crystallographic studies: (Ru—F(bridge) = 1.995–2.007 Å, Ru—F—Ru = 136.8° and 140.8°).[416] The diffuse reflectance UV–vis spectra of $[RuF_5]$ and $[OsF_5]$ have been recorded and assigned from the strong-field model and optical electronegativity approach.[417]

$[OsF_5]_4$ and salts of $[OsF_6]^-$ have been described in *CCC* (1987). The Os—F distance of $K[OsF_6]$ has been determined by EXAFS: d(Os—F) = 1.882 Å.[357]

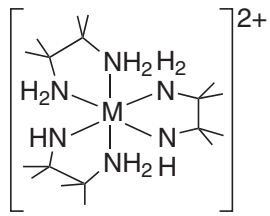
5.6.6 RUTHENIUM(IV) AND OSMIUM(IV)

5.6.6.1 Amido Complexes

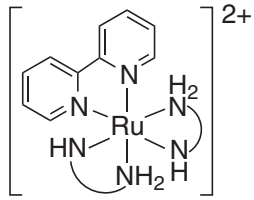
5.6.6.1.1 Nitrogen donor ligands

A number of ruthenium(IV) and osmium(IV) complexes containing deprotonated ethylenediamine ligands are known. Reaction of $(NBu^n_4)[Ru(N)(Cl)_4]$ with tmen produces $[Ru^{IV}(tmen\text{-}H)_2(tmen)]^{2+}$ (**115a**).[418] The two Ru—N(amide) bonds are *cis* to each other with rather short bond distances of 1.835 Å and 1.850 Å. Cyclic voltammetry shows reversible $[Ru^{III}(tmen)_3]^{3+}/[Ru^{II}(tmen)_3]^{2+}$ and $[Ru^{IV}(tmen\text{-}H)_2(tmen)]^{2+}/[Ru^{III}(tmen)_3]^{3+}$ couples at 0.09 V and 0.29 V vs. SCE (pH = 1.0), respectively. At pH ≥ 3.0 these two couples merge to the $[Ru^{IV}(tmen\text{-}H)_2(tmen)]^{2+}/[Ru^{II}(tmen)_3]^{2+}$ couple. Oxidation of $[Ru^{II}(bpy)(tmen)_2]^{2+}$ with Br_2 gives $[Ru^{IV}(bpy)(tmen\text{-}H)_2]^{2+}$ (**115c**), with Ru—N(amide) bond distances of 1.856 Å.[418] Cyclic voltammetry shows reversible $[Ru^{III}(bpy)(tmen)_2]^{3+}/[Ru^{II}(bpy)(tmen)_2]^{2+}$ and $[Ru^{IV}(bpy)(tmen\text{-}H)_2]^{2+}/[Ru^{III}(bpy)(tmen)_2]^{3+}$ couples at 0.38 V and 0.46 V vs. SCE, respectively. These two couples merge to form a $[Ru^{IV}(bpy)(tmen\text{-}H)_2]^{2+}/[Ru^{II}(bpy)(tmen)_2]^{2+}$ couple at pH ≥ 2.0.

Reaction of $(NH_4)_2[OsBr_6]$ with an excess of tmen also gives $[Os^{IV}(tmen\text{-}H)_2(tmen)]^{2+}$ (**115b**).[419] This species is more stable than $[Os^{IV}(en\text{-}H)_2(en)]^{2+}$, which undergoes oxidative dehydrogenation.[420] The Os—NH distances are 1.896 Å, which are 0.3 Å shorter than the average Os—NH_2 distance, indicative of substantial π-bonding. Cyclic voltammetry of (**115b**) shows a pH-dependent irreversible wave. However, a reversible pH-dependent $Os^{IV/III}$ couple is observed for *trans*-$[Os^{III}(tmen)_2(Cl)_2]^+$.[421]

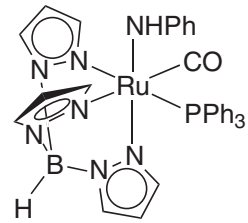


(**115**)
(**a**) Ru
(**b**) Os



$H_2N^{\wedge}NH_2$ = tmen

(**115c**)

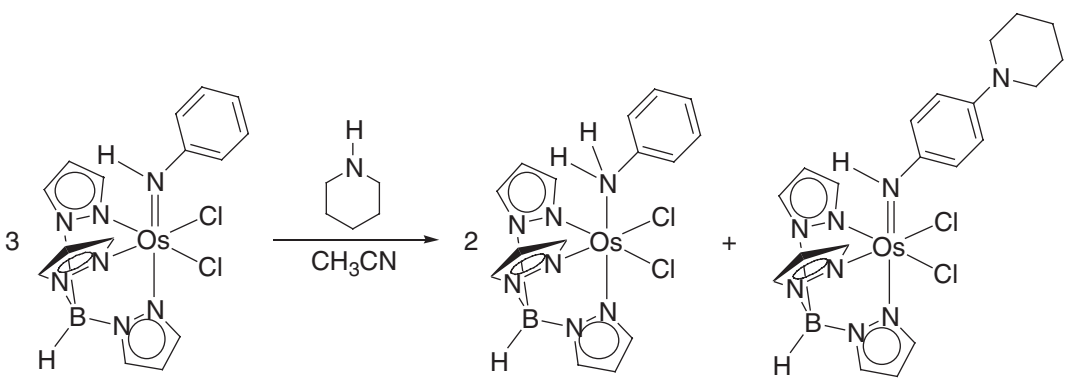


(**115d**)

It has been proposed that Ru^{IV} plays an important role in the oxidation of amines coordinated to ruthenium. A ruthenium(IV) amido species, $[Ru(sar\text{-}H)]^{3+}$, characterized by UV–vis spectroscopy, has been generated by two-electron oxidation of $[Ru(sar)]^{2+}$ (sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane).[422] This species is short lived and is rapidly transformed into a Ru(II) imine species.

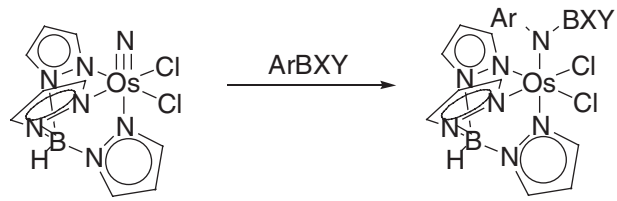
Reaction of the ruthenium(II) amido complex $[Ru^{II}(NHPh)(Tp)(CO)(PPh_3)]$ with two equivalents of AgOTf in the presence of excess NEt_3 or lutidine generates $[Ru^{IV}(NHPh)(Tp)(CO)(PPh_3)](OTf)_2$ (**115d**). The $BAr'_4{}^-$ ($Ar' = C_6H_3(CF_3)_2$-3,5) salt was also prepared.[609]

Treatment of $[Os^{VI}(N)(Tp)(Cl)_2]$ with PhMgBr followed by H_2O produces $[Os^{IV}(Tp)(NHPh)(Cl)_2]$ (Os—N(amide) = 1.919 Å, Os—N—C = 133.8°).[166,167] A similar reaction occurs with tolylmagnesium bromide or *p*-toluidine to give $[OsTp(NHTol)(Cl)_2]$.[167] $[Os^{IV}(Tp)(NHPh)(Cl)_2]$ exhibits low acidity and low basicity; it is less acidic and less basic than aniline.[423] It was suggested that this is a result of both Os—N(amide) π bonding and the inductive effect of the oxidizing Os(IV) center. Reaction of $[Os^{IV}(Tp)(NHPh)(Cl)_2]$ with MeOTf at 80 °C for 6*d* produces $[Os^{IV}(Tp)(NHPh)(OTf)_2]$ and CH_3Cl. The X-ray structure of $[Os^{IV}(Tp)(NHPh)(OTf)_2]$ shows a distorted octahedral structure: Os—N(amido) = 1.939 Å and Os—N—C = 134.8°. Interestingly, the anilido ligand is activated towards nucleophilic attack by secondary amines. Reaction of $[Os^{IV}(Tp)(NHPh)(Cl)_2]$ with piperidine (Equation (61)) and pyrrolidine gives $[Os^{IV}(Tp)\{NH\text{-}p\text{-}C_6H_4N(c\text{-}C_5H_{10})\}(Cl)_2]$ (Os—N(amide) = 1.945 Å) and $[Os^{IV}(Tp)\{NH\text{-}p\text{-}C_6H_4N(c\text{-}C_4H_8)\}(Cl)_2]$ (Os—N(amide) = 1.922 Å), respectively.[424] The Os—N(amide) N(amide) bond lengths are much shorter than the Os(III)–amine distance of 2.129 Å in the related $[Os(Tp)(NHEt_2)(Cl)_2]$ complex, indicating some multiple bond character.



(61)

Reaction of $[Os^{VI}(N)(Tp)(Cl)_2]$ with the organoboranes ArBXY (Equation (62)) yields the borylamido complexes $[Os(Tp)\{N(Ar)(B)(X)(Y)\}(Cl)_2]$ (Ar = X = Y = Ph; Ar = X = Ph, Y = $OBPh_2$; Ar = X = Y = C_6F_5).[167] The Os—N(amide) distances for these complexes are 1.880 Å, 1.937 Å, and 2.057 Å, respectively, indicating the presence of Os—N π-bonding. The B—N bond lengths are in the range of single bonds and vary in the reverse order 1.602 Å, 1.509 Å, and 1.408 Å.



(62)

Ar = X = Y =Ph;
Ar = X = Ph, Y = $OBPh_2$;
Ar = X = Y = C_6F_5

The alkyl boranes BEt_3 and $BEt_2(OMe)$ also add to $[Os^{VI}(N)(Tp)(Cl)_2]$ to form [Os(Tp){N(Et)-B(Et)X}$(Cl)_2$] (X = Et, OMe).[167]

[4 + 1] cycloaddition reactions are found to occur between $[Os^{VI}(N)(L)(Cl)_2]$ (L = Tp, tpm, tpy) and 1,3-cyclohexadienes at elevated temperature to produce the bicyclic osmium amido complexes $[Os^{IV}(L)(NC_6H_8)(Cl)_2]$[425] (Scheme 8).

The Os—N(amido) bond (1.859 Å) is significantly shorter than the corresponding distance in the anilido complex $[Os^{IV}(NHPh)(Tp)(Cl)_2]$ (1.919 Å), suggesting that the bicyclic amide is a stronger π-donor than the anilide.[166,425]

5.6.6.1.2 Oxygen donor ligands

The amidoruthenium(IV) complexes $[Ru^{IV}\{NH(c\text{-}C_6H_{11})\{OCEt(R)CO_2\}_2\}]^-$ (R = Me or Et) have been synthesized by the interaction of $[Ru^{V}(O)\{OCEt(R)CO_2\}_2]^-$ with excess cyclohexyl isocyanate in toluene or THF.[369] X-ray crystallography of $[Ru^{IV}\{NH(c\text{-}C_6H_{11})\}\{OCEt_2CO_2\}_2]^-$ (**116**) reveals a trigonal bipyramidal structure. The Ru—N distance is 1.818 Å, indicative of strong d_π–p_π interaction. The Ru—N—C angle is 132.1°, consistent with an amido ligand.

5.6.6.1.3 Mixed donor atom ligands

A paramagnetic Ru^{IV} species with a tetraanionic bis(amido) ligand, $[Ru^{IV}(CHBA\text{-}Et)(PPh_3)(py)]$ ($\mu_{eff} = 3.08\,\mu_B$ at 25 °C), has been obtained as a bluish green solid by the reaction of $[Ru(PPh_3)_3C1_2]$ with H_4CHBA-Et in the presence of air.[426] The X-ray crystal structure has been determined (Ru^{IV}—N(amide) = 1.987–2.044 Å). Analogous Os^{IV} complexes [Os(CHBA-Et)$(py)_2$] and [Os(CHBA-DCB)(bpy)] are also known (Figure 12).[314]

5.6.6.1.4 Porphyrin and related ligands

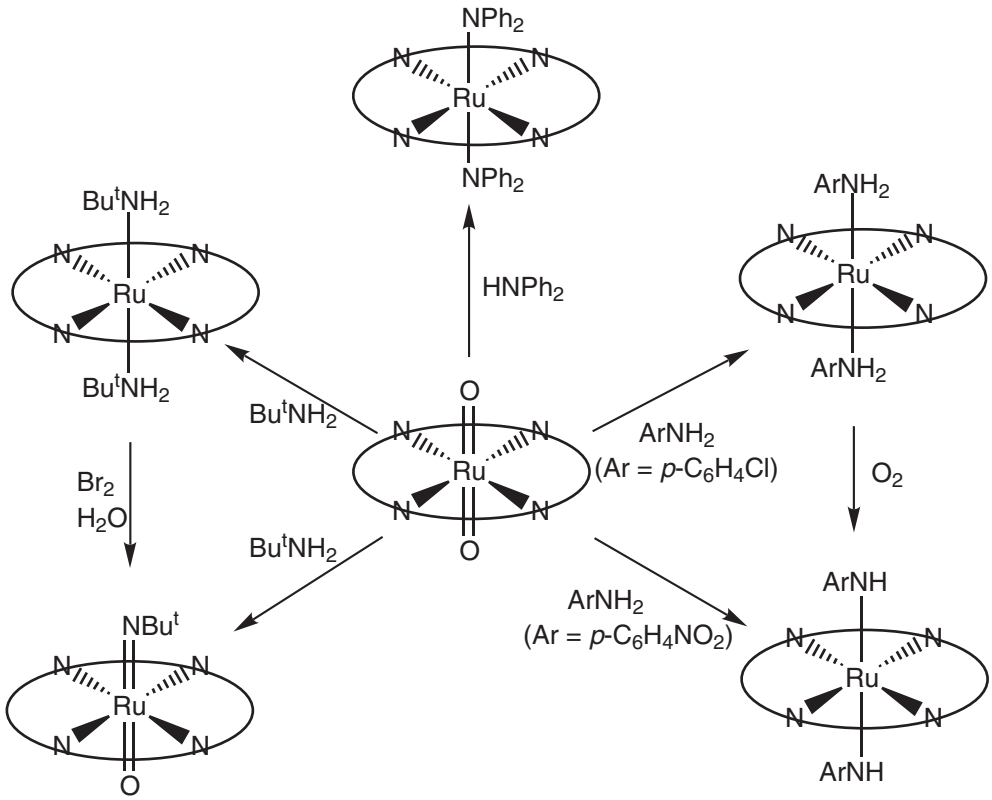
Reaction of $[Ru^{VI}(por)(NTs)_2]$ (por = TPP, OEP) with styrene or ethylbenzene in the presence of pyrazole produces the tosylamidoruthenium(IV) complex $[Ru^{IV}(por)(NHTs)(pz)]$ (Scheme 5).[146,147] It has a Ru—N(amido) distance of 2.025 Å and Ru—N—S angle of 136.4°.[147] In contrast to bis(amido)-ruthenium(IV) porphyrins, these complexes are paramagnetic with two unpaired electrons.

A number of bis(arylamido)- and bis(diarylamido)ruthenium(IV) porphyrin complexes have been reported. In general, these complexes can be prepared by the reduction of $[Ru(O)_2(por)]$ with corresponding aromatic amines or by the oxidative deprotonation of $[Ru^{II}(por)(ArNH_2)_2]$, as shown in Scheme 18.[135,427]

The X-ray structure of $[Ru^{IV}(TPP)(4\text{-}Cl\text{-}C_6H_4NH)_2]$ (**116a**) reveals a C_2 rotation axis where the ruthenium(IV) ion is located at the center of the porphyrinato ring and has a distorted octahedral environment.[135] The Ru—N(imido) bond lengths are both 1.956 Å, and the Ru—N—C angles are 135.8°.

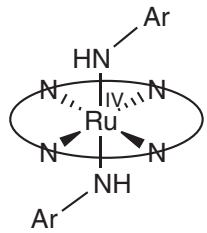
The osmium analog, $[Os^{IV}(por)(NHAr)_2]$ (por = OEP, TPP, 3,4,5-MeO-TPP; Ar = Ph, 4-F-Ph), can be obtained by the reaction of $[Os^{II}(por)(N_2)(THF)]$ with arylamines under aerobic conditions.[134]

These bis(amido)ruthenium(IV) and bis(amido)osmium(IV) porphyrin complexes show well-resolved ^{1}H NMR spectra with the signals of the porphyrinato ligands appearing at normal fields, indicating that they are all diamagnetic.



N_4 = por

Scheme 18



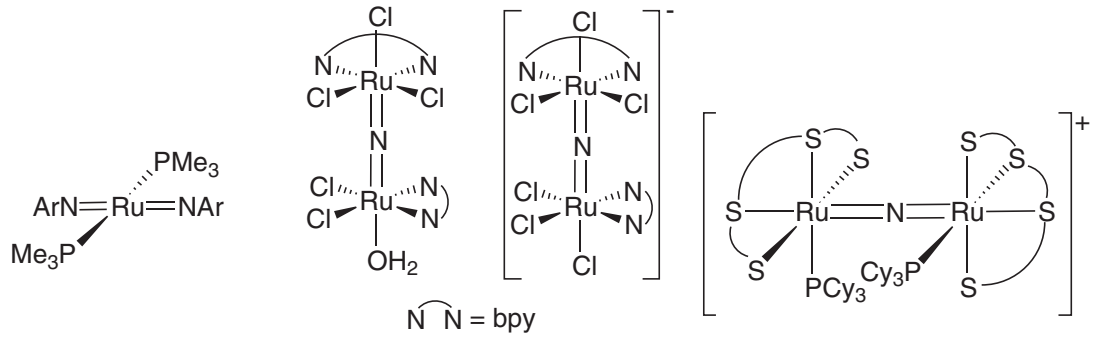
Ar = C_6H_4Cl-4, N_4 = TPP

(**116a**)

5.6.6.2 Imido Complexes

Treatment of *trans*-$[Ru(Cl)_2(PMe_3)_4]$ with Li(ArNH) in THF followed by O_2 oxidation produces the blue-green diamagnetic ruthenium(IV) imido species *trans*-$[Ru^{IV}(NAr)_2(PMe_3)_2]$ (**117**) ($Ar = C_6H_3Pr^i$-2,6).[428] The molecule has a square planar coordination geometry with a N—Ru—p angle of 90.1°. The Ru—N—C angle is 178.7°.[428] The Ru—N (1.785 Å) and Ru—P (2.372 Å) lengths are very similar to those of the osmium analog, *trans*-$[Os(NAr)_2(PMe_2Ph)_2]$.[151]

trans-$[Os^{IV}(NAr)_2(PMe_2Ph)_2]$ (**6**) ($Ar = C_6H_3Pr^i_2$-2,6) is prepared by the interaction of $[Os(NAr)_3]$ (**5**) with PMe_2Ph.[17,151] It is a square planar complex in which there is a crystallographic inversion center. The Os—N and Os—P distances are 1.790 Å and 2.374 Å, respectively.

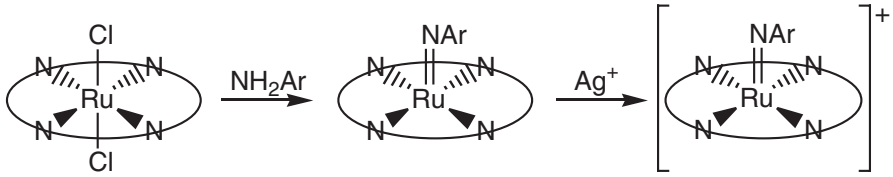


(**117**) (**118a**) (**118b**) (**119**)

The imido ligands are virtually linear (Os—N—C = 177.9°).[151] The same method has been used to prepare $[Os(NAr)_2(L)_2]$ (L = PMe_3, PMe_2Ph, $P(OMe)_3$).[17,151] Reduction of $[Os(O)_2(NAr)_2]$ with a few equivalents of L (L = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) also gives $[Os(NAr)_2(L)_2]$.[18] The reactivity of $[Os(NAr)_2(L)_2]$ are summarized in Scheme 4. $[Os(NAr)_2(PhC{\equiv}CPh)]$ is isolated when $[Os(NAr)_2(PPh_3)_2]$ is treated with PhC≡CPh in the presence of CuCl.[18]

An osmium(IV) imido species, $[Os(NH)(tpy)(bpy)]^{2+}$, has been proposed to be the active intermediate in the formation of nitrosamines from the oxidation of coordinated ammonia in the presence of secondary amines.[429] Deprotonation of $[Ru^{IV}(NHPh)(Tp)(CO)(PPh_3)]^{2+}$ gives the unstable imido complex $[Ru^{IV}(NPh)(Tp)(CO)(PPh_3)]^{+}$.[609]

A number of arylimido complexes of ruthenium(IV) porphyrins are known. Reactions of $[Ru^{IV}(por)(Cl)_2]$ (por = 4-Bu^t-TPP, TTP) with $ArNH_2$ give the paramagnetic $[Ru^{IV}(por)(NAr)]$ ($\mu_{eff} = 2.8\mu_B$, $\nu(Ru{=}NR) = 1{,}200$–$1{,}210\ cm^{-1}$) (Equation (62a)).[371] The cyclic voltammogram of $[Ru^{IV}$(4-Bu^t-TPP)(NAr)] exhibits reversible $Ru^{V/IV}$ and $Ru^{IV/III}$ couples. [Ru(4-Bu^t-TPP)(NAr)] undergoes imido group transfer with tertiary phosphines to give $ArN{=}PR_3$ and $[Ru(4\text{-Bu}^t\text{-TPP})(PR_3)_2]$. The reduction of $[Ru^{IV}$(4-Bu^t-TPP)(NAr)] by PMe_2Ph shows saturation kinetics, in which the rate is first order in $[Ru^{IV}]$. The proposed mechanism involves reversible binding of phosphine to Ru^{IV} and rate-limiting intramolecular imido group transfer.



(62a)

por = 4-Bu^t-TPP, Ar = *p*-XC_6H_4 (X = Me, H, Cl or I); por = TTP, Ar = *p*-MeC_6H_4

5.6.6.3 Nitrido Complexes

5.6.6.3.1 Mononuclear complexes

No mononuclear nitrido complexes of Ru(IV) and Os(IV) have been reported.

5.6.6.3.2 Binuclear and trinuclear nitrido-bridged complexes

There are quite a number of μ-nitrido ruthenium(IV) and osmium(IV) complexes, including $[Ru_2(N)(X)_8(H_2O)_2]^{3-}$ (X = Cl, Br, NCS), $[Ru_2(N)(X)_8(CO)_2]^{3-}$, $[Ru_2(N)(CN)_{10}]^{5-}$, $[Ru_2(N)(X)_2(NH_3)_8]^{3+}$ (X = Cl, Br, NO_3), $[Ru_2(N)(X)_3(NH_3)_6(OH_2)]^{2+}$ (X = Cl, NCS, N_3), $[Os_2(N)(NH_3)_8(X)_2]^{3+}$

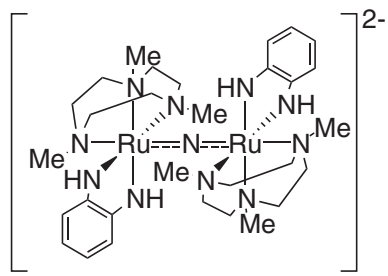
(X = Cl, Br, I, NCS, N_3, NO_3), $[Os_2(N)(Cl)_8(H_2O)_2]$, $[Os_2(N)(Cl)_{10}]^{5-}$, and $[Os_2(N)(S_2CNR_2)_5]$ (R = Me, Et), that have been discussed in *CCC* (1987).

Prolonged treatment of $[Ru_2(N)(Cl)_8(OH_2)_2]^{3+}$ with en produces $[Ru_2(\mu\text{-}N)(en)_5]^{5+}$, the X-ray structure of which shows a bridging en ligand with Ru—N(nitride) = 1.742 Å and Ru—N—Ru = 175.6°.[430] Treatment of $[Ru(bpy)(CO)_2(Cl)_2]$ with HCl/HNO_3 at 240 °C for 12 h produces a small amount of the red μ-nitrido species $[Ru_2(\mu\text{-}N)(bpy)_2(Cl)_5(H_2O)]$ (**118a**) (Ru—N = 1.744 and 1.728 Å, ν(Ru—N—Ru) = 1,071 cm^{-1}). Under the same conditions but with a mixture of $[Ru(bpy)(CO)_2(Cl)_2]$ and *fac*- and *mer*-$[Ru(bpy)(Cl)_3(NO)]$, a few dark red crystals of $(H_5O_2)[Ru_2(\mu\text{-}N)(bpy)_2(Cl)_6]$ (**118b**) were obtained. The X-ray structure of (**118b**) shows symmetric Ru=N=Ru bridges (Ru—N = 1.734 Å).[431]

$[\{Ru(PCy_3)(\text{“}S_4\text{”})\}_2(\mu\text{-}N)](PF_6)$ (**119**) (“S_4”$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2-); Cy = cyclohexyl) is formed by the reaction of $[Ru(N_3)(PCy_3)(\text{“}S_4\text{”})]$ with HBF_4.[432] IR monitoring of the reaction shows an unstable intermediate exhibiting an IR band at 2,070 cm^{-1}, proposed to be a N_2 complex $[Ru(N_2)(PCy_3)(\text{“}S_4\text{”})]$. The two Ru centers are strongly bent, probably due to steric crowding. The Ru—N distances are 1.762 Å and 1.804 Å.

There are a number of μ-nitrido ruthenium complexes containing macrocyclic ligands. The $Ru^{III}Ru^{IV}$ species [(Pc)Ru—N—Ru(Pc)] (Pc = phthalocyanine) has been prepared by heating [Ru(Pc)] or $[Ru(Pc)(py)_2]$ with NaN_3 (ν(Ru—N—Ru) = 1,040 cm^{-1}, $\mu_{eff} = 1.8\,\mu_B$).[433] A $Ru^{IV}Ru^{IV}$ dimer containing the tetraanionic macrocyclic ligand *meso*-octamethylporphyrinogen L, $[Ru_2(N)(L)_2]^{3-}$ (**120a**), is formed when $[Ru^{VI}(N)(L)]^{-}$ is treated with one equivalent of $[Ru^{II}L]^{2-}$. (**120a**) undergoes a reversible one-electron reduction to $[Ru_2(N)(L)_2]^{4-}$ (**120b**) (Scheme 12), which contains an unpaired electron ($\mu_{eff} = 1.60\,\mu_B$ at 293 K). The two nitrido-bridged complexes differ significantly in their bond distances. The Ru—N—Ru skeleton is linear in both cases, but the Ru—N_{av} distance changes from 1.768 Å in Ru^{IV}—N—Ru^{IV} to 1.826 Å in Ru^{IV}—N—Ru^{III}.[209]

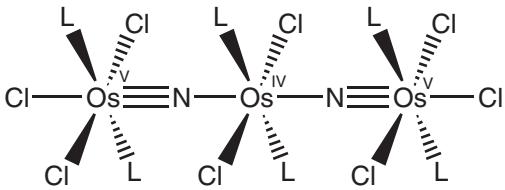
The nitrido-bridged complex $[\{Ru(Me_3tacn)(o\text{-}C_6H_4(NH)_2)\}_2(\mu\text{-}N)](PF_6)_2$ (**120c**) is obtained by heating solid $[(Me_3tacn)Ru(o\text{-}C_6H_4(NH)_2)(N_3)](PF_6)\cdot H_2O$ in vacuum at 160 °C.[434] Magnetic measurement shows that the complex is a mixed-valence, paramagnetic species containing one unpaired electron per dinuclear unit. X-ray crystallography reveals the o-$C_6H_4(NH)_2$ ligand in the complex has *o*-phenylenediamide character, which would render the complex formally a mixed-valence $Ru^{IV}Ru^{V}$ species. However, the Ru—N bond lengths of 1.802 Å and 1.767 Å are significantly longer than in other Ru^{IV}=N=Ru^{IV} units (1.72–1.74 Å). Apparently the $C_6H_4(NH)_2$ ligand is noninnocent and that formal oxidation state assignments to the ligands or metal centers are not possible.[434]



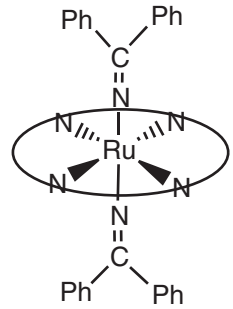
(**120c**)

The complex $[Os_2(N)(NH_3)_8(Cl)_2]Cl_3$ has been prepared by heating $Na_2[OsCl_6]$ with aqueous ammonia under pressure[435] Reaction of $(NH_4)_2[OsCl_6]$ with $N_2H_4\cdot H_2O$ under refluxing conditions gives the golden yellow $[Os_2(N)(NH_3)_{10}]Cl_5$, which shows a ν(Os=N=Os) stretch at 1,100 cm^{-1}.[436] A μ-nitrido complex, $[(Tp)Os(Cl)_2(\mu\text{-}N)Mo(S_2CNEt_2)_3]$, where the osmium probably has an oxidation state between +4 and +5, is described in Section 5.6.4.2.2(ii).

A trinuclear nitrido-bridged osmium complex, $[Os_3(N)_2(CN)_{10}(OH_2)_4]^{4-}$, has been reported.[437] A series of Os^{V}≡N—Os^{IV}—N≡Os^{V} complexes, $[Os_3(N)_2(Cl)_8(R\text{-}py)_6]$ (R-py = 4-methylpyridine (4-Mepy), 3-picoline, 4-ethylpyridine (4-Etpy) and 4-*t*-butylpyridine (4-Bu^tpy)), have been prepared by thermolysis of $[Os(N)(Cl)_3(R\text{-}py)_2]$ in a noncoordinating solvent.[156,158] X-ray structural studies of $[Os_3(N)_2(Cl)_8(4\text{-}Etpy)_6]$ (**121a**) and $[Os_3(N)_2(Cl)_8$ (4-Bu^tpy)$_6$] (**121b**) reveal a linear $Os_3(N)_2$ unit with multiple bonding significantly localized in the outer osmium–nitrogen bonds; Os_{outer}—$N_{nitrido}$ = 1.702–1.719 Å, $d(Os_{inner}$–$N_{nitrido})$ = 1.895–1.911 Å.[158]



(**121**)
(**a**) 4-Etpy
(**b**) 4-Bu^{t}py



(**121c**)

N_4 = 3,4,5-MeO-TPP

5.6.6.4 Miscellaneous Nitrogen Ligands

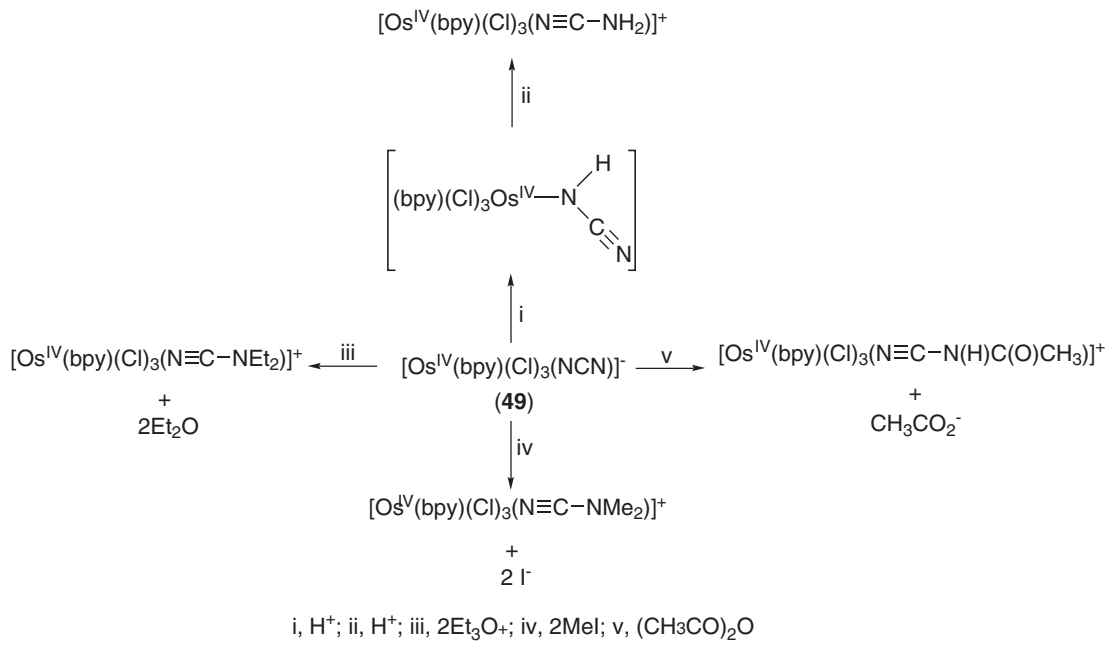
5.6.6.4.1 Cyanoimido complexes (NCN)

Osmium(IV) cyanoimido complexes can be prepared by the interaction of osmium(VI) nitrido complexes with CN^- (Equations (62b) and (62c); see also Scheme 6 and Section 5.6.4.2.2(ii)).

The X-ray crystal structure of $(NEt_4)[Os^{IV}(bpy)(Cl)_3(NCN)]$ shows an Os—N(CN) distance of 1.914 Å, consistent with an Os═N bond. The Os—N—C angle of 131.0° appears to be the smallest known for cyanoimido and substituted cyanoimido complexes.[606] The reactions of $[Os^{IV}(bpy)(Cl)_3(NCN)]^-$ with acids, alkylating agents, and acid anhydride are summarized in Scheme 19.

$$[Os^{VI}(N)(tpy)(Cl)_2]^+ + CN^- \longrightarrow [Os^{IV}(tpy)(Cl)_2(NCN)] \quad (62b)$$

$$[Os^{VI}(N)(bpy)(Cl)_3] + CN^- \longrightarrow [Os^{IV}(bpy)(Cl)_3(NCN)]^- \quad (62c)$$



i, H^+; ii, H^+; iii, $2Et_3O_+$; iv, 2MeI; v, $(CH_3CO)_2O$

Scheme 19

5.6.6.4.2 Methyleneamido complexes ($N{=}CR_2$)

The chemical and electrochemical oxidation of $[Ru(tpy)(bpy)(NH_2CHRR')]^{2+}$ ($NH_2CHRR' = Pr^iNH_2$, cyclohexylamine, (α-methylbenzyl)amine) produces the ruthenium(IV) complexes $[Ru(tpy)(bpy)(N{=}CRR')]^{2+}$. The X-ray structure of $[Ru(tpy)(bpy)(N{=}CMe_2)](ClO_4)_3{\cdot}H_2O$ shows a linear Ru—N—C linkage with a Ru—N bond length of 1.831 Å, indicating multiple bonding.[438]

Reaction of $[Ru^{VI}(O)_2(3,4,5\text{-MeO-TPP})]$ with $Ph_2C{=}NH$ produces the ruthenium(IV) bis(methyleneamido) complex $[Ru^{IV}(3,4,5\text{-MeO-TPP})(N{=}CPh_2)_2]$ (**121c**).[439] The structure of the complex includes two linear, axial $N{=}CPh_2$ group (Ru—N—C = 175.9°) with a linear C=N—Ru-N=C backbone. The Ru—N(methyleneamido) distance of 1.896 Å again indicates multiple bonding character.

5.6.6.4.3 Azidoimido complexes (NN_3)

Reaction of *mer*-$[Os^{VI}(N)(bpy)(Cl)_3]$ with N_3^- results in the formation of the stable diamagnetic osmium(IV) azidoimido product $[Os^{IV}(bpy)(Cl)_3(N_4)]^-$, which contains the first example of an unbridged N_4^{2-} ligand (Equation (62d)).[440] This product is characterized by elemental analysis, NMR, and IR ($\nu_{sym}(N_3^-) = 2058\,cm^{-1}$, $\nu(Os{-}N) = 1{,}092\,cm^{-1}$). The cyclic voltammogram of this complex in CH_3CN shows three reversible waves at $E_{1/2} = +1.40$ V, +0.88 V, and −0.82 V (vs. SSCE) for the $Os^{VI/V}$, $Os^{V/IV}$, and $Os^{IV/III}$ couples, respectively. Reaction of the cyanoimido complex with $ONMe_3{\cdot}3H_2O$ in dry CH_3CN produces an osmium(IV) azidohydroxoamido complex, $[Os^{IV}(bpy)(Cl)_3\{N(OH)N_3\}]$, which appears to contain the first example of the $N(OH)N_3^-$ ligand:[440]

$$mer\text{-}[Os^{VI}(N)(bpy)(Cl)_3] + N_3^- \longrightarrow mer\text{-}[Os^{IV}(N_4)(bpy)(Cl)_3]^- \tag{62d}$$

Addition of OH^- to $[Os^{IV}(N(OH)N_3)(bpy)(Cl)_3]$ results in the formation of $[Os^{II}(N_2O)(bpy)(Cl)_3]^-$ (Equation (63)). This reaction may occur by deprotonation followed by internal redox (Equation (64)):

$$mer\text{-}[Os\{N(OH)N_3\}(bpy)(Cl)_3] + OH^- \longrightarrow mer\text{-}[Os(N_2O)(bpy)(Cl)_3]^- + N_2 + H_2O \tag{63}$$

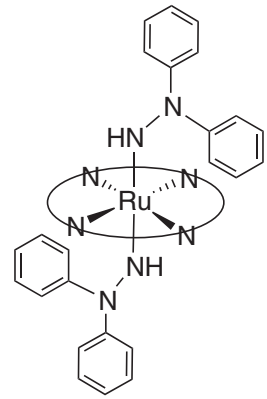
$$mer\text{-}[Os^{IV}\{N(OH)N_3\}(bpy)(Cl)_3] + OH^- \longrightarrow H_2O + mer\text{-}[Os^{IV}\{N(O)N_3\}(bpy)(Cl)_3]^- \longrightarrow mer\text{-}[Os^{II}\{N(=O)N_3\}(bpy)(Cl)_3]^- \longrightarrow mer\text{-}[Os^{II}(N_2O)(bpy)(Cl)_3]^- + N_2 \tag{64}$$

5.6.6.4.4 Hydrazido complexes (NNR_2)

High oxidation state hydrazido complexes have been proposed as key intermediates in biological and chemical nitrogen fixation.[441–443]

Reaction of dioxoruthenium(VI) porphyrins with 1,1-diphenylhydrazine in ethanol produces bis(1,1-diphenylhydrazido)ruthenium(IV) porphyrins, $[Ru^{IV}(por)(NHNPh_2)_2]$ (por = TPP, TTP, 4-Cl-TPP, 4-MeO-TPP)[444] (see Figure 1). The X-ray structure of $[Ru(TPP)(NHNPh_2)_2]$ (**122**) has been determined. The average Ru—N(N) distance and average Ru—N—N angle are 1.911 Å and 141.1°, respectively.

There is an extensive chemistry involving hydrazido complexes of osmium(IV), -(V), and -(VI). Electrochemical oxidation of $[Os(tpy)(bpy)(NH_3)](PF_6)_2$ in aqueous solutions in the presence of a secondary aliphatic amine produces the formally osmium(V) hydrazido(2-) complex $[Os^V(NNR_2)(tpy)(bpy)](PF_6)_3$, which can be reduced electrochemically to $[Os^{IV}(NNR_2)(tpy)(bpy)](PF_6)_2$.[377] The X-ray structures of $[Os^{IV}(NNR_2)(tpy)(bpy)](PF_6)_2$ for $NR_2 =$ diethylamide and morpholide have been determined; both complexes show bent hydrazido(2-) coordination (Os—N—N = 137°). The Os—N(N) distances are 1.89 Å and 1.85 Å for the $NNEt_2$ and the $NN(CH_2)_4O$ complex, respectively, indicating multiple bonding. Other osmium(IV) hydrazido complexes such as *cis*-$[Os^{IV}\{NN(CH_2)_4O\}(tpy)(Cl)(CH_3CN)]^+$ and *cis*-$[Os^{IV}\{NN(CH_2)_4O\}(tpy)(CH_3CN)_2]^{2+}$, as well as the corresponding osmium(V) and -(VI) hydrazido complexes $[Os^V(L)(Cl)_2(NNR_2)]^+$ (L = tpy (2,2′:6′,2″-terpyridine), tpm (tris-(1-pyrazolyl)methane); $NNR_2 = NN(CH_2)_4CH_2$, $NN(CH_2)_4O$, $NNEt_2$) and *trans*-$[Os^{VI}(NN(CH_2)_4O)(tpy)(Cl)_2]^{2+}$ have also been prepared and structurally characterized.[177,178,377] The Os—N(N) distance decreases from d^4 Os^{IV} to d^3 Os^V by 0.11 Å, and



(**122**)

from d^3 Os^V to d^2 Os^{VI} by another 0.08 Å (Table 14). The Os—N—N angle increases from 130° for Os^{IV} to 148–157° for Os^V to 170° for Os^{VI}. These differences are rationalized by a bonding model in which there is stepwise electron loss from a π^* MO on going from Os^{IV} to Os^{VI}, thereby increasing multiple bond character and decreasing bond length. The bending of Os—N—N in Os^{IV} reduces electron–electron repulsion caused by electrons in the π^* orbital. Removal of electrons from the π^* orbital would increase the bond angle.

The species *trans*-$[Os^{IV}\{NN(CH_2)_4O\}(tpy)(Cl)_2]$ can be protonated to give the hydrazido(1-) species *trans*-$[Os^{IV}\{N(H)N(CH_2)_4O\}(tpy)(Cl)_2]^+$. The protonated species undergoes rapid oxidation by benzoquinone, Q, to give *trans*-$[Os^{V}\{NN(CH_2)_4O\}(tpy)(Cl)_2]^+$ and H_2Q.[378] This reaction occurs with a remarkable N—H/N—D kinetic isotope effect of 41.4, consistent with a proton-coupled electron transfer mechanism.

5.6.6.4.5 *Sulfilimido and sulfoximido complexes*

cis- and *trans*-$[Os^{VI}(N)(tpy)(Cl)_2]^+$ react rapidly with 3,5-$Me_2C_6H_3SH$ to give the osmium(IV) sulfilimido complexes *cis*- and *trans*-$[Os^{IV}\{NS(H)C_6H_3Me_2\}(tpy)(Cl)_2]^+$ (see Scheme 6).[445,446] The N—S—C angles are 102.8° and 101.6°, respectively, for the *cis* and *trans* isomers, consistent with pseudo sp^3-hybridization and protonation at the S atom. The bond lengths Os—N = 1.947 Å (*cis*), 1.906 Å (*trans*) and N—S = 1.645 Å (*cis*), 1.706 Å (*trans*) and the angles Os—N—S = 125.6° (*cis*), 130.4° (*trans*) are consistent with an osmium(IV) complex with an Os=N double bond and a N—S single bond. A pK_a of 1.31 has been determined for the acid–base equilibrium (Equation (64a)):[445,447]

$$\textit{trans}\text{-}[Os^{IV}\{NS(H)C_6H_3Me_2\}(tpy)(Cl)_2]^+ \rightleftharpoons \textit{trans}\text{-}[Os^{IV}\{NSC_6H_3Me_2\}(tpy)(Cl)_2] + H^+ \quad (64a)$$

The structure of the deprotonated form has also been determined by X-ray crystallography. For *trans*-$[Os^{IV}(NSC_6H_3Me_2)(tpy)(Cl)_2]$ the Os—N(S) and N—S bond lengths are 1.890 Å and 1.596 Å, respectively, and the N—S—C and Os—N—S bond angles are 104.28° and 129.52°, respectively.[446]

trans-$[Os^{IV}\{NS(H)C_6H_3Me_2\}(tpy)(Cl)_2]^+$ is readily oxidized by benzoquinone (Q) (Equation (65)). This reaction has a remarkable S—H/S—D kinetic isotope effect of 31.1, consistent with a proton-coupled electron transfer mechanism, which may have important implications for the electron transfer reactivity of Fe—S proteins.[448–454]

Cyclic voltammetry in CH_3CN in the presence of HPF_6 shows reversible $[Os^{V/IV}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^{2+/+}$ and $[Os^{IV/III}(tpy)(Cl)_2(NS(H)C_6H_3Me_2)]^{+/0}$ waves at $E_{1/2} = +1.17$ V and -0.08 V for the *trans* complex, and $E_{1/2} = +1.21$ V and -0.09 V (vs. SSCE) for the *cis* complex:[466]

$$2\textit{trans}\text{-}[Os^{IV}(tpy)(Cl)_2\{NS(H)C_6H_3Me_2\}]^+ + Q \longrightarrow 2\textit{trans}\text{-}[Os^{V}(tpy)(Cl)_2\{NSC_6H_3Me_2\}]^+ + H_2Q \quad (65)$$

There is also a reversible oxygen atom transfer chemistry based on the sulfilimido ligand. *cis*- and *trans*-$[Os^{IV}\{NS(H)C_6H_3Me_2\}(tpy)(Cl)_2]^+$ react readily with Me_3NO in CH_3CN to give the corresponding Os^{IV} sulfoximido complex ($\nu(S{=}O) = 1{,}250\,cm^{-1}$ (*trans*) and $1{,}275\,cm^{-1}$ (*cis*)) (Equation (65a)). The same products are also formed rapidly when the deprotonated sulfilimido complexes are exposed to O_2 (Equation (66)). The sulfoximido complexes are able to transfer the O atom to PPh_3 and to *trans*-stilbene (Equation (67)):

$$[Os^{IV}(NS(H)C_6H_3Me_2)(tpy)(Cl)_2]^+ + ONMe_3 \longrightarrow [Os^{IV}(NS(O)C_6H_3Me_2)(tpy)(Cl)_2] + HNMe_3^+ \quad (65a)$$

$$[Os^{IV}(NSC_6H_3Me_2)(tpy)(Cl)_2] + 1/2O_2 \longrightarrow [Os^{IV}(N(O)SC_6H_3Me_2)(tpy)(Cl)_2] \quad (66)$$

$$[Os^{IV}\{N(O)SC_6H_3Me_2\}(tpy)(Cl)_2] + PPh_3 \longrightarrow [Os^{IV}(NSC_6H_3Me_2)(tpy)(Cl)_2] + OPPh_3 \quad (67)$$

An irreversible O-atom transfer also occurs in DMSO; *cis*- and *trans*-$[Os^{IV}\{NS(H)C_6H_3Me_2\}(tpy)(Cl)_2]^+$ are converted to the sulfoximido complexes $[Os^{IV}\{NS(O)Me_2\}(tpy)(Cl)_2]^+$. In the X-ray structure of *trans*-$[Os^{IV}(NS(O)Me_2)(tpy)(Cl)_2]^+$, the average angle of 109.035° at the S-atom is consistent with sp^3-hybridization. The long Os—N(S) bond length of 2.119 Å is consistent with an Os—N(S) single bond.

A remarkable O_2 evolution chemistry was observed with these complexes.[447] When one equivalent of HPF_6 is added to CH_3CN solutions of either *cis*- or *trans*-$[Os^{IV}(tpy)(Cl)_2\ \{N(O)SC_6H_3Me_2\}]$, O_2 is produced in a very rapid reaction (Equation (68)). When a stoichiometric amount of bpy in air-saturated CH_3CN is added the osmium(IV) sulfoximido is regenerated (Equation (69)). This O_2 evolution can be made catalytic by adding large excess of HPF_6 in the presence of Me_3NO (Equation (70)):

$$2cis\text{-}[Os^{IV}(NS(O)C_6H_3Me_2)(tpy)(Cl)_2] + 2H^+ \longrightarrow 2cis\text{-}[Os^{IV}(NS(H)C_6H_3Me_2)(tpy)(Cl)_2]^+ + O_2 \quad (68)$$

$$cis\text{-}[Os^{IV}(NS(H)C_6H_3Me_2)(tpy)(Cl)_2]^+ + bpy + 1/2O_2 \longrightarrow cis\text{-}[Os^{IV}(NS(O)C_6H_3Me_2)(tpy)(Cl)_2] + Hbpy^+ \quad (69)$$

$$H^+ + ONMe_3 \xrightarrow[MeCN/HPF_6]{[Os\{NS(O)C_6H_3Me_2\text{-}3,5\}(tpy)(Cl)_2]} 1/2\ O_2 + HNMe_3^+ \quad (70)$$

Novel two-electron group transfer reactions also occur with the osmium(IV) sulfilimido complexes (Equations (71) and (72)):[380]

$$[Os^{IV}(NS(H)C_6H_3Me_2)(tpy)(Cl)_2]^+ + PPh_3 + MeCN \longrightarrow [Os^{II}(tpy)(Cl)_2(MeCN)]^+ + Ph_3P{=}N\text{-}SC_6H_3Me_2 + H^+ \quad (71)$$

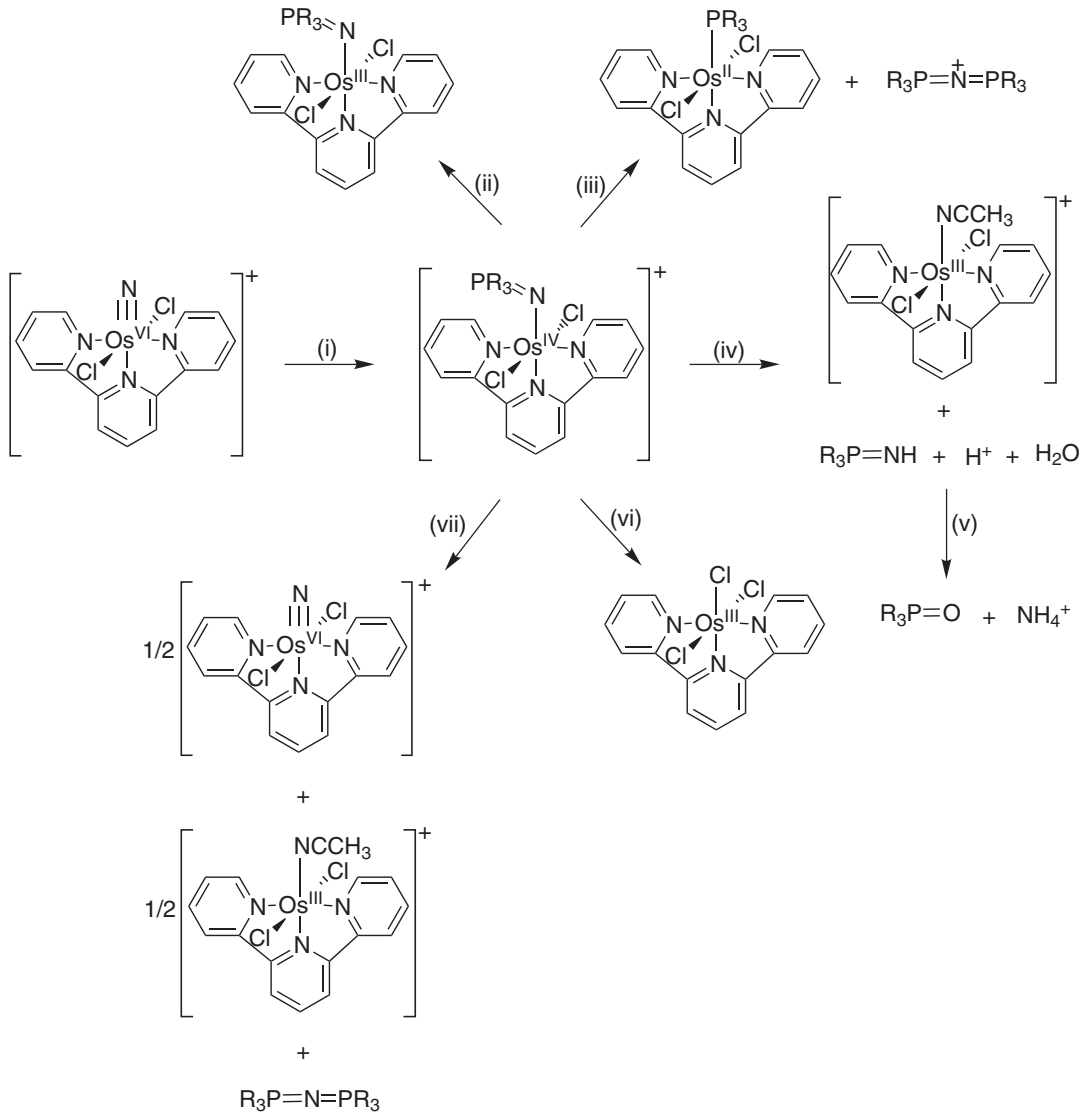
$$[Os^{IV}(NS(H)C_6H_3Me_2)(tpy)(Cl)_2]^+ + p\text{-}MeOC_6H_4NH_2 + MeCN \longrightarrow [Os^{II}(tpy)(Cl)_2(MeCN)] + p\text{-}MeOC_6H_3Me_2 + H^+ \quad (72)$$

5.6.6.4.6 *Phosphoraniminato (NPR_3) and phosphineaminato ($NHPR_3$) complexes*

Ruthenium(IV) and osmium(IV) phosphoraniminato complexes are formed by nucleophilic attack of phosphines on the nitrido ligand of ruthenium(VI) or osmium(VI). The first examples of this type of complexes are $[Os^{IV}(NPR_3)(PR_3)_2(Cl)_3]$ and $[Ru^{IV}(NPEt_2Ph)(Cl)_3(PEt_2Ph)_2]$, which have been documented in *CCC* (1987). While there are quite a few osmium complexes of this class, there appears to be only one structurally characterized ruthenium complex.

Rapid reactions occur between $[Os^{VI}(N)(tpy)(Cl)_2]^+$ and PR_3 ($R = Ph_3$, Ph_2Me, $PhMe_2$, Me_3, Et_3) to give $[Os^{IV}(NPR_3)(tpy)(Cl)_2]^+$ (Scheme 20).[379,455] The X-ray structures of *trans*-$[Os^{IV}(NPPh_3)(tpy)(Cl)_2](PF_6)\cdot CH_3CN$ and *cis*-$[Os^{IV}(NPPh_2Me)\ (tpy)(Cl)_2](PF_6)\cdot CH_3CN$

show long Os—N(P) bond distances (2.093 Å and 2.061 Å), acute Os—N—P bond angles (132.5° and 132.2°), and little structural *trans* effect. These properties indicate that the Os—N(P) bond is essentially a single bond. A room temperature magnetic moment of $1.8\mu_B$ was found for *trans*-$[Os^{IV}(NPPh_3)(tpy)(Cl)_2](PF_6)$, consistent with the d^4 Os^{IV} formulation.[379,455] The cyclic voltammogram of *trans*-$[Os^{IV}(NPPh_3)(tpy)(Cl)_2](PF_6)$ in CH_3CN shows reversible $Os^{IV/III}$ and $Os^{III/II}$ couples at 0.92 V and −0.27 V vs. SSCE, respectively.



i, PR_3; ii, 1 e^- reduction; iii, xs PR_3; iv, HBF_4; v, hydrolysis; vi, HCl; vii, 1 e^- oxidation;

Scheme 20

Reaction of $[Os^{VI}(N)(Tp)(Cl)_2]$ with $HPEt_2$ generates $[Os^{IV}\{NP(H)Et_2\}(Tp)(Cl)_2]$, which reacts rapidly with benzoquinone (Q) according to Equation (73):

$$2[Os^{IV}\{NP(H)Et_2\}(Tp)(Cl)_2] + Q \longrightarrow 2[Os^{V}\{NPEt_2\}(Tp)(Cl)_2] + H_2Q \qquad (73)$$

The observed rate law is consistent with competing pathways involving the oxidation of Os^{IV}–$NP(H)Et_2$ and Os^{IV}–$NPEt_2$ by Q. A remarkable P—H/P—D kinetic isotope of 178 is observed, consistent with a proton-coupled electron transfer mechanism.[456]

An osmium(IV) phosphoraniminato complex containing the anionic ligand L_{OEt} is known. The complex $[OsL_{OEt}(NPPh_3)(Cl)_2]$ has Os—N = 1.893 Å, Os—N—P = 137.5° and $\mu_{eff} = 2.0\,\mu_B$.[188]

A series of osmium complexes containing the Schiff base ligand salophen have been reported, $[Os^{IV}(NPPh_3)(L)(Cl)]$ (L = 5,5′-disubstituted salophen).[205] These complexes exhibit reversible $Os^{V/IV}$ and $Os^{IV/III}$ couples, the $E_{1/2}$ values showing linear correlations with the Hammett constant σ_p of the substituent on the Schiff base ligand. The X-ray structure of $[Os^{IV}(NPPh_3)(salophen)(Cl)]$ also shows a rather long Os—N(P) bond length (1.92 Å) and an acute Os—N—P bond angle (149.6°).

An Os^{IV} phosphoraniminato complex has also been obtained via the reaction of an osmium(II) thionitrosyl complex with PPh_3 (Equation (74)):[457]

$$[Os^{II}(NS)(tpm)(Cl)_2]^+ + 2PPh_3 \rightarrow [Os^{IV}(NPPh_3)(tpm)(Cl)_2]^+ + S{=}PPh_3 \quad (74)$$

Bond length, bond angle, and electrochemistry data for some osmium phosphoraminato complexes are collected in Table 16.

5.6.6.4.7 Other nitrogen ligands

A number of $[M^{IV}(por)(X)_2]$ (X = Cl, Br, I) complexes are known. These are generally prepared by the reduction of $[Os^{VI}(O)_2(por)]$[414,458,459] or by treatment of $[Ru(por)]_2$ (por = TPP) with HBr, HCl, or I_2. A more convenient, one-pot synthesis is by simply heating [Ru(por)(CO)] in CX_4.[460,461] The X-ray structure of $[Ru(TPP)(Br)_2]$ has been determined (Ru—Br = 2.425 Å).[462]

A chiral dichlororuthenium(IV) complex of a D_4-symmetric porphyrin, $[Ru^{IV}(D_4\text{-por*})(Cl)_2]$, has been prepared by heating $[Ru^{II}(D_4\text{-por*})(CO)(MeOH)]$ in CCl_4.[463] The complex is characterized by ^1H NMR (paramagnetically shifted pyrrolic protons at $\delta_H = -52.3$ ppm), FAB-MS, and magnetic susceptibility measurement ($\mu_{eff} = 3.1\,\mu_B$). It is a very active catalyst for enantioselective alkene epoxidations using 2,6-dichloropyridine *N*-oxide as the terminal oxidant, with a turnover number of up to 2000; the ee of the epoxides is 50–80%. The complex can be incorporated into sol–gel and turnovers of over 10^4 can be achieved.[463]

$[Os^{IV}(Tp)(OTf)(Cl)_2]$ can abstract a nitrogen atom from MeCN upon heating to give the osmium nitrido compound $[Os^{VI}(N)(Tp)(Cl)_2]$ (Equation (75)).[168] The suggested mechanism is hydrolysis at Os^{IV} followed by redox disproportionation to Os^{VI} and Os^{III}:

$$3[Os^{IV}(Tp)(OTf)(Cl)_2] + MeCN + 2H_2O \rightarrow [Os^{VI}(N)(Tp)(Cl)_2] + 2[Os^{III}(MeCN)(Tp)(Cl)_2] + HOAc + 3HOTf \quad (75)$$

Reaction of *trans*-$[Ru^{VI}(O)_2(por)]$ with alkenes in the presence of pyrazole (Hpz) produces *trans*-$[Ru^{IV}(por)(pz)_2]$ (**122c**). These complexes are paramagnetic with two unpaired electrons. The

Table 16 Selected bond length, bond angle, and electrochemistry of osmium phosphoraminato complexes.

			Vs. $Cp_2Fe^{+/0}$		
Complex	*d(Os—N)*(Å)	∠*Os—N—P*(°)	$E_{1/2}{}^{V/IV}$(V)	$E_{1/2}{}^{IV/III}$(V)	*References*
$[Os(NPPh_3)(salophen)Cl]$	1.92(1)	149.6(10)	0.14	−0.21	205
trans-$[Os(NPPh_3)(tpy)(Cl)_2](PF_6)$	2.093(5)	132.5(3)	0.92[a]	−0.27[a]	379,455
trans-$[Os(NPPh_2Me)(tpy)(Cl)_2](PF_6)$	2.061(6)	132.2(4)			455
cis-$[Os(NPPh_3)(tpy)(Cl)_2](PF_6)$	2.071(6)	138.4(4)			605
$[Os(NPPh_3)(L_{OEt})(Cl)_2]$	1.893(5)	137.5(3)		−0.718	188

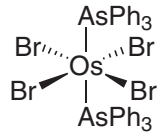
[a] Vs. SSCE.

IR spectrum shows an oxidation marker band at 1,006 cm^{-1}, consistent with a Ru^{IV} formation. The structure of $[Ru^{IV}(DPP)(pz)_2]$ has been established by X-ray crystallography. The Ru—N(pz) distances are 2.022 Å and 2.083 Å.[321]

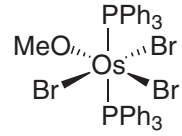
5.6.6.5 Phosphine, Arsine, and Stibine Ligands

Phosphines and arsines occur as coligands in Ru^{IV}=O complexes (Section 5.6.6.6.1(i)(b)).

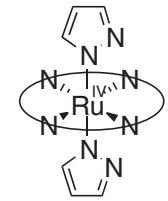
Osmium(IV) complexes of the type *trans*-$[Os(L)_2(X)_4]$, *mer*-$[Os(L)_3(X)_3]^+$, *trans*-$[Os(L)_4(X)_2]^{2+}$, and *trans*-$[Os(L\text{-}L)_2(X)_2]^{2+}$ (L = various PR_3, AsR_3, $SbPh_3$; L-L = diphosphine sphine or diarsine; X = Cl, Br, I) are known.[277,464–468] These are generally prepared either by reaction of $[OsO_4]$ with L and HX or by the oxidation of the corresponding Os^{III} or Os^{II} complex. Cyclic voltammetry shows that the $Os^{IV/III}$ couples are generally reversible.[466] For *trans*-$[Os(L)_2(X)_4]$ the redox potentials of the $Os^{IV/III}$ couples correlate with the energies of the lowest charge transfer transitions in the UV–vis spectra.[468] The X-ray structures of *trans*-$[Os(AsPh_3)_2(Br)_4]$[469] (**122a**) (Os—As = 2.569 Å, Os—Br = 2.451–2.472 Å) and *trans*-$[Os(PPh_3)_2(MeO)(Br)_3]$[470] (**122b**) (Os—P = 2.413–2.424 Å, Os—Br = 2.471–2.494 Å) have been determined.



(**122a**)



(**122b**)



N_4 = DPP

(**122c**)

5.6.6.6 Oxo Complexes

5.6.6.6.1 *Mononuclear complexes*

(i) Synthesis

(a) Nitrogen ligands. Extensive work on terminal Ru^{IV}=O complexes containing nonlabile oxidation-resistant nitrogen donor ligands has been reported.[23,24,471,472] In general, these complexes are prepared either by oxidation of Ru^{II}—OH_2 or Ru^{III}—OH_2 precursors,[240,269,473–476] or by reduction of *trans*-dioxoruthenium(VI) complexes.[241–243,477] Selected examples are shown in Equations (76)–(79):

$$[Ru^{II}(tpy)(diamine)(H_2O)]^{2+} + 2Ce^{IV} \rightarrow [Ru^{IV}(O)(tpy)(diamine)]^{2+} + 2Ce^{III} + 2H^+ \quad (76)$$

$$[Ru^{III}(14\text{-}TMC)(OH)(OH_2)]^{2+} + X^- + H_2O_2 + H^+ \rightarrow [Ru^{IV}(O)(14\text{-}TMC)(X)]^{n+} + 3H_2O \ (X = NCO, N_3, n = 1; X = H_2O, n = 2) \quad (77)$$

$$[Ru^{VI}(O)_2(14\text{-}TMC)]^{2+} + PPh_3 + CH_3CN \rightarrow [Ru^{IV}(O)(14\text{-}TMC)(CH_3CN)]^{2+} + O{=}PPh_3 \quad (78)$$

$$[Ru^{VI}(O)_2(TMP)] + PPh_3 \rightarrow [Ru^{IV}(O)(TMP)] + O{=}PPh_3 \quad (79)$$

Six-coordinate Ru^{IV}=O complexes are paramagnetic with measured μ_{eff} ranging from 2.7 to 2.95 μ_B at room temperature. Their IR spectra exhibit a Ru=O stretch ranging from 750 cm^{-1} to

845 cm^{-1} (Table 4). The first complex of this type is *cis*-$[Ru(O)(bpy)_2(py)](ClO_4)_2$, prepared by Ce^{IV} oxidation of *cis*-$[Ru(bpy)_2(py)(OH_2)](ClO_4)_2$.[473,474] The Ru=O stretching vibration occurs at 792 cm^{-1}, this assignment being supported by ^{18}O-labeling experiments.[474] Its room temperature magnetic moment is 2.95 μ_B. Detailed studies on the temperature variation of the magnetic susceptibility revealed a singlet $(d\pi_1)^2(d\pi_2)^1(d\pi_3)^1$ ground state with the triplet state $(d\pi_1)^2(d\pi_2)^2(d\pi_3)^0$ lying slightly higher, at 79 cm^{-1} in the solid state and 56 cm^{-1} in CD_3CN.[478] The complex is unstable toward self-reduction in basic solutions; the mechanism involves metal–ligand redox reactions.[479]

Optically active forms of *cis*-$[Ru(O)(bpy)_2(py)](ClO_4)_2$ have been resolved.[480] Related Ru^{IV}=O complexes, such as $[Ru(O)(tpy)(bpy)]^{2+}$,[481] and *para*-substituted derivatives,[482] $[Ru(O)(tpy)(6,6'\text{-}Cl_2bpy)]^{2+}$[269] and $[Ru(O)(tpm)(bpy)]^{2+}$,[483] have also been prepared. $[Ru^{IV}(O)(tpy)(6,6'\text{-}Cl_2bpy)]^{2+}$ is an active and robust catalyst for the oxidation of saturated hydrocarbons by TBHP.[269] This Ru^{IV} oxo complex has a high $E°(Ru^{IV/III})$ value of 1.13 V vs. SCE at pH 1.0 and is capable of oxidizing the tertiary C—H bond of adamantane to give adamantan-1-ol exclusively.

Ru^{IV}=O complexes containing chiral ligands are also known. $[Ru(O)(PPz^*)(Y_2\text{-}bpy)]^{2+}$ (PPz* = 2,6-bis[(4*S*,7*R*)-7,8,8-trimethyl-4,5,6,7-tetrahydro-4,7-methanoindazol-2-yl]pyridine, $Y_2 = H_2$, 6,6′-Cl_2) epoxidize alkenes with ee of up to 60%.[515] $[Ru(O)(tpy)(1R,2R\text{-cxhn})](ClO_4)_2$(cxhn = *N,N,N′,N′*-tetramethyl-1,2-diaminocyclohexane) and $[Ru(O)(Me_3tacn)(cbpy)](ClO_4)_2$(cbpy = (−)-3,3′-[(4*S*-*trans*)-1,3-dioxolane-4,5-dimethyl]-2,2′-bipyridine) have also been reported.[484] Stoichiometric oxidation of styrene and 4-chlorostyrene by $[Ru(O)(tpy)(1R,2R\text{-cxhn})](ClO_4)_2$ gave the corresponding epoxide with no enantiomeric excess. Using $[Ru(O)(Me_3tacn)(cbpy)](ClO_4)_2$, a 9% ee of *R*-styrene and *R*-4-chlorostyrene oxide were found in the oxidation of styrene and 4-chlorostyrene, respectively. Ru^{IV}=O complexes containing chiral bis(oxazoline) ligands, $[Ru(O)(tpy)(L)](ClO_4)_2$ (L = (*S*)- or (*R*)-bpop = 2,2-bis[2-[4(*S*)- or 4(*R*)-phenyl-1,3-oxazolinyl]]propane), are also known.[485] These chiral ruthenium oxo complexes oxidize methyl *p*-tolyl sulfide to the corresponding sulfoxide with ~12% ee, and racemic methyl *p*-tolyl sulfoxide to the corresponding sulfone with ~25% ee.

NaOCl oxidation of *trans*-$[Ru^{II}X(NO_2)(Y\text{-}py)_4]^n$ ($n = 0$ for X = Cl, $n = 1+$ for $X = H_2O$; Y = H, Me)[486,487] produces *trans*-$[Ru(O)X(Y\text{-}py)_4]^+$ (X = Cl, NO_2). Interestingly, *trans*-$[RuCl(NO_2)(py)_4]$ is oxidized to *trans*-$[Ru(O)Cl(py)_4]^+$, while *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$ is oxidized to *trans*-$[Ru(O)(ONO)(py)_4]^+$ with retention of the nitro nitrogen. *trans*-$[Ru^{IV}(O)(py)_4Cl]ClO_4$ has a long Ru=O distance of 1.862 Å,[488] and yet it has a stretching frequency (ν(Ru=O) = 805 cm^{-1}) similar to that found for *trans*-$[Ru^{IV}(O)(L)(X)]^{n+}$ (815–820 cm^{-1}, L = 14-TMC)[240] and $[Ru^{IV}(O)(tpy)(bpy)](ClO_4)_2$ (792 cm^{-1}).[481]

A number of ruthenium(IV) oxo complexes bearing tertiary phosphine or arsine ligands, $[Ru(O)(bpy)_2(PnR_3)]^{2+}$[489,490] and $[Ru(O)(bpy)(biq)(PnR_3)]^{2+}$ (biq = 2,2′-biquinoline, PnR_3 = tertiary rtiary phosphine or arsine),[475] have been synthesized through oxidation of the corresponding aqua-ruthenium(II) species by Ce^{IV} or by electrochemical means. Although tertiary phosphine ligands are susceptible to oxidation, these ligands are found to be stable within the coordination sphere of the Ru^{IV} center. These complexes are powerful oxidants that oxidize a wide variety of organic substrates.

Ru^{IV}=O complexes containing chelating tertiary amines such as $[Ru^{IV}(O)(tpy)(TMEA)]^{2+}$[476] and $[Ru^{IV}(O)(tpy)(tmcn)]^{2+}$[491] (TMEA = *N,N,N′,N′*-tetramethylethylenediamine; tmcn = *N,N,N′,N′*-tetramethyl-cyclohexanediamine) have been prepared by oxidation of their Ru^{II}—OH_2 precursors by Ce^{IV}.

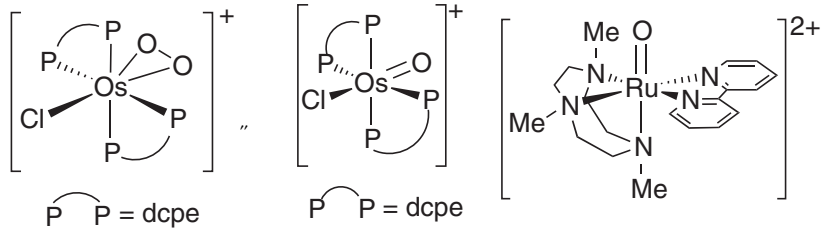
A ruthenium(IV) oxo complex containing pyridyl-type ligands, $[Ru^{IV}(O)(N_4O)]^+$(see Figure 14 for structures of ligand), has been generated by electrochemical oxidation of $[Ru^{III}(N_4O)(OH_2)]^{2+}$ in aqueous solution (pH > 3.5). This species was found to disproportionate to Ru^{III} and Ru^{V} in acidic solution.[492]

(b) Phosphine ligands. Reaction of *trans*-$[Os(\eta^2\text{-}O_2)(dcpe)_2(Cl)]^+$ (**130**) (dcpe = 1,2-bis(dicyclohexylphosphino)ethane) with anhydrous HCl and a reductant (I^- or PPh_3) produces *trans*-$[Os^{IV}(O)(dcpe)_2(Cl)]^+$ (**123**), the first stable and structurally characterized Os^{IV}=O species.[494]

(**123**) has a μ_{eff} of 3.05 μ_B at 300 K, consistent with the $(d_{xy})^2(d_{xz})^1(d_{yz})^1$ configuration. The X-ray structure shows a distorted octahedral coordination with a Os=O distance of 1.834 Å similar to that in Os^{IV}—O—Os^{IV} species (1.78–1.83 Å), but longer than that in the Os^{VI} oxo complexes $[Os(O)(tmen\text{-}2H)(tmen\text{-}H)]ClO_4$ (~1.72 Å)[250] and $[OsO(O_2C_2H_4)_2]$ (1.670 Å).[493] This complex is unreactive towards organic substrates. *trans*-$[Os^{IV}(O)(dcpe)_2(Br)]^+$ and *trans*-$[Os^{IV}(O)(depe)_2(Cl)]^+$ (depe = 1,2-bis(diethylphosphino)ethane) have also been prepared in a similar way.[494]

(c) Oxygen ligands. A Ru^{IV}=O active intermediate is proposed in the aerobic hydroxylation of adamantane by the ruthenium-substituted "sandwich"-type polyoxometalate

$[WZnRu^{III}{}_2(XW_9O_{34})_2]^{11-}$.[495] Similarly, a Ru^{IV}=O intermediate, formulated as $[Ru(O)(Cl)_2(PPh_3O)_3]$, is proposed in the catalytic oxidation of *N*-Boc hydroxylamine to the corresponding nitroso dienophile by $[Ru(Cl)_2(PPh_3)_4]$/TBHP.[496]



(130) (123) (124)

(d) Macrocyclic tertiary amine ligands. Apart from polypyridyl ligands, macrocyclic tertiary amine ligands are also found to be oxidation resistant upon coordination and can stabilize high-valent ruthenium oxo complexes. There is an extensive series of Ru^{IV}=O complexes containing macrocyclic tertiary amine ligands, *trans*-$[Ru^{IV}(O)(L)(X)]^{n+}$ (L = 14-TMC, 15-TMC, 16-TMC, $(TMEA)_2$; $n = 1$, X = Cl, N_3, NCO; $n = 2$, X = CH_3CN) (see Figure 3 for structures of ligands).[240] These complexes are prepared either by the reduction of the corresponding *trans*-dioxoruthenium(VI) complex *trans*-$[Ru^{VI}(O)_2(L)]^{2+}$ (see Section 5.6.4.4.2) with excess PPh_3 or by the oxidation of *trans*-$[Ru^{III}(L)(OH)(OH_2)]^{2+}$ with H_2O_2 in the presence of excess X^- (NCO^- or N_3^-) (Equations (80)–(83)). Interestingly, reduction of the perchlorate salt produces the chloro complex, suggesting ClO_4^- is involved in the redox reaction:

$$[Ru^{III}(14\text{-TMC})Cl_2]^+ \xrightarrow[H_2O]{Ag^+} [Ru^{III}(14\text{-TMC})(OH)(OH_2)]^{2+} \quad (80)$$

$$[Ru^{III}(14\text{-TMC})(OH)(OH_2)]^{2+} \xrightarrow[X^-]{H_2O_2(aq)} [Ru^{IV}(O)(14\text{-TMC})(X)]^+ \quad (X = NCO^-, N_3^-) \quad (81)$$

$$[Ru^{VI}(O)_2(14\text{-TMC})](PF_6)_2 \xrightarrow[(CH_3)_2CO/CH_3CN]{PPh_3} [Ru^{IV}(O)(14\text{-TMC})(CH_3CN)](PF_6)_2 \quad (82)$$

$$[Ru^{VI}(O)_2(14\text{-TMC})](ClO_4)_2 \xrightarrow[(CH_3)_2CO]{PPh_3} [Ru^{IV}(O)(14\text{-TMC})Cl]ClO_4 \quad (83)$$

The X-ray crystal structures of *trans*-$[Ru^{IV}(O)(14\text{-TMC})(X)]^{n+}$ (X = Cl, NCO, N_3, $n = 1$ and X = CH_3CN, $n = 2$) have been determined. The Ru=O bond distances for these complexes were found to be 1.765 Å, being relatively insensitive to the nature of X (see Table 4 for bond distances).[240–243]

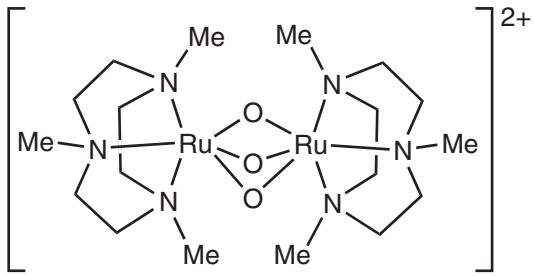
trans-$[Ru^{IV}(O)(16\text{-TMC})(Cl)]^+$ can also be produced via disproportionation of a Ru^{III}–NO_2 intermediate.[497] Reaction of *trans*-$[Ru^{III}(16\text{-TMC})(Cl)_2]^+$ with NO_2^- in water at 60 °C leads to the formation of *trans*-$[Ru^{IV}(O)(16\text{-TMC})(Cl)]^+$ and *trans*-$[Ru^{II}(16\text{-TMC})(OH)(NO)]^{2+}$. The Ru^{IV}=O species has been characterized by X-ray crystallography, and the Ru=O distance is 1.75 Å.[497]

A Ru^{IV}=O complex with a N_3py (N = tertiary amine) macrocyclic ligand, $[Ru^{IV}(O)(CRMe_3)(NCO)]C1O_4$, has been prepared by H_2O_2 oxidation of $[Ru^{III}(CRMe_3)(OH)(OH_2)]^{2+}$ in the presence of NaNCO. The X-ray structure revealed a Ru=O distance of 1.777 Å.[243]

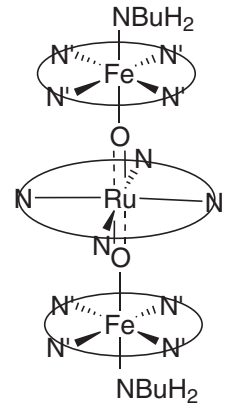
An oxoaquaruthenium(IV) complex of a macrocyclic N_2O_2 ligand, $[Ru^{IV}(O)(H_2O)(N_2O_2)]^{2+}$, has been prepared by electrochemical oxidation of $[Ru^{III}(N_2O_2)\text{-}(OH)(OH_2)]^{2+}$ and characterized by X-ray crystallography.[247] This complex shows an exceptionally high Ru=O stretching frequency of 845 cm^{-1}.[247] The stronger Ru=O bond is also consistent with the measured Ru=O distance of 1.739 Å,[247] the shortest one ever reported for oxoruthenium(IV) complexes. The difference in the

d(Ru=O) values between *trans*-$[Ru^{IV}(O)(H_2O)(N_2O_2)]^{2+}$ and $[Ru^{IV}(O)(14\text{-TMC})(X)]^{n+}$ has been discussed in terms of the weaker donor strength of N_2O_2 compared to 14-TMC, leading to enhanced p_π(O)—d_π(Ru) bonding interactions.

A Ru^{IV}=O species containing a tridentate macrocyclic ligand Me_3tacn, $[Ru^{IV}(O)(Me_3tacn)(bpy)]^{2+}$ (**124**), has been synthesized by oxidation of $[Ru^{II}(Me_3tacn)(bpy)(OH_2)]^{2+}$ with Ce^{IV}.[498] X-ray diffraction studies reveal that the complex has a distorted octahedral geometry with the Me_3tacn facially coordinated to Ru. The Ru=O distance is 1.815 Å, which is longer than the Ru—O(bridging) distances of 1.899–1.937 Å in $[(Me_3tacn)Ru(\mu\text{-}O)_3Ru(Me_3tacn)]^{2+}$ (**126**) (see Section 5.6.6.6.2(i)). The Ru=O stretch occurs at 780 cm^{-1}. $E°(Ru^{IV/III})$ for $[Ru^{IV}(O)(Me_3tacn)(bpy)]^{2+}$ at pH = 7 is 0.54 V, which is lower than the corresponding value of 0.62 V for $[Ru^{IV}(O)(tpy)(bpy)]^{2+}$. $[Ru^{IV}(O)(Me_3tacn)(bpy)]^{2+}$ is an active oxidant for alkenes and alkanes; the rate constants for the oxidation of styrene and norbornene are 1.30×10^{-3} M^{-1} s^{-1} and 2.5×10^{-4} M^{-1} s^{-1}, respectively at 25.0 °C.



(**126**)



(**127**)

trans-Dioxoosmium(IV) complexes of macrocyclic tertiary amine ligands have also been generated in the cyclic voltammetric scans of *trans*-$[Os^{VI}(O)_2(L)]^{2+}$ (L = 14-TMC, 15-TMC, 16-TMC, $CRMe_3$) in MeCN[251] (see Section 5.6.4.4.2(ii)).

(e) Porphyrins and related complexes. Stoichiometric reduction of $[Ru^{VI}(O)_2(TMP)]$ with PPh_3[477] gives the oxoruthenium(IV) species $[Ru^{IV}(O)(TMP)]$. This species is characterized by magnetic susceptibility measurement ($\mu_{eff} = 2.4\,\mu_B$) and ^{1}H NMR spectroscopy, and it is unstable towards disproportionation to Ru^{II} and Ru^{VI}. Monmeric ruthenium(IV) oxo species containing nonsterically encumbered porphyrins, formulated as either $[Ru^{IV}(O)(por)(ROH)]$ or $[Ru^{IV}(por)(OH)_2]$, are also known.[318,319] The success of the synthesis of these monomeric species depends on the solvent. Weakly coordinating solvents such as ethanol are thought to occupy the vacant coordination site of the $[Ru^{IV}(O)(por)]$ intermediate, thus inhibiting the μ-oxo dimerization process that leads to the formation of $[Ru^{IV}(por)(OH)]_2(\mu\text{-}O)$.[318,319] [Ru(O)(por)(ROH)] (or $[Ru(por)(OH)_2]$) has a measured $\mu_{eff} = 3.1\,\mu_B$, consistent with the $(d_{xy})^2(d_{yz})^1(d_{xz})^1$ electronic configuration. The cyclic voltammogram of [Ru(O)(OEP)(EtOH)] in CH_2Cl_2/py displays a reversible reduction wave at −0.86 V and an irreversible oxidative wave at 0.6 V vs. $Cp_2Fe^{+/0}$. The reduction wave has been assigned to the $Ru^{IV/III}$ couple.[499] A summary of the d(Ru=O) and ν(Ru=O) data is collected in Table 4.

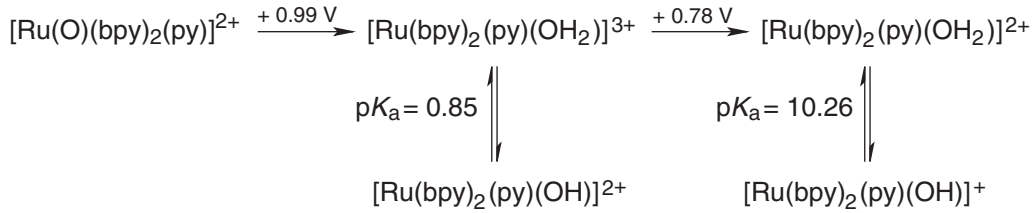
(ii) Electrochemistry

The electrochemical behavior of ruthenium(IV) oxo complexes has been extensively studied. They exhibit interesting electrochemical behavior, particularly in aqueous solutions, where proton-coupled electron transfer processes occur. In general, two couples are observed in the cyclic voltammetry of a Ru^{IV}=O complex in aqueous solutions (Equations (84) and (85)):

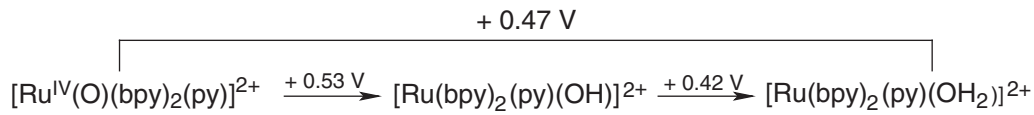
$$Ru^{IV}{=}O + H^+ + e^- \rightleftharpoons Ru^{III}{-}OH \text{ or } Ru^{IV}{=}O + 2H^+ + e^- \rightleftharpoons Ru^{III}{-}OH_2 \quad (84)$$

$$Ru^{III}{-}OH + e^- + H^+ \rightleftharpoons Ru^{II}{-}OH_2 \quad (85)$$

In general, the Ru^{III}–OH/Ru^{II}–OH_2 couple is reversible, whereas the reversibility of the Ru^{IV}=O/Ru^{III}–OH couple is strongly affected by the pretreatment of the electrode.[500,501] Smaller currents are usually observed at gold, platinum, and untreated glassy carbon electrodes, but improved reversibility can be achieved using oxidatively activated glassy carbon and pyrolytic graphite electrodes.[269,474,476,500] This is attributed to the presence of oxygen-containing functional groups, such as carbonyl, phenolic, or carboxylic, on the surface of the electrodes which would facilitate the proton transfer step. The E° values of the Ru^{IV}=O/Ru^{III}—OH_2 and Ru^{IV}=O/Ru^{III}—OH couples shift cathodically with increase in pH in a manner predicted by the Nernst equation for a two-proton one-electron and a one-proton one-electron transfer couple, respectively. A Latimer diagram that summarizes the redox and acid–base behavior of $[Ru^{IV}(O)(bpy)_2(py)]^{2+}$, a representative example of a Ru^{IV}=O species, is shown in Scheme 21.[474]



pH 7 ; 1 *M* $LiClO_4$; vs SCE



Scheme 21

The electrochemical behavior of $[Ru(tpy)(bpy)(OH_2)]^{2+}$ in aqueous solution and when incorporated in Nafion coatings has been studied in detail.[500]

The effect of ligand variations on the redox potentials of Ru^{IV}=O systems is summarized in Table 6. In general, Ru^{IV}=O is stabilized by strong σ-donor ligands, which is reflected in a relatively low E°. For example, in $[Ru(O)(tpy)(diamine)]^{2+}$, the E° values are in the order of diamine: TMEA < 4,4′-$(MeO)_2$bpy < bpy < 6,6′-Cl_2bpy, while the relative σ-donor strengths of the diamines are TMEA > 4,4′-$(MeO)_2$bpy > bpy > 6,6′-Cl_2bpy. A similar trend is observed in $[Ru(O)(bpy)(L)]^{2+}$, where E° values for L: Me_3tacn < tpy < tpm.

The electrochemical behavior of ruthenium(IV) oxo complexes of tertiary amines is similar to that of polypyridyls. For the $[Ru^{IV}(O)(L)(OH_2)]^{2+}/[Ru^{III}(L)(OH)(OH_2)]^{2+}$ couples, the ring size of the macrocycle L has little effect on E°. However, replacement of a tertiary amine nitrogen by a pyridyl nitrogen leads to an increase in E°.

In nonaqueous solutions, oxoruthenium(IV) species undergo simple one-electron transfer reactions. For *trans*-$[Ru^{IV}(O)(L)(X)]^+$ (L = 14-TMC, 15-TMC, $(TMEA)_2$; X = Cl, NCO, N_3), a reversible oxidative couple is observed in the cyclic voltammogram in MeCN, which is due to the *trans*-$[Ru^{V}(O)(L)(X)]^{2+}/$*trans*-$[Ru^{IV}(O)(L)(X)]^+$ couple. The $E^\circ(Ru^{V/IV})$ values for this series of complexes range from 0.70 to 1.10 V vs. $Ag/AgNO_3$ (Table 6). The electrochemically generated Ru^V species is an active oxidant for alcohols, as indicated by the catalytic oxidative current in the presence of alcohols (see Section 5.6.5.4.1(ii) for Ru(V)).

Proton-coupled electron transfer reactions are also observed in the electrochemistry of osmium oxo complexes. Cyclic voltammetry of $[Os^{II}(tpy)(bpy)(OH_2)]^{2+}$ in aqueous solution show pH-dependent Os^{IV}=O/Os^{II}—OH_2 or Os^{IV}=O/Os^{III}—OH couples depending on the pH of the solution.[248] E° for the $[Os^{IV}(O)(tpy)(bpy)]^{2+}/[Os^{III}(O)(tpy)(bpy)]^{2+}$ couple is 0.41 V at pH 7, which is only 0.2 V lower than the corresponding ruthenium couple.

(iii) Reactivities

As shown by their redox potentials oxoruthenium(IV) species containing polypyridyl ligands are strong oxidants and they oxidize a variety of substrates. The complex $[Ru(O)(bpy)_2(py)]^{2+}$ has also been used electrocatalytically for the oxidation of alcohols, aldehydes, alkenes, and aromatics.[471,502] Electrocatalytic oxidation has also been performed on this complex that has been incorporated into poly-4-vinylpyridine.[503,504]

The oxidation of triphenylphosphine by $[Ru(O)(bpy)_2(py)]^{2+}$ has been studied in acetonitrile solution. An ^{18}O-labeling experiment shows that oxygen transfer from Ru(IV)=O to PPh_3 is quantitative; $k_2 = 1.75 \times 10^5\ M^{-1}\ s^{-1}$ at 298 K.[505]

The oxidation of dimethyl sulfide to dimethyl sulfoxide and dimethyl sulfoxide to dimethyl sulfone by $[Ru(O)(bpy)_2(py)]^{2+}$ also occurs by O-atom transfer with respective rate constants of $17.1\ M^{-1}\ s^{-1}$ and $0.13\ M^{-1}\ s^{-1}$ in MeCN at 298 K.[506] The rate-determining step in the oxidation of thioanisole by $[Ru(O)(bpy)_2(PR_3)]^{2+}$ appears to involve primarily single-electron transfer, whereas the rate-determining step for the oxidation of methyl phenyl sulfoxide probably has an S_N2 mechanism.[507] The aerobic oxidation of methyl *p*-tolyl sulfide catalyzed by a remarkably labile heteroscorpionate ruthenium(II) aqua complex, *fac*-$[Ru^{II}(H_2O)(dpp)(tpmm)]^{2+}$ (dpp = di(pyrazol-1-yl)propane and tpmm = tris(pyrid-2-yl)methoxymethane), has been reported.[508a] The reaction occurs without a peroxide intermediate. The active intermediate is the ruthenium(IV) oxo species *fac*-$[Ru^{IV}(O)(dpp)(tpmm)]^{2+}$.

$[Ru(O)(bpy)_2(py)]^{2+}$ oxidizes $HCOO^-$ to CO_2 according to Equation (86). The pH dependence of the reaction rates is consistent with paths involving oxidation of HCO_2H, $k = 0.01\ M^{-1}\ s^{-1}$, and of HCO_2^-, $k = 4.2\ M^{-1}\ s^{-1}$ (25 °C, $\mu = 0.1$ M). The path involving Ru^{IV} and HCO_2^- is proposed to occur by a two-electron hydride transfer from the α-carbon of the alcohol to the oxo group of the ruthenium(IV), with a large kinetic isotope effect, $k(HCO_2^-)/k(DCO_2^-) = 19$:[508b]

$$[Ru(O)(bpy)_2(py)]^{2+} + HCO_2^- + H^+ \rightarrow [Ru(bpy)_2(py)(H_2O)]^{2+} + CO_2 \quad (86)$$

The oxidation of alcohols by $[Ru(O)(bpy)_2(py)]^{2+}$ and related complexes probably occurs by a hydride transfer mechanism with large C—H kinetic isotope effects ranging from 9 (CD_3OH) to 50 ($C_6H_5CD_2OH$), but solvent isotope effects are negligible.[410,411] The rate constants for the oxidation of 2-propanol by the three ruthenium(IV) oxo complexes $[Ru(O)(tpy)(6,6'\text{-}Cl_2bpy)]^{2+}$, $[Ru(O)(bpy)_2(py)]^{2+}$, and $[Ru(O)(tpy)(tmen)]^{2+}$ differ by a factor of only about two despite the $E^\circ(Ru^{IV/III})$ values ranging over 200 mV.[269] The oxidation of primary alcohols by $[Ru(O)(bpy)_2(PPh_3)]^{2+}$ in aqueous solutions increases with the hydrophobicity of the alcohol. The oxidation of allyl alcohol by $[Ru(O)(bpy)_2(PPh_3)]^{2+}$ is 250 times the rate of oxidation by $[Ru(O)(bpy)_2(PEt_3)]^{2+}$, again showing hydrophobic selectivity.[509,510] A mechanism involving a preassociation of target alcohol and coordinated phosphine ligand prior to hydride transfer is proposed.[509] In the oxidation of benzyl alcohols by oxoruthenium(IV) complexes containing *para*-substituted triphenylphosphine ligands a mechanism that involves a partial hydrogen atom abstraction from the benzylic carbon in the rate-determining step is proposed.[511] A molecular orbital analysis of the oxidation of methanol by $[Ru(O)(N)_5]^{2+}$ suggests a pathway that involves precoordination of the alcohol to the metal is competitive with one that involves C—H activation by the oxo alone.[512]

Oxidation of alkenes by polypyridyl ruthenium(IV) oxo complexes is in general not selective.[269,476,490,513,514] In the oxidation of aromatic alkenes such as styrene both epoxide and benzaldehyde, which arise from the oxidative cleavage of C=C bonds, have been observed. The epoxidation of *cis*-stilbene and *cis*-β-methylstyrene are not stereoretentive. In the oxidation of cyclohexene, allylic oxidation occurs preferentially over epoxidation. The oxidation has been investigated in acetonitrile and is found to obey second-order kinetics: rate = $k_2[Ru^{IV}{=}O][alkene]$. In the oxidation of aromatic alkenes by $[Ru^{IV}(O)(tpy)(6,6'\text{-}Cl_2bpy)](ClO_4)_2$, $[Ru^{IV}(O)(tpy)(TMEA)](ClO_4)_2$, and $[Ru^{IV}(O)(Me_3tacn)(bpy)](ClO_4)_2$, the rates are rather insensitive to changes in $E^\circ(Ru^{IV/III})$ (see Section 5.6.4.4.2, Table 11), suggesting that an alkene-derived cation radical or a carbocation intermediate is unlikely.[514] There is a linear free energy relationship between the rate constants for the oxidation of *para*-substituted styrene and the total substituent effect (TE) parameter, which supports the rate-limiting formation of a benzylic radical intermediate. Oxidation of styrene and *cis*- and *trans*-β-methylstyrenes by the chiral oxoruthenium(IV) complex $[Ru^{IV}(O)(PPz^*)(bpy)](ClO_4)_2$ attains moderate enantioselectivities, in which the production

of *cis*-epoxide is more enantioselective than the *trans* counterpart.[514] This complex also catalyzes the epoxidation of alkenes by PhIO, again with moderate enantioselectivity.[515]

$[Ru(Cl)_2(PPh_3)_3]$ catalyzes the oxidation of alkanes and alkylaromatics with *t*-butylhydroperoxides and peracetic acid, and an oxoruthenium(IV) active intermediate has been proposed.[516]

The kinetics of oxidation of phenol and alkylated phenols to the corresponding quinones by $[Ru^{IV}(O)(bpy)_2(py)]^{2+}$ have been investigated.[517] The reactions are first order in both phenol and $Ru^{IV}{=}O$, and on the basis of the magnitude of OH/OD and CH/CD kinetic isotope effects and ^{18}O-labeling experiments, the mechanism appears to be electrophilic attack of Ru=O on the aromatic ring. In the oxidation of hydroquinones (QH_2) to the corresponding quinones by the same oxidant, pathways involving the oxidation of QH_3^+, QH_2, and QH^- occur within the pH range 1–8. The oxidation of QH_2 proceeds with a proton-coupled electron transfer mechanism, with a large H_2O/D_2O kinetic isotope effect of 30.[518]

Kinetic studies on the oxidations of cyclohexene, benzyl alcohol, phenol, and *trans*-stilbene by $[Ru^{IV}(O)(tpy)(bpy(PO_3H_2)_2)]^{2+}$ (bpy($PO_3H_2)_2$) = 2,2′-bipyridine-4,4′-diphosphonic acid adsorbed to thin films of TiO_2 nanoparticles on glass have been reported.[519] There is evidence for initial two-electron steps to give Ru^{II} intermediates in all four cases.

The kinetics and mechanisms of the oxidation of DNA, nucleic acid sugars, and nucleotides by $[Ru(O)(tpy)(bpy)]^{2+}$ and its derivatives have been reported.[520–527] The $Ru^{IV}{=}O$ species is an efficient DNA cleavage agent: it cleaves DNA by sugar oxidation at the 1′ position, which is indicated by the termini formed with and without piperidine treatment and by the production of free bases and 5-methylene-2(5*H*)-furanone. Kinetic studies show that the 1′-C—H activation is rate determining and a hydride transfer mechanism is proposed. The $Ru^{IV}{=}O$ species also oxidizes guanine bases via an oxo transfer mechanism to produce piperidine-labile cleavages.

Kinetic studies on the reduction of $Ru^{IV}{=}O$ species by inorganic complexes have been reported. Hydrogen peroxide is rapidly oxidized to O_2 by $[Ru^{IV}(O)(bpy)_2(py)]^{2+}$. The rate law over the pH range 2–10 shows parallel pathways involving the oxidation of H_2O_2 and HO_2^-.[528,529] The oxidation of H_2O_2 has a kinetic isotope effect, $k_{H_2O}/k_{D_2O} = 22.1$ at 25.0 °C, consisting of a H-atom transfer mechanism. The pathway involving the oxidation of HO_2^- is likely to be outer sphere, with $k_{H_2O}/k_{D_2O} = 9.91$, a considerable fraction of this effect being from acid–base equilibrium for H_2O_2, $K_a(H_2O)/K_a(D_2O) = 7.28$.

The comproportionation reaction between $[Ru^{IV}(O)(bpy)_2(py)]^{2+}$ and $[Ru^{II}(bpy)_2(py)(OH_2)]^{2+}$ to form two equivalents of $[Ru^{III}(bpy)_2(py)(OH)]^{2+}$ occurs via a H-atom transfer mechanism with a solvent isotope effect (k_{H_2O}/k_{D_2O}) of 16.1 (Equation (86a)):

$$[Ru^{IV}(O)(bpy)_2(py)]^{2+} + [Ru^{II}(bpy)_2(py)(OH_2)]^{2+} \rightarrow 2\,[Ru^{III}(bpy)_2(py)(OH)]^{2+} \qquad (86a)$$

The closely related comproportionation reaction of $[Ru^{IV}(O)(tpy)(bpy)]^{2+}$ with $[Ru^{II}(tpy)(bpy)(OH_2)]^{2+}$ to produce $[Ru^{III}(tpy)(bpy)(OH)]^{2+}$ shows a linear dependence of its rate constant on the driving force when a series of complexes with substituents on the 4′ position of the tpy ligand or the 4 and 4′ positions of the bpy ligand are studied. The slopes of 0.66 in H_2O and 0.64 in D_2O are in reasonably good agreement with the value of 0.5 predicted by Marcus theory.[530]

The reduction of *cis*-$[Ru^{IV}(O)(bpy)_2(py)]^{2+}$ by $[Os^{II}(bpy)_3]^{2+}$ occurs by an outer-sphere mechanism and is uncoupled from proton transfer.[531] Reduction of $[Ru^{IV}(O)(OH_2)(N_2O_2)]^{2+}$ (see Figure 3 for structure of ligand) to $[Ru^{III}(N_2O_2)(OH)(OH_2)]^{2+}$ by *cis*-$[Ru^{II}(NH_3)_4(isn)_2]^{2+}$ (isn = isonicotinamide) involves prior protonation with $[Ru^{IV}(N_2O_2)(OH)(OH_2)]^{3+}$ as the reactive intermediate.[532] The self-exchange rate constant of the $[Ru(N_2O_2)(OH)(OH_2)]^{3+/2+}$ couple is determined to be 3.1×10^{-4} M^{-1} s^{-1}.

The reactivities of $[Ru^{IV}(O)(14\text{-TMC})(X)]^{n+}$ and its related 15-TMC, 16-TMC, and $CRMe_3$ complexes with organic substrates have also been examined.[240,243] In contrast to polypyridyl $Ru^{IV}{=}O$ species, these macrocyclic $Ru^{IV}{=}O$ complexes are weak oxidants. They oxidize benzyl alcohol to benzaldehyde but do not react with alkenes at room temperature. The lower oxidizing ability of these systems than the polypyridyl systems is due to their lower E° values.[240] However, $[Ru^{IV}(O)(H_2O)(N_2O_2)](ClO_4)_2$, which has a higher E° value, is able to catalyze the oxidation of norbornylene, styrene, and cyclooctene by PhIO.[247]

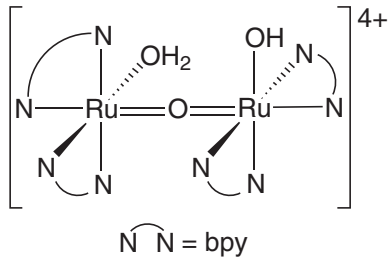
There are very few osmium(IV) oxo species. There is evidence that the $Os^{IV}{=}O$ species is more reactive than the corresponding $Os^{VI}(O)_2$ species. $[Os^{VI}(O)_2(phenba)]$ (see Figure 12 for structure of ligand) is able to oxidize benzyl alcohol in the presence of one equivalent of PPh_3, the active oxidant being probably a $Os^{IV}{=}O$ species. No oxidation occurs in the absence of PPh_3.[312] The

complex $[Os^{IV}(O)(tpy)(bpy)]^{2+}$ has been generated by the electrochemical oxidation of $[Os^{II}(tpy)(bpy)(OH_2)]^{2+}$.[481] As in the case of ruthenium, pH-dependent $Os^{IV}{=}O/Os^{III}{-}OH_2$ and $Os^{IV}{=}O/Os^{III}{-}OH$ couples were observed. Interestingly, E° of the $[Os^{IV}(O)(tpy)(bpy)]^{2+}/[Os^{III}(tpy)(bpy)(OH)]^{2+}$ couple, which is 0.41 V vs. SSCE at pH 7, is only about 200 mV smaller than that for the related ruthenium system under similar conditions. Electrochemical oxidation of *cis*-$[Os^{II}(bpy)_2(OH_2)_2]^{2+}$ via a series of sequential one-electron oxidations to $[Os^{IV}(O)(bpy)_2(OH_2)]^{2+}$ has also been reported.[237]

5.6.6.6.2 Oxo-bridged dimers

(i) Nitrogen ligands

The species $[(bpy)_2(H_2O)Ru^{III}(\mu\text{-}O)Ru^{IV}(OH)(bpy)_2]^{4+}$ (**125**), which is a water oxidation catalyst (see Section 5.6.4.4.2), has been prepared by the oxidation of $[(bpy)_2(H_2O)Ru^{III}(\mu\text{-}O)Ru^{III}(OH_2)(bpy)_2]^{4+}$ with Ce^{IV}.[398a,533] Its structure has been determined by X-ray crystallography. Further oxidation of (**125**) produces $[(bpy)_2(O)Ru^{IV}(\mu\text{-}O)Ru^{V}(O)(bpy)_2]^{3+}$ (see Section 5.6.4.4.2).[408] $[(b)_2(O)Ru^{IV}(\mu\text{-}O)Ru^{V}(O)(b)_2]^{3+}$ (b = 5,5′-$(COOH)_2$bpy) can also be generated in a similar manner. This species is able to oxidize water to oxygen.[534]



(**125**)

A novel tri-oxo-bridged diruthenium(IV) complex with the ligand Me_3tacn,[535] $[(Me_3tacn)Ru^{IV}(\mu\text{-}O)_3Ru^{IV}(Me_3tacn)]^{2+}$ (**126**), has been prepared by aerial oxidation of $[(Me_3tacn)Ru^{III}(\mu\text{-}OH)_3Ru^{III}(Me_3tacn)]^{2+}$ in alkaline medium. This dark green species has a temperature-dependent magnetic moment with $\mu_{eff} = 2.26\,\mu_B$ per binuclear unit at 298 K, which corresponds to almost two unpaired electrons per binuclear unit. The X-ray structure reveals a short Ru—Ru distance of 2.363 Å, consistent with a bond order of 2. The measured Ru—O (bridge) distances range from 1.899 Å to 1.937 Å. This complex undergoes a reversible one-electron oxidation ($E^\circ = 1.05$ V vs. $Cp_2Fe^{+/0}$) in acetonitrile to give a bright green mixed-valence Ru^{IV}—Ru^{V} species, $[(Me_3tacn)Ru^{IV}(\mu\text{-}O)_3Ru^{V}(Me_3tacn)]^{3+}$.

The bpy analog of ruthenium red, $[(bpy)_2(H_2O)Ru^{III}ORu^{IV}(bpy)_2ORu^{III}(OH_2)(bpy)_2]^{6+}$, has been synthesized and characterized by XPS measurements.[536] Electrochemical studies in aqueous solutions reveal seven distinct valence states from [2, 2, 2] to [4, 5, 4]. Its optical spectrum in 0.1 M acid displays an intense peak at 653 nm ($\varepsilon_{max} = 1.05 \times 10^5\ M^{-1}\,cm^{-1}$).

The complex $[(Cl)(NH_3)_4Ru^{III}(\mu\text{-}O)Ru^{IV}(NH_3)_4(Cl)]^{3+}$ constitutes a significant portion of the "ruthenium red" cytological stain,[537] and the hydroxyl analog readily forms in water. The formato derivative of this species, $[(HCO_2)(NH_3)_4Ru^{III}(\mu\text{-}O)Ru^{IV}(NH_3)_4(HCO_2)]^{3+}$, has been structurally characterized; the Ru—O(bridge) distance is 1.8240 Å.[538]

Dimeric μ-oxo-Ru^{IV} porphyrins, $[\{Ru^{IV}(por)(OH)\}_2(\mu\text{-}O)]$ (por = OEP, TPP), are formed by the oxidation of $[Ru^{II}(por)(CO)]$ with TBHP, or by the oxidation of $[Ru(por)]_2$ with O_2 in the presence of a trace amount of H_2O, or by the reduction of $[Ru^{VI}(O)_2(por)]$ with alkenes in noncoordinating solvents.[318,539–541] $[Ru^{IV}(OEP)(OH)]_2(\mu\text{-}O)$ has a linear Ru—O—Ru backbone with Ru—O(bridge) = 1.847 Å and a staggered conformation of the porphyrin rings.[539] A range of related dimeric Ru^{IV} species $[Ru(por)(X)]_2(\mu\text{-}O)$ (por = OEP, TPP, TPr^nP (*meso*-tetra-n-propylporphyrinato-dianion); $X = Cl^-$, Br^-, OAc^-, CF_3COO^-, HSO_4^-, MeO^-, EtO^-, 2-HO-$C_6H_4O^-$, 4-HO-$C_6H_4O^-$) have also been prepared.[541] The structures of $[Ru(OEP)(Cl)]_2(\mu\text{-}O)$ and $[Ru(TP\ P)(OR)]_2$ (μ-O) (OR = OC_6H_4Me-4) have also been established by X-ray crystallography ($[Ru(OEP)Cl]_2$ (μ-O): Ru—O(bridge) = 1.793 Å; $[Ru^{IV}(TPP)(OR)]_2(\mu\text{-}O)$: Ru—O (bridge) = 1.789 Å).[541]

The reduction of various dioxoruthenium(VI) porphyrin complexes $[Ru^{VI}(O)_2(por)]$ by M^{II} porphyrin and salicylaldimine complexes produces heterotrimetallic oxo-bridged complexes $[(L)M^{III}(\mu\text{-}O)Ru^{IV}(por)(\mu\text{-}O)M^{III}(L)]$ (M = Fe, Cr, Mn; por = TPP, TMP, OEP; L = TMP, TPP, OEP, salen, salmah (the dianion of *N*,*N*′-(4-methyl-4-azaheptane-1,7-diyl)bis(salicylaldimine))). A detailed study of the temperature- and field-dependent magnetic properties of these complexes show that the spin states of the metal centers are Ru^{IV}, $S_{Ru} = 1$; Fe^{III}, $S_{Fe} = 5/2$; Cr^{III}, $S_{Cr} = 3/2$; Mn^{III}, $S_{Mn} = 4/2$.[542] Similar heterotrimetallic oxo-bridged species, $[(L)(N_4)Fe^{III}(\mu\text{-}O)Ru^{IV}$-(4-MeO-TPP)$(\mu\text{-}O)Fe^{III}(N_4)(L)]$ (N_4 = ((DMG)BF_2)$_2$ (DMG)BF_2 = (diphenylboryl)dimethylglyoximate, ((DMG)BPh_2)$_2$ (DMG)BPh_2 = (difluoroboryl)dimethylglyoximate, ((DPG)BF_2)$_2$ (DPG)BF_2 = (difluoroboryl)diphenylglyoximate; L = Bu^nNH_2, MeCN, py, 1-MeIm, $(BuO)_3P$), have also been reported. The X-ray structure of the complex for L = Bu^nNH_2 and N_4 = ((DPG)BF_2)$_2$ (**127**) has been determined.[543]

A number of μ-oxoosmium(IV) complexes have been reported in *CCC* (1987). The mixed-valence species $[(H_2O)(bpy)_2Os^{III}(\mu\text{-}O)Os^{IV}(bpy)_2(OH)]^{4+}$ and $[(tpy)(bpy)Os^{III}(\mu\text{-}O)Os^{IV}(bpy)(tpy)]^{5+}$ have been isolated.[544] The osmium complex $[(bpy)_2(O)Os^{V}(\mu\text{-}O)Os^{V}(O)(bpy)_2]^{4+}$ has also been generated in a manner similar to that of its ruthenium analog.[544] Electrochemically, the redox couples Os^{II}—Os^{II}, Os^{III}—Os^{III}, Os^{III}—Os^{IV}, Os^{IV}—Os^{IV}, Os^{IV}—Os^{V}, and Os^{V}—Os^{V} are all accessible. The Pourbaix diagrams for $[(bpy)_2(H_2O)Ru^{III}(\mu\text{-}O)Ru^{III}(OH_2)(bpy)_2]^{4+}$ and $[(bpy)_2$-$(H_2O)Os^{III}(\mu\text{-}O)Os^{IV}(OH)(bpy)_2]^{4+}$ have been studied and are shown in Figures 17 and 18.

Interaction of $K_2[Os(O)_2(CHBA\text{-}Et)]$ with PPh_3 affords the μ-oxo dimer $K_2[Os_2O(CHBA\text{-}Et)_2(OPPh_3)_2]$ (**153**), which has been structurally characterized.[545] The equatorial ligands are eclipsed, and the Os—O—Os bridge is not quite linear (Os—O—Os = 175°, Os—O(bridge) = 1.795 Å). Reaction of *trans*-$[Os(O)_2(C1)_2(PPh_3)_2]$ with acetic acid/acetic anhydride produces $[Os_2(\mu\text{-}O)(\mu\text{-}OAc)_2Cl_4(PPh_3)_2]$ (**154**), which has a bent oxo-bridge (Os—O—Os = 140.2°, Os—O (bridge) = 1.829 Å).[546] The cyclic voltammogram shows a reversible one-electron reduction, and the purple paramagnetic Os^{III}—Os^{IV} anion $[Os_2(O)(OAc)_2(C1)_4(PPh_3)_2]^-$ has been isolated. Other $[Os_2(O)(OCOR)_2(Cl)_4(PR'_3)_2]$ complexes (R = Me, Et; X = Cl, Br; $PR'_3 = PPh_3$, PEt_2Ph) have also been prepared.[546] A similar reaction of *trans*-$[Os(O)_2(Cl)_2(py)_2]$ with acetic acid/acetic anhydride, however, produces a linear μ-oxo complex $[Os^{IV}_2(\mu\text{-}O)(Cl)_5(OAc)(py)_4]$ with the coordination of

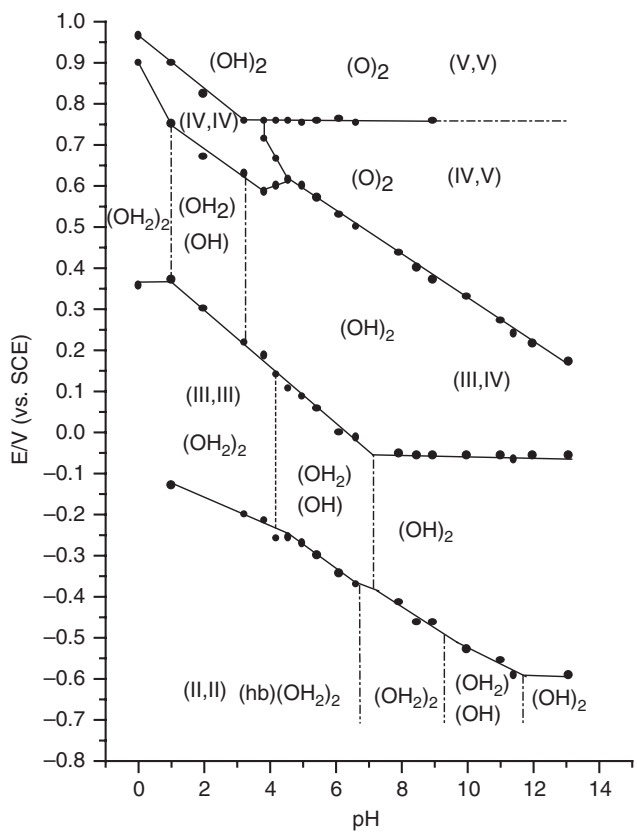
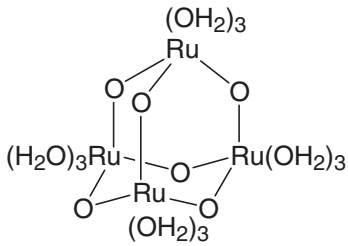
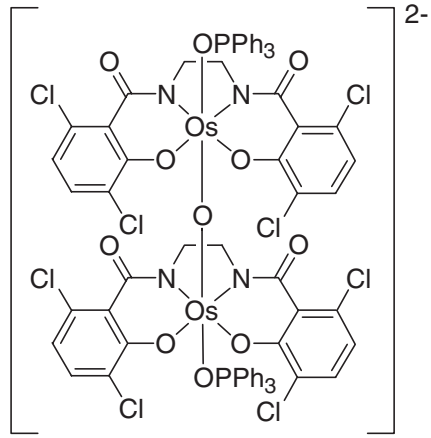


Figure 18 Pourbaix diagram for $[(bpy)_2(OH_2)Os^{III}(\mu\text{-}O)Os^{IV}(OH_2)(bpy)_2]^{4+}$.

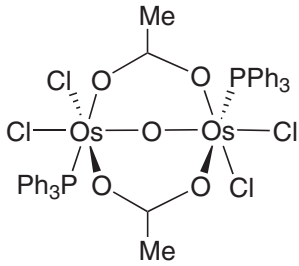


(152)

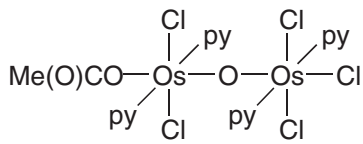


(153)

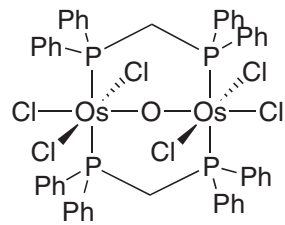
acetate *trans* to the oxide instead of the *cis* position necessary for bridge formation.[547] The two Os atoms have unsymmetrical ligand environment with Os—O distances of 1.826 Å and 1.790 Å. Reduction of $[Os^{IV}_2\text{-}(\mu\text{-O})(Cl)_5(OAc)(py)_4]$ (**155**) with hydrazine hydrate generates the mixed-valence $Os^{III}Os^{IV}$ dimer $[Os^{III}Os^{IV}(\mu\text{-O})(Cl)_5(OAc)(py)_4]^-$. The overall structure is similar to that of the Os^{IV}_2 dimer; the Os—O—Os moiety remains linear but the Os—O distances (1.847 and 1.857 Å) become longer. E° for the $Os^{IV}Os^{IV}/Os^{IV}Os^{III}$ and the $Os^{IV}Os^{III}/Os^{III}Os^{III}$ couples are 0.03 V and −1.15 V (vs. Ag/AgCl), respectively, by cyclic voltammetry. A linear μ-oxo-diosmium(IV) molecule bridged by two dppm ligands, $[Os_2(\mu\text{-O})(\mu\text{-dppm})_2(Cl)_6]$ (**156**), has been prepared by reacting $OsCl_3$ with dppm.[548] The Os—O bond distance is 1.792 Å. Interestingly, it undergoes a reversible one-electron oxidation to give formally an Os^{IV}—O—Os^{V} complex, $[Os_2(\mu\text{-O})(\mu\text{-dppm})_2(Cl)_6]^+$ (Figure 19).



(154)



(155)



(156)

A number of μ-oxo-osmium(IV) porphyrin complexes have been prepared by aerial oxidation of $[Os^{II}(OEP)(CO)(MeOH)]$ in the presence 2,3-dimethylindole in CH_2Cl_2.[549] Cyclic voltammetric studies show that $[Os_2(O)(OEP)_2(OMe)_2]$ can undergo reduction to give an Os^{IV}—O—Os^{III} dimer. The X-ray crystal structure of $[Os(OEP)(OMe)]_2(\mu\text{-O})$ shows a linear Os—O—Os backbone with Os—O and Os—OCH_3 distances of 1.808 Å and 1.997 Å, respectively.[550]

(ii) Oxygen ligands

The diamagnetic red-brown $Ru^{IV}(aq)$ cation has been known since the 1950s. It has been prepared by anodic oxidation of $[Ru(H_2O)_6]^{2+}$ or $[Ru(H_2O)_6]^{3+}$, or by reduction of RuO_4 with H_2O_2.[551] Results of Ru K-edge EXAFS are consistent with the formulation $[Ru_4(\mu\text{-O})_6(H_2O)_{12}]^{4+}$ (**152**) with an adamantine-like structure.[552]

Oxidation of $[Ru^{III}(edta)(OH_2)]^-$ produces the $Ru^{III}Ru^{IV}$ μ-oxo ion $[\{Ru(edta)\}_2(\mu\text{-O})]^{3-}$,[553,554] which was characterized by Raman spectroscopy.[554] Further one-electron oxidation with Ce^{IV}

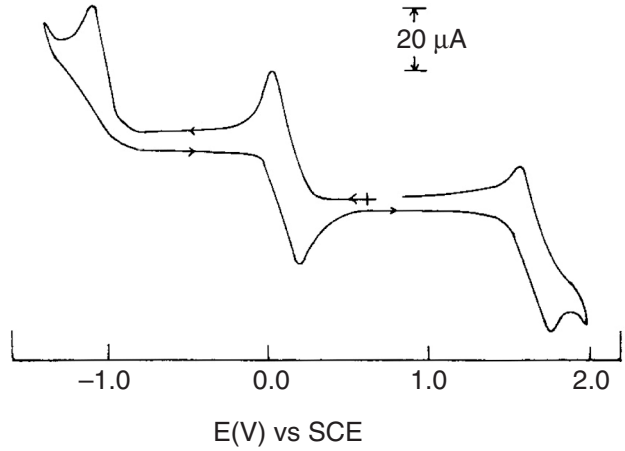
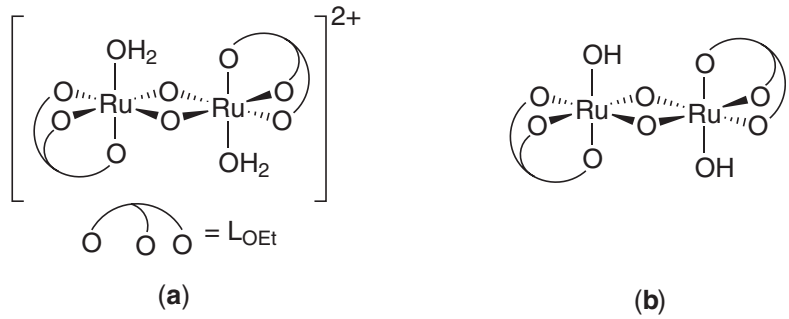


Figure 19 Cyclic voltammogram of $Os_2O(dppm)_2Cl_6$ in dichloromethane (0.1 M TBAP) at a platinum electrode (scan rate, 40 mV s^{-1}; concentration, 1×10^{-3} M) (after Chakravarty *et al.*[548]).

produces the $Ru^{IV}Ru^{IV}$ ion $[\{Ru(edta)\}_2(\mu\text{-}O)]^{2-}$. This species decomposes in the presence of excess oxidant to produce CO_2, apparently due to ligand oxidation.[554]

The anionic cobalt(III)-based oxygen tripod ligand L_{OEt}^- (= $[(Cp)Co(OP(OEt)_2)_3]^-$) is oxidatively robust and should stabilize high-valent metal centers.[555a] Reaction of $Na(L_{OEt})$ in 1% H_2SO_4 with $[RuO_4]$ in CCl_4 produces the edge-sharing bioctahedral $Ru^{IV}-Ru^{IV}$ complex $[(L_{OEt})(H_2O)Ru(\mu\text{-}O)_2Ru(OH_2)(L_{OEt})]^{2+}$ (**128a**), which is converted to $[(L_{OEt})(HO)Ru(\mu\text{-}O)_2Ru(OH)(L_{OEt})]$ (**128b**) on treatment with Na_2CO_3.[413] Both complexes have been characterized by X-ray crystallography. The Ru—Ru distances are 2.452 Å in (**128b**) and 2.505 Å in (**128a**), indicating substantial metal–metal interactions.



(**128**)

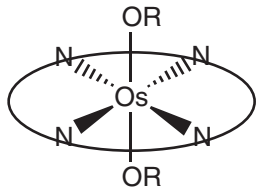
(iii) Halide ligands

MO calculations on the linear μ-oxo ion $[(Cl)_5Ru(\mu\text{-}O)Ru(Cl)_5]^{4-}$ have been performed.[556]

5.6.6.7 Miscellaneous Oxygen Ligands

5.6.6.7.1 Complexes containing alkoxo ligands

A series of dialkoxyosmium(IV) porphyrins $[Os^{IV}(por)(OR)_2]$ (por = *p*-X-TPP, $(MeO)_{12}TPP$, OEP, MIX-DME; R = Me, Et, Pr^i, Ph) have been prepared either by reduction of $[Os^{VI}(por)(O)_2]$ with PPh_3, N_2H_4, or ascorbic acid in the presence of ROH; or by the treatment of $[Os(por)(N_2)(THF)]$ with ROH in THF in the presence of air. These complexes are characterized by UV–vis, IR, and ^1H NMR. The "oxidation state marker" IR bands appear at 1,014–1,016 cm^{-1}. Reversible/quasi-reversible $Os^{V/IV}$ and $Os^{IV/III}$ waves are found in the cyclic voltammograms of these osmium(IV)



(**129**)

(**a**) Et

(**b**) Pr^i

(**c**) Ph

complexes. The X-ray structures of $[Os(TPP)(OEt)_2]$ (**129a**), $[Os(TPP)(OPr^i)_2]$ (**129b**), and $[Os(TPP)(OPh)_2]$ (**129c**) have been determined. The RO—Os—OR axes are all linear; the Os—OR distances range from 1.909 Å to 1.938 Å, indicating some d_π (Os)–p_π (O) interactions.[555b]

5.6.6.7.2 Complexes containing peroxo ligands

There are few well-characterized high-valent peroxo complexes of ruthenium and osmium, presumably because they decompose readily to give oxo complexes.

The five-coordinate complexes $[Os(X)(dcpe)_2](BPh_4)$ (X = H, Cl) react quantitatively with O_2 at room temperature and atmospheric pressure in a noncoordinating solvent to afford the diamagnetic species $[Os(O_2)(X)(dcpe)_2](BPh_4)$.[557] The X-ray structure of $[Os(O_2)(H)(dcpe)_2](BPh_4)$ (**130**) has been determined. The Os—O distances are identical (2.041 Å), and the Os—H distance is 1.83 Å. The O—O distance of 1.45 Å is close to that of peroxide ion (1.49 Å). Thus this complex should be formulated as an osmium(IV) peroxo species. The ruthenium analog $[Ru(O_2)(H)(dippe)_2](BPh_4)$ (dippe = 1,2-bis(diisopropylphosphino)ethane) has a much longer O—O distance of 1.360 Å.[557–559] This may be formulated either as a ruthenium(IV) peroxo or a ruthenium(II) dioxygen species.

5.6.6.7.3 Complexes containing dioxolene ligands

A series of novel ruthenium(IV) dioxolene complexes, formally [3 + 2] cycloadducts, have been obtained via the reaction of *cis*-$[Ru^{VI}(O)_2(Me_3tacn)(CF_3CO_2)]^+$ with trimethylsilylacetylenes (Scheme 14).[270] These dark blue complexes display a characteristic UV–vis absorption band at 550–680 nm. They are also characterized by electrospray mass spectrometry. The X-ray structure of the complex formed with bis(trimethylsilyl)acetylene has been determined; the two Ru—O bonds of the metallocycle are of the same length (1.978 Å).[270]

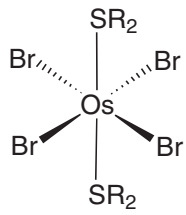
5.6.6.8 Sulfur Ligands

5.6.6.8.1 Thioether complexes

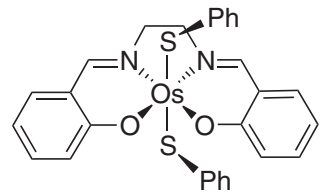
The cationic ruthenium(IV) complex $[Ru(\eta^5\text{-}C_5Me_5)(SC_4H_8)_2Br_2]^+$ has been reported.[560]

Species of the form $[Os(L)(X)_4]$ ($L = S(CH_2CH_2CH_2SMe)_2$, $MeC(CH_2SMe)_3$, X = Cl, Br and X = Cl, $L = S(CH_2)_2S(CH_2)_3S(CH_2)_3$) and $[Os(L')(X)_4]$ (X = Cl, L = RSCH=CHR, RSH_2CH_2R, *o*-$C_6H_4(SR)_2$, R = Me, Ph; X = Br, L′ = MeSCH=CHSMe, $MeSCH_2CH_2SMe$) have been documented in *CCC* (1987).

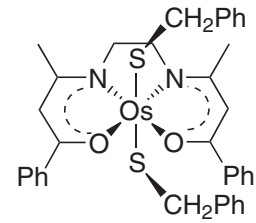
A few other osmium(IV) thioether complexes have been reported. A series of *trans*-$[Os^{IV}(Br)_4(SR_2)_2]$ (**131**) complexes have been synthesized by oxidative bromination of *mer*-$[Os(Br)_3(SR_2)_3]$.[561] These complexes have magnetic moments of about 1.7μ_B at 295 K. The X-ray structures of *trans*-$[Os(Br)_4(SR_2)_2]$ ($SR_2 = (PhCH_2)_2S$, $(CH_2)_4S$) reveals a centrosymmetric *trans* geometry (Os—S = 2.420 Å and 2.401 Å, respectively).



(**131**)



(**132**)



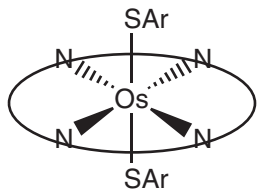
(**133**)

5.6.6.8.2 Thiolato complexes

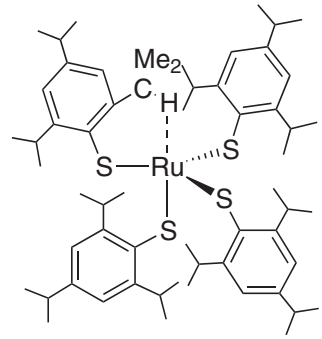
The first osmium(IV) thiolato complex, [Os(salen)(SPh)$_2$] (**132**), was prepared by the reduction of [Os(O)$_2$(salen)] with thiophenol in CH_2Cl_2.[310] The complex has a distorted octahedral structure, and both phenyl groups tilt away from the methylene bridge of the salen ligand, which is in the *gauche* confirmation. The mean Os—S distance is 2.32 Å, which is shorter than that (2.415 Å) in [Os$_2$(Et$_2$dtc)$_6$](PF$_6$)$_2$[562](Et$_2$dtc = *N*,*N*-diethyldithiocarbamate).

A series of bisthiolato osmium(IV) complexes, *trans*-[Os^{IV}{(Ba)$_2$en}(SR)$_2$] (R = C_6H_5, $CH_2C_6H_5$, Np, $C_6H_4CH_3$, C_6H_4F, Et, Bu, C_6H_{11}), have also been prepared by treatment of [Os^{VI}(O)$_2${(Ba)$_2$en}] with RSH.[313] The X-ray crystallography of [Os^{IV}{(Ba)$_2$en}(SCH$_2$C$_6$H$_5$)]·1/2H$_2$O (**133**) reveals two independent molecules (Os—S = 2.298–2.323 Å).

The diamagnetic bis(thiolato)osmium(IV) porphyrin complexes [Os(por)(SAr)$_2$] (**134**) (por = TTP, OEP; Ar = *p*-tolyl, C_6F_4H, C_6F_5, 2,6-Me$_2$C$_6$H$_3$) are prepared by a method similar to that of [Os(salen)(SPh)$_2$].[563] The X-ray structure of [Os(TTP)(SC$_6$F$_4$H)$_2$] reveals a short Os—S distance of 2.294 Å.



(**134**)
(**a**) *p*-tolyl
(**b**) C_6F_4H
(**c**) C_6F_5
(**d**) $C_6H_3Me_2$-2,6



(**135**)

The geometric features and electronic structures of dithiolato complexes of osmium(IV) porphyrins have been investigated by density functional calculations.[563] The diamagnetic properties are the result of a strong Os(*d*)–S(*p*) π interaction, causing a large splitting between two of the three "t_2g" orbitals when the two dithiolate ligands are coplanar.

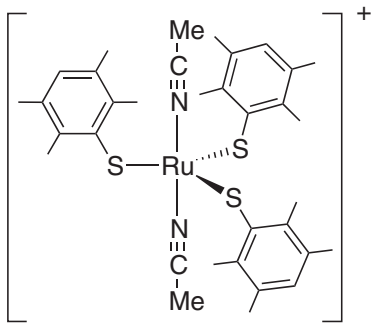
Transition metal complexes of sterically hindered thiolate ligands have been reviewed.[564] These ligands give rise to unusual geometries and oxidation states, and low coordination numbers in their complexes.

The trigonal bipyramidal tetrathiolate ruthenium(IV) and osmium(IV) complexes [M(SAr)$_4$(L)] (M = Ru, Os; SAr = SC_6HMe_4-2,3,5,6, $SC_6H_2Pr^i_3$-2,4,6; L = MeCN, CO) have been described in *CCC* (1987). [Ru($SC_6H_2Pr^i_3$-2,4,6)$_4$L] (L = MeOH, DMSO, CH_3CN) can be prepared by heating [Ru(NO)($SC_6H_2Pr^i_3$-2,4,6)$_4$]$^-$ in solvent L.[565] Removal of the MeOH in [Ru($SC_6H_2Pr^i_3$-2,4,6)$_4$(MeOH)] by heating produces [Ru($SC_6H_2Pr^i_3$-2,4,6)$_4$] (**135**). The X-ray structure reveals the complex to be pentacoordinate; in addition to the four thiolates the ruthenium is also coordinated to the methane C—H of an *ortho* isopropyl group. The reaction of [M(SAr)$_4$(CH_3CN)] (M = Ru, Os; SAr = SC_6HMe_4-2,3,5,6, $SC_6H_2Pr^i_3$-2,4,6)[566] with HBF_4 or

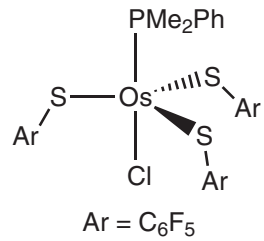
HPF_6 in CH_3CN produces $[M(SAr)_3(MeCN)_2]^+$.[567] The X-ray structure of $[Ru(SC_6HMe_4\text{-}2,3,5,6)_3(MeCN)_2](PF_6)$ (**136**) shows a trigonal bipyramidal geometry with d(Ru—S) = 2.195–2.208 Å. The reaction of $[M(SAr)_4(CH_3CN)]$ (M = Ru, Os; SAr = SC_6HMe_4-2,3,5,6, $SC_6H_2Pr^i_3$-2,4,6) with HCl in THF produces $[M(SAr)_3Cl(MeCN)]$.[567]

An alternative method for the preparation of $[Ru(SR)_4(MeCN)]$ and $[Ru(SR)_3(MeCN)(Cl)]$ (R = 2,6-dimethylphenol) has been reported.[568]

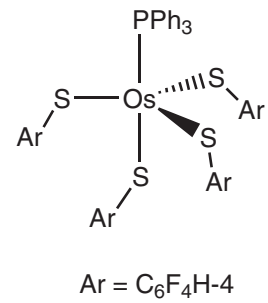
Platinum group metals complexes, including Ru^{IV} and Os^{IV}, containing pentafluorobenzenethiolato ligands have been reviewed.[569] Reactions of $[Os(SAr)_3(PMe_2Ph)_2]$ (Ar = C_6F_5 or C_6F_4H) with HCl in acetone produce the diamagnetic osmium(IV) complexes $[Os(Cl)(SAr)_3(PMe_2Ph)]$.[570] The X-ray crystallography of $[Os(Cl)(SC_6F_5)_3(PMe_2Ph)]$ (**137**) (Os—S = 2.195–2.201 Å) reveals a trigonal bipyramidal structure. The less sterically hindered thiolate ligands occupy the equatorial positions and are all "down" towards and around the smaller chloride ligand.[570] $[Os(SAr)_4(PMe_2Ph)]$ (Ar = C_6F_5, C_6F_4H-4, C_6H_4F-4, Ph) can be prepared either by reaction of $[OsCl(SAr)_3(PMe_2Ph)]$ with $Pb(SAr)_2$ or by interaction of $[OsO_4]$ with RSH and PMe_2Ph.[571] $[Os(SAr)_4(PPh_3)]$ are also known.[571] The trigonal bipyramidal structure with phenyl group in the "down" configuration of $[Os(SC_6F_4H\text{-}4)_4(PPh_3)]$ (**138**) is confirmed by X-ray crystal-



(**136**)



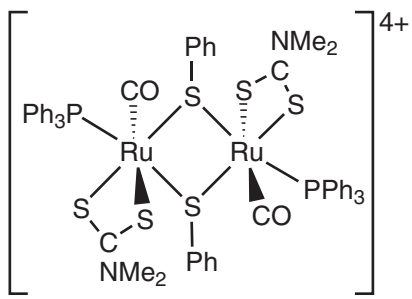
(**137**)



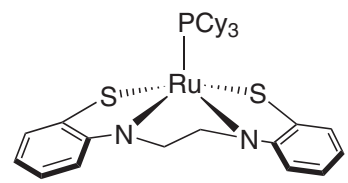
(**138**)

lography (Os—S_{axial} = 2.414 Å and Os—$S_{equatorial}$ = 2.207 Å). Treatment of $Pb(SC_6H_4X)_2$ (X = F or CF_3) with $[Os(Cl)(SC_6F_5)_3(PMe_2Ph)]$ gives $[Os(Cl)(SC_6F_5)_2(SC_6H_4X)(PMe_2Ph)]$ (Os–SC_6F_5 = 2.206 Å and Os–$SC_6H_4CF_3$ = 2.187 Å).[571] The electrochemistry of the Os^{IV} complexes $[Os(X)(SR)_3(PR_{13})]$ (X = Cl, Br or SR; R = C_6F_4H-4 or C_6F_5; PR_{13} = PMe_2Ph, PPh_3, $P(C_6H_4Y\text{-}4)_3$ (Y = F, OMe, CF_3, Me or Cl)) has been studied.[572]

$[Ru^{IV}(\mu\text{-SPh})(S_2CNMe_2)(CO)(PPh_3)]_2(NO_3)_4$ (**139**) is synthesized by oxidation of $[Ru^{II}(\mu\text{-SPh})(S_2CNMe_2)(CO)(PPh_3)]_2$ with nitric acid in MeCN at room temperature.[573] This complex has a planar Ru_2S_2 core and Ru···Ru distance of 2.876 Å, indicative of the presence of a metal–metal bond. It shows an unusual four-electron reversible $Ru^{IV,IV}/Ru^{II,II}$ couple at 0.496 V vs. SCE (ΔE = 28 mV) in the cyclic voltammogram ($MeCN + CH_2Cl_2$).



(**139**)

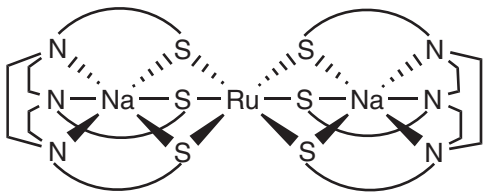


(**140**)

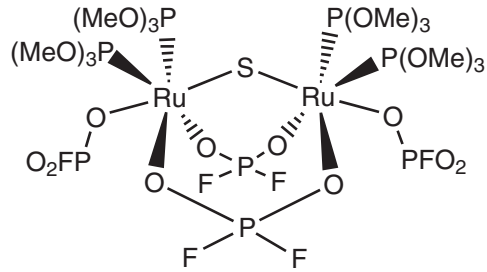
The diamagnetic [Ru(PCy$_3$)("S_2N_2")] (**140**) complex ("S_2N_2"$^{4-}$ = 1,2-ethanediamide-*N*,*N*′-bis (2-benzenethiolate)(4-) (cy = cyclohexyl)) can be prepared by reacting either [Ru(Cl)$_2$(DMSO)$_4$] or RuCl$_3$·3H$_2$O with PCy$_3$, "$S_2N_2H_4$" and LiOMe.[574] The relatively short average Ru—S and Ru—N distances (2.290 and 1.974 Å, respectively) indicate the presence of π-bonding in Ru—S and Ru—N which stabilize the Ru^{IV} oxidation state.

5.6.6.8.3 Metallothioanions as ligands

The trinuclear complexes [LNaM^{IV}NaL] (M = Ru, Os; H_3L = 1,4,7-tris(4-*t*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane) were obtained by the reaction of methanolic Na_3L with [Ru(DMSO)$_4$(Cl)$_2$] and K_2[OsCl$_6$], respectively.[575] The X-ray structure of [LNaRu^{IV}NaL] (**141**) reveals an octahedral Ru$^{IV}S_6$ central core and two trigonal prismatic terminal LNa units with an N_3S_3 set (average Ru—S distance = 2.414 Å). Both complexes exhibit reversible M$^{V/IV}$ and M$^{IV/III}$ couples in their cyclic voltammograms.



(**141**)



(**142**)

5.6.6.8.4 Sulfido complexes

The interaction of K[Ru(Hedta)(Cl)] with elemental sulfur in a water/ethanol mixture was reported to give [Ru^{IV}(Hedta)]$_2$(μ-S_2), which can be further converted to [Ru^{IV}(Hedta)]$_2$(μ-S) by prolong refluxing in 1:1 water/ethanol.[576] Both complexes are able to stoichiometrically and catalytically transfer the sulfur atom to cyclohexene to yield cyclohexene sulfide. However, further characterizations of these complexes are desirable.

Reaction of [{Ru(MeCN)$_3$[P(OMe)$_3$]$_2$}$_2$(μ-S_2)](PF$_6$)$_3$ with a mixture of acetylene and O_2 gives a Ru^{IV} dimer, [{Ru^{IV}(PFO$_3$)[P(OMe)$_3$]$_2$}$_2$(μ-S)(μ-PF_2O_2)$_2$] (**142**) (Ru—S = 2.158 and 2.165 Å).[577] The newly formed bridging and terminal ligands $PF_2O_2^-$ and PFO_3^{2-} are probably produced from the reaction of PF_6^- with trace amounts of H_2O in the solvent.

5.6.6.8.5 Miscellaneous sulfur ligands

(i) Dithiocarbamato ($S_2CNR_2^-$) complexes

The osmium(IV) complexes containing $S_2CNR_2^-$ ligands, such as [Os(S$_2$CNEt$_2$)$_4$], [Os(S$_2$CNEt$_2$)$_3$]$^+$, [Os(S$_2$CNEt$_2$)$_3$X] (X = Cl, I), and [Os$_2$N(S$_2$CNEt$_2$)$_5$], have been documented in *CCC* (1987).

(ii) Dithiolene complexes

A ruthenium(IV) complex with six sulfur donor atoms, [Ru^{IV}(mnt)$_3$]$^{2-}$ (**143**), is formed by oxidation of [Ru^{III}(mnt)$_3$]$^{3-}$ (mnt = 1,2-dicyanoethylene dithiolate) with I_2, H_2O_2, or Ce^{IV}. The complex is paramagnetic with a magnetic moment of 2.84 μ_B.[579] The Ru—S distances range from 2.3349 Å to 2.3512 Å.

5.6.6.9 Halide Ligands

Deep pink polycrystalline solid RuF_4 has been prepared by treatment of AsF_5 with $[Ru(F)_6]^{2-}$ in anhydrous HF solution.[416] A combination of X-ray synchrotron and neutron powder diffraction data reveal that each Ru-atom has six F^- ligands with an octahedral framework, four in the same plane, each shared with another Ru-atom, to form a puckered-sheet array: (Ru—F (bridge) = 2.00 Å and 2.00 Å, Ru—F—Ru 133°).[416]

The synthesis and properties $K_2[Ru(F)_6]$ have been described in *CCC* (1987). A Ru—F distance of 1.916 Å has been determined by EXAFS.[355]

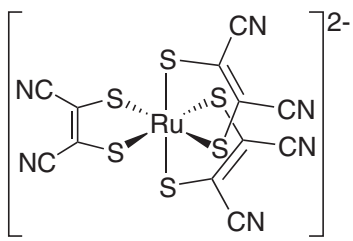
New synthetic methods for $[OsF_4]$ have been described.[580,581] The X-ray structure of *trans*-$[Os(F)_4(Cl)_2]^{2-}$ has been determined (Os—F = 1.924–1.944 Å).[582] The stepwise replacement of ligands in $[OsCl_6]^{2-}$ by oxidation with BrF_3 generates the mixed complexes $[Os(F)_n(Cl)_{6-n}]^{2-}$ (n = 1–5); the species with n = 2–4 have *cis* configurations.[583] They are characterized by vibrational spectroscopy. The X-ray structure of *cis*-$[(py)_2CH_2][Os^{IV}(F)_4(Cl)_2]$ has been determined (Os—F = 1.941–1.953 Å, Os—Cl = 2.329 Å).[584]

The low-temperature optical spectra of $[Os(Cl)_5(Br)]^{2-}$, *cis*- and *trans*-$[Os(Cl)_4(Br)_2]^{2-}$, $[Os(Br)_5(Cl)]^{2-}$, *cis*-$[Os(Br)_4(Cl)_2]^{2-}$, *trans*-$[Os(Cl)_4(I)_2]^{2-}$, and *fac*- and *mer*-$[Os(Cl)_3(I)_3]^{2-}$ have been measured.[585,586] The linkage isomers $[Os(Cl)_5(NCS)]^{2-}$ and $[Os(Cl)_5(SCN)]^{2-}$ have been separated by ion exchange chromatography from the reaction of $[Os(Cl)_5(I)]^{2-}$ with $(SCN)_2$.[587] The species $[Os(Cl)_5(H_2O)]^-$ has been prepared by the reduction of $[OsO_4]$ with Na_2SO_3 in the presence of NaCl, followed by extraction with *n*-tributyl phosphate (IR: Os—Cl = 316 cm^{-1}, Os—O = 467 cm^{-1}).[588] This species can be readily converted to $[Os(Cl)_5(EtOH)]^-$, $[Os(Cl)_5(py)]^-$, and $[(Cl)_5Os(pyz)Os(Cl)_5]^{2-}$. The X-ray structures of $(AsPh_4)[Os(Cl)_5(H_2O)]\cdot 2EtOH$ and $(AsPh_4)[Os(Cl)_5(EtOH)]$ have been determined (Os—Cl = 2.305–2.352 Å).

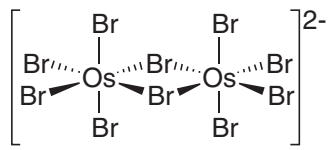
The mixed-valence $Os^{III}Os^{IV}$ species $[Os_2(Cl)_8]^-$ has been electrogenerated from $[Os_2(Cl)_8]^{2-}$ at low temperatures in nonaqueous solvents and characterized by the $\delta_2\delta^* \rightarrow \delta\delta^*_2$ band at 4600 cm^{-1}, with distinctive Os—Os vibrational progression of 220 cm^{-1}.[589]

$[OsBr_4]$ has been obtained by reaction of $OsCl_4$ with Br_2 in a closed system at 330 °C and 120 bar Br_2 pressure. The compound crystallizes in a $TcCl_4$-type structure.[590]

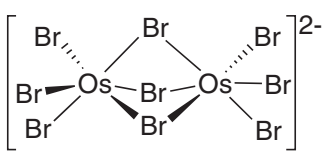
The species $[Os_2(Cl)_{10}]^{2-}$ and $[Os_2(Br)_{10}]^{2-}$ (**144**) are known.[591,592] $(NBu^n_4)_2$ $[Os_2(Br)_{10}]$ can be prepared by refluxing $(NBu^n_4)[Os(Br)_6]$ in trifluoroacetic acid (TFA) for several hours.[593] The X-ray structure shows that it contains edge-sharing bioctahedral $[(Br)_4Os(\mu\text{-}Br)_2Os(Br)_4]^{2-}$ anions; Os—Os = 3.788 Å, av. Os—Br(bridge) = 2.544 Å, av. Os—Br (terminal) = 2.454 Å, and av. Os—Br—Os = 96.3°. The magnetic moment at 296 K is 0.26 μ_B. Further reflux yields dark blue $(NBu^n_4)_2[Os_2(Br)_9]$ (**145**), which is characterized by IR, UV–vis, CV, and magnetic measurements. A triply bridged structure (**145**) has been suggested.



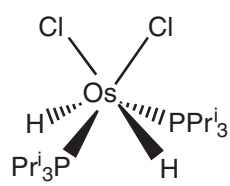
(**143**)



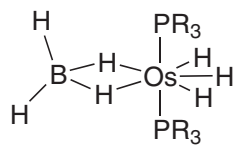
(**144**)



(**145**)



(**146**)



(**147**)

5.6.6.10 Hydride Ligands

There are a number of osmium(IV) phosphine hydrido species, some of which have been described in *CCC* (1987). The six-coordinate diamagnetic osmium(IV) complexes $[Os(H)_2(Cl)_2(PR_3)_2]$ ($PR_3 = PPr^i_3$, $PMeBu^t_2$) have been prepared from $OsCl_3{\cdot}xH_2O$ and PR_3 in boiling 2-propanol.[366] They are characterized by IR, NMR, and MS. The X-ray structure of $[Os(H)_2(Cl)_2(PPr^i_3)_2]$ (**146**) has been determined (Os—H = 1.663 Å). ^1H and ^{31}P NMR data reveal that $[Os(H)_2(X)_2(PR_3)_2]$ (X = halide, $PR_3 = PPr^i_3$) exist in solution as two rapidly interconverting isomers, one having C_2 symmetry (as in the solid-state structure) and one having no symmetry. $[Os(H)_2(Cl)_2(PPr^i_3)_2]$ reacts with CH_3CO_2K and CH_3CO_2Ag to give $[Os(H)_2(Cl)(\kappa^2\text{-}O_2CCH_3)(PPr^i_3)_2]$ and $[OsH_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(PPr^i_3)_2]$, respectively. The X-ray structure of the latter species has been determined.[594] Reaction of $[Os(H)_2(\kappa^2\text{-}O_2CCH_3)\{\kappa^1\text{-}OC(O)CH_3\}(PPr^i_3)_2]$ with $1/2HBF_4{\cdot}OEt_2$ leads to the dimer $[\{Os(H)_2(\kappa^2\text{-}OCOCH_3)(PPr^i_3)_2\}_2(\mu\text{-}OCOCH_3)](BF_4)$, while the reaction with $HBF_4{\cdot}OH_2$ gives the aqua derivative $[Os(H)_2(\kappa^2\text{-}OCOCH_3)(H_2O)(PPr^i_3)_2](BF_4)$.[595] The cationic dichlorohydridoosmium(IV) species containing the bulky chelating phosphine 1,2-bis(diisopropylphosphino)ethane(dippe), $[Os(H)(Cl)_2(dippe)_2](BPh_4)$, was prepared by treatment of $[Os(Cl)(dippe)_2](BPh_4)$ with HCl in CH_2Cl_2.[596] The trihydride $[Os(H)_3(dippe)_2](BPh_4)$ was prepared by the reaction of *cis*-$[Os(Cl)_2(dippe)_2]$ with $NaBH_4/NaBPh_4$ in EtOH.[596]

Reaction of $[Os(H)_6\{P(c\text{-}C_5H_9)_3\}_2]$ with $BH_3{\cdot}THF$ affords $[Os(BH_4)(H)_3\{P(c\text{-}C_5H_9)_3\}_2]$ (**147**). The X-ray structure has been determined (Os—H(bridged) = 1.90 Å, Os—H(terminal) = 1.57 Å). The BH_4^- ligand is bound to the osmium via two bridging H atoms, which, at 90 °C, it exchanges rapidly only with the hydride ligands on osmium.[364]

The pentahydride $[Os(H)_5(PMe_2Ph)_3]^+$ (as its BF_4^- salt) is characterized by neutron diffraction as a dodecahedral pentahydride. However, the H/H separations are as short as 1.49 Å.[597] Pentahydrides with mixed phosphines are also known. Treatment of $[Os(H)_4(PHPh_2)(PPr^i_3)_2]$ with HBF_4 gives $[Os(H)_5(PHPh_2)(PPr^i_3)_2](BF_4)$, which reacts with MeOH and H_2O to give $[Os(H)_5\{P(OMe)Ph_2\}(PPr^i_3)_2](BF_4)$ and $[Os(H)_5\{P(OH)Ph_2\}(PPr^i_3)_2](BF_4)$, respectively.[598] X-ray diffraction, IR, and NMR are consistent with the structure of $[Os(H)_5(PHPh_2)(PPr^i_3)_2](BF_4)$.

Monohydrido complexes of Os^{IV} amines are also known. Oxidation of $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{2+}$ and $[Os(en)_2(\eta^2\text{-}H_2)]^{2+}$ by $[FeCp_2]^+$ produces the hydrido species $[Os(H)(NH_3)_5(MeOH)]^{3+}$ and $[Os(H)(en)_2(MeOH)]^{3+}$, respectively.[599] Both complexes are paramagnetic and give broad ^1H NMR signals in D_2O. A series of mixed-valence species, $[Os^{IV}(H)(en)_2\{M^{II}(CN)_6\}(H_2O)]^-$ (M = Fe, Ru, Os), have been prepared by first mixing $[Os(en)_2(\eta^2\text{-}H_2)(H_2O)]^{2+}$ with $[M(CN)_6]^{4-}$ to produce $[Os(en)_2(\eta^2\text{-}H_2)\{M(CN)_6\}]^{2-}$, followed by oxidation with $[S_2O_8]^{2-}$ or $[FeCp_2]^+$; or by direct reaction of $[Os(H)(en)_2(H_2O)_2]^{3+}$ with $[M(CN)_6]^{4-}$.[600] These complexes have a blue color arising from $M(CN)_6^{4-} \rightarrow Os^{IV}$ charge transfer absorption.

5.6.7 REFERENCES

1. Che, C. M.; Yam, V. W. W. *Adv. Inorg. Chem.* **1992**, *39*, 233–325.
2. Lay, P. A.; Harman, W. D. *Adv. Inorg. Chem.* **1991**, *37*, 291–379.
3. Dehnicke, K.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955–978.
4. Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds* **1988**, Wiley: New York.
5. Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, *7*, 639–666.
6. Griffith, W. P. *Chem. Soc. Rev.* **1992**, *21*, 179–185.
7. Che, C. M.; Yam, V. W. W. *Advances in Transition Metal Coordination Chemistry*; JAI Press: London, 1996; Vol. 1, pp 209–237.
8. Meunier, B., Ed. *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Imperial College Press: London, 1999.
9. Meunier, B.; Bernadou, J. *Struct. Bond.* **2000**, *97*, 1.
10. Watanabe, Y. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 4, pp 97–117.
11. Groves, K. J. T.; Shalyaev, J. L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds., Academic Press: San Diego, CA, 2000; Vol. 4, pp 17–40.
12. Meunier, B., Ed. *Metal-oxo and Metal-peroxo Species in Catalytic Oxidations*; Springer-Verlag: Berlin, 2000.
13. Mansuy, D.; Battioni, P.; Mahy, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4487–4489.
14. Groves, J. T.; Takeuchi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073–2074.
15. Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 269–275.
16. Rankin, D. W. H.; Robertson, H. E.; Danopoulos, A. A.; Lyne, P. D.; Mingos, D. M. P.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1994**, 1563–1569.

17. Schofield, M. H.; Kee, T. P.; Anhaus, J. T.; Schrock, R. R.; Johnson, K. H.; Davis, W. M. *Inorg. Chem.* **1991**, *30*, 3595–3604.
18. Wolf, J. R.; Bazan, G. C.; Schrock, R. R. *Inorg. Chem.* **1993**, *32*, 4155–4156.
19. Leung, W. H.; Chim, J. L. C.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1996**, 3153–3154.
20. Leung, W. H.; Chim, J. L. C.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1997**, 3277–3282.
21. Leung, W. H.; Chim, J. L. C.; Lai, W.; Lam, L.; Wong, W. T.; Chan, W. H.; Yeung, C. H. *Inorg. Chim. Acta* **1999**, *290*, 28–35.
22. Zheng, H.; Leung, W. H.; Chim, J. L. C.; Lai, W.; Lam, C.-H.; Williams, I. D.; Wong, W. T. *Inorg. Chim. Acta* **2000**, *306*, 184–192.
23. Griffith, W. P. *Chem. Soc. Rev.* **1992**, *21*, 179–185.
24. Griffith, W. P. *Transition Met. Chem.* **1990**, *15*, 251–256.
25. Courtney, J. L. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., deJonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; pp 445–467.
26. Gao, Y.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 7538–7539.
27. Liliana, G. M.; Lasalvia, M.; Piccialli, V.; Sica, D. *Tetrahedron Lett.* **1996**, *37*, 527–530.
28. Shing, T. K. M.; Tai, V. W. F.; Tam, E. K. W. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2312–2313.
29. Kasai, M.; Ziffer, H. *J. Org. Chem.* **1983**, *48*, 2346–2349.
30. Meier, M. S.; Kiegiel, *Org. Lett.* **2001**, *11*, 1717–1719.
31. Creaser, C. S.; Fernandes, A. R.; Ayres, D. C. *Chem. Ind. (London)* **1988**, 499–500.
32. Ayres, D. C. *Platinum Met. Rev.* **1988**, *32*, 186.
33. Beattie, J. K. *Pure Appl. Chem.* **1990**, *62*, 1145–1146.
34. Mendez, A.; Bermejo, J.; Santamaria, R.; Blanco, C. G.; Menendez, R. *Energy & Fuels* **2000**, *14*, 936–942.
35. Boucher, R. J.; Standen, G.; Eglinton, G. *Fuel* **1991**, *70*, 695–702.
36. Lee, D. G.; Congson, L. N. *Can. J. Chem.* **1990**, *68*, 1774–1779.
37. Lai, S.; Lepage, C. J.; Lee, D. G. *Inorg. Chem.* **2002**, *41*, 1954–1957.
38. Lee, D. G.; Gai, H. *Can. J. Chem.* **1995**, *73*, 49–55.
39. Hansen, K. C.; Lin, Q.; Aminabhavi, T. M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3643–3646.
40. Boelrijk, A. E. M.; Reedijk, J. *J. Mol. Catal.* **1994**, *89*, 63–76.
41. Zimmerman, G. L.; Riviello, S. J.; Glauser, T. A.; Kay, J. G. *J. Phys. Chem.* **1990**, *94*, 2399–2404.
42. Swartzendruber, D. C.; Manganaro, A.; Madison, K. C.; Kremer, M.; Wertz, P. W.; Squier, C. A. *Cell Tissue Res.* **1995**, *279*, 271–276.
43. Swartzendruber, D. C.; Burnett, I. H.; Wertz, P. W.; Squier, C. A. *J. Invest. Dermatol.* **1995**, *104*, 417–420.
44. Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263–4265.
45. Jacobsen, E. N.; Marko, I.; Mungall, W. S.; Schröder, G.; Sharples, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968–1970.
46. Wai, J. S. M.; Marko, I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 1123–1125.
47. Jacobsen, E. N.; Marko, I.; France, M. B.; Svendsen, J. S.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 737–739.
48. Svendsen, J. B.; Marko, I.; Jacobsen, E. N.; Rao, C. P.; Bott, S.; Sharpless, K. B. *J. Org. Chem.* **1989**, *54*, 2263–2264.
49. Tomioka, K.; Nakajima, M.; Koga, K. *J. Am. Chem. Soc.* **1987**, *109*, 6213–6215.
50. Annunziata, R.; Cinquin, M.; Cozzi, F.; Raimondi, L.; Stefanelli, S. *Tetrahedron Lett.* **1987**, *28*, 3139–3142.
51. Corey, E. J.; Sarshar, S.; Azimioara, M. D.; Newbold, R. C.; Noe, M. C. *J. Am. Chem. Soc.* **1996**, *118*, 7851–7852.
52. Bailey, A. J.; Bhowon, M. G.; Griffith, W. P.; Shoair, A. G. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 3245–3250.
53. Beller, M.; Bolm, C. In *Transition Metals for Organic Synthesis*; Kolb, H. C.; Sharpless, K. B.; Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, pp 219–242.
54. Cornils, B.; Herrmann, W. A. In *Applied Homogeneous Catalysis with Organometallic Compounds*, 2nd ed.; Beller, M.; Sharpless K.B.; Eds.; Wiley-VCH: Weinheim, Germany, 2002; Vol.3, pp 1149–1164.
55. Beller, M.; Bolm, C. In *Transition Metals for Organic Synthesis*; Kolb, H. C., Sharpless, K. B., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, pp 219–242.
56. Lohnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 357–398.
57. Markó, I. E.; Svendsen, J. S. In *Comprehensive Asymmetric Catalysis II*; Jacobson, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999; pp 713–787.
58. Li, G.; Chang, H. T.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 451–454.
59. Rubin, A. E.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2637–2640.
60. Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 3455–3457.
61. Andersson, M. A.; Epple, R.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 472–475.
62. Beller, M.; Bolm, C. In *Transition Metals for Organic Synthesis*; Kolb, H. C.; Sharpless, K. B.; Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 2, pp 243–260.
63. Bolm, C.; Hildebrand, J. P.; Muniz, K. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, 2000; pp 399–428.
64. Travis, B. R.; Narayan, R. S.; Borhan, B. *J. Am. Chem. Soc.* **2002**, *124*, 3824–3825.
65. Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312–313.
66. Hawkins, J. M.; Lewis, T. A.; Loren, S. D.; Meyer, A.; Heath, J. R.; Shibato, Y.; Saykally, R. J. *J. Org. Chem.* **1990**, *55*, 6250–6252.
67. Hawkins, J. M.; Loren, S.; Meyer, A.; Nunlist, R. *J. Am. Chem. Soc.* **1991**, *113*, 7770–7771.
68. Hawkins, J. M. *Acc. Chem. Res.* **1992**, *25*, 150–156.
69. Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Bunz, U.; Nunlist, R.; Ball, G. E.; Ebbesen, T. W.; Tanigaki, K. *J. Am. Chem. Soc.* **1992**, *114*, 7954–7955.
70. Wallis, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 8207–8223.
71. Wallis, J. M.; Kochi, J. K. *J. Org. Chem.* **1988**, *53*, 1679–1686.
72. Kunkely, H.; Vogler, A. *Inorg. Chem. Commun.* **1998**, *1*, 7–9.
73. Cotton, R. G. H.; Rodrigues, N. R.; Campell, R. D. *Proc. Natl. Acad. Sci. USA* **1988**, *85*, 4397–4401.
74. Jelen, F.; Karlovsky, P; Makaturava, E.; Pecinka, E.; Palecek, E. *Gen. Physiol. Biophys.* **1991**, *10*, 461–473.

75. Kuderova-Krejcova, A.; Poverenny, A. M.; Palecek, E. *Nucleic Acids Res.* **1991**, *19*, 6811–6817.
76. Kabakov, A. E.; Podgorodnichenko, V. K.; Poverennyi, A. M. *Immunol. Lett.* **1991**, *30*, 23–26.
77. Palecek, E. *Methods Enzymol.* **1992**, *212*, 305–318.
78. Palecek, E. *Methods Enzymol.* **1992**, *212*, 139–155.
79. Palecek, E.; Robert-Nicoud, M.; Jovin, T. M. *J. Cell Sci.* **1993**, *104*, 653–661.
80. Kabakov, A. E.; Poverenny, A. M. *Anal. Biochem.* **1993**, *211*, 224–232.
81. Palecek, E.; Vlk, D.; Vojtiskova, M.; Boublikova, P. *J. Biomolec. Struct. Dynamics* **1995**, *13*, 537–546.
82. Nevskii, N. N.; Ivanov-Emin, B. N.; Nevskaya, N. A. *Dokl. Akad. Nauk SSSR* **1982**, *266*, 628–630.
83. Nevskii, N. N.; Ivanov-Emin, B. N.; Nevskaya, N. A.; Belov, N. V. *Dokl. Akad. Nauk SSSR* **1982**, *266*, 1138–1141.
84. Ivanov-Emin, B.; Nevskaya, N. A.; Zaitsev, B. E.; Nevskii, N. N.; Izmailovich, A. S. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1984**, *29*, 710.
85. Nevskii, N. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk SSSR* **1983**, *272*, 1123–1125.
86. Jewiss, H. C.; Levason, W.; Tajik, M.; Webster, M.; Walker, N. P. C. *J. Chem. Soc., Dalton. Trans.* **1985**, 199–203.
87. Nevskii, N. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk SSSR Ser. Cryst.* **1983**, *270*, 1392–1395.
88. Holloway, J. H.; Laycock, D. *Adv. Inorg. Chem. Radiochem.* **1984**, *28*, 73–99.
89. Hope, E. G.; Levason, W.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1988**, 61–65.
90. (a) Bougon, R.; Buu, B.; Seppelt, K. *Chem. Ber.* **1993**, *126*, 1331–1336. (b) Veldakamp, A.; Frenking, G. *Chem. Ber.* **1993**, *126*, 1325–1330.
91. Christe, K. O.; Bougon, R. *Chem. Commun.* **1992**, 1056.
92. Christe, K. O.; Dixon, D. A.; Mack, H. G.; Oberhammer, H.; Pagelot, A.; Sanders, J. C. P.; Schrobilgen, G. J. *J. Am. Chem. Soc.* **1993**, *115*, 11279–11284.
93. Casteel, W. J.; Dixon, D. A.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* **1996**, *35*, 4310–4322.
94. Gerken, M.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2002**, *41*, 259–277.
95. Gerken, M.; Dixon, D. A.; Schrobilgen, G. J. *Inorg. Chem.* **2000**, *39*, 4244–4255.
96. Weber, R.; Dehnicke, K.; Muller, U.; Fenske, D. *Z. Anorg. Allg. Chem.* **1984**, *516*, 214.
97. Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 1855–1860.
98. Seddon, E. A.; Seddon, K. R. *Chemistry of Ruthenium* **1984**, Elsevier: Amsterdam.
99. Lee, D. G.; Congson, L. N.; Spitzer, U. A.; Olson, M. E. *Can. J. Chem.* **l984**, *62*, 1835–1839.
100. Green, G.; Griffith, W. P.; Hollinshead, D. M.; Ley, S. V.; Schröder, M. *J. Chem. Soc., Perkin Trans.* **1984**, *1*, 681–686.
101. Griffith, W. P.; Ley, S. V. *Aldrichim. Acta* **1990**, *23*, 13–19.
102. Griffith, W. P.; Ley, S. V.; Whitcombe, G. P.; White, A. D. *Chem. Commun.* **1987**, 1625–1627.
103. Bailey, A. J.; Griffith, W. P.; Mostafa, S. I.; Sherwood, P. A. *Inorg. Chem.* **1993**, *32*, 268–271.
104. Dengel, A. C.; Gibson, J. F.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1991**, 2799–2800.
105. Dengel, A. C.; Griffith, W. P. *Inorg. Chem.* **1991**, *30*, 869–871.
106. Bloch, R.; Brillet, C. *Synlett* **1991**, 829–830.
107. Moreno, M. J. S.; Sáe Melo, M. L.; Campo Neves, A. S. *Tetrahedron Lett.* **1991**, *32*, 3201–3204.
108. Tokunaga, Yuji; Ihara, Masataka; Fukumoto, Keiichiro. *J. Chem. Soc., Perkin Trans. 1* **1997**, *3*, 207–209.
109. Lee, D. G.; Congson, L. N. *Can. J. Chem.* **1990**, *68*, 1774–1779.
110. Berthold, H.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1998**, *1*, 1–2.
111. Pagliaro, M.; Ciriminna, R. *Tetrahedron Lett.* **2001**, *42*, 4511–4514.
112. Latham, K.; Thompsett, D.; Williams, C. D.; Round, C. I. *J. Mater. Chem.* **2000**, *10*, 1235–1240.
113. Bleloch, A.; Johnson, B. F. G.; Ley, S. V.; Price, A. J.; Shephard, D. S.; Thomas, A. W. *Chem. Commun.* **1999**, *18*, 1907–1908.
114. Berthold, H.; Lenz, R.; Ley, S. V. *Synthesis.* **1998**, *7*, 977–979.
115. Brown, D. S.; Kerr, W. J.; Lindsay, D. M.; Pike, K. G.; Ratcliffe, P. D.; AstraZeneca, M. *Synlett* **2001**, *8*, 1257–1259.
116. Marko, I. E.; Giles, P. R.; Tsukazaki, M.; Chelle-Regnaut, I.; Urch, C. J.; Brown, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 12661–12662.
117. Coleman, K. S.; Lorber, C. Y.; Osborn, J. A. *Eur. J. Inorg. Chem.* **1998**, *11*, 1673–1675.
118. Hasan, M.; Musawir, M.; Davey, P. N.; Kozhevnikov, I. V. *J. Mol. Catal. A: Chem.* **2002**, *180*, 77–84.
119. Lenz, R.; Ley, S. V. *J. Chem. Soc., Perkin Trans. 1* **1997**, *22*, 3291–3292.
120. Farmer, V.; Welton, T. *Green Chem.* **2002**, *4*, 97–102.
121. Ley, S. V.; Ramarao, C.; Smith, M. D. *Chem. Commun.* **2001**, *21*, 2278–2279.
122. Lau, T. C.; Kong, S. L. L. *J. Chem. Soc., Dalton Trans.* **1995**, *13*, 2221–2223.
123. Bilger, E.; Pebler, J.; Weber, R.; Dehnicke, K. *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **1984**, *39(B)*, 259–261.
124. Levason, W. L.; Tojah, M.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1735–1736.
125. Dengel, A. C.; Griffith, W. P. *Transition Met. Chem.* **1989**, *14*, 230–232.
126. Holloway, J. H.; Hope, E. G.; Raynor, J. B.; Townson, P. T. *J. Chem. Soc., Dalton Trans.* **1992**, 1131–1134.
127. Hope, E. G.; Levason, W.; Ogden, J. S. *J. Chem. Soc., Dalton Trans.* **1988**, 997–999.
128. Shapley, P. A.; Kim, H. S.; Wilson, S. R. *Organometallics* **1988**, *7*, 928–933.
129. Marshman, R. W.; Shusta, J. M.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1991**, *10*, 1671–1676.
130. Weber, R.; Dehnicke, K.; Schweda, E.; Strähle, J. *Z. Anorg. Allg. Chem.* **1982**, *490*, 159–170.
131. Abel, E. W.; Stone, F. G. A.; Wilkinson, G. Eds., *Comprehensive Organometallic Chemistry II*; Pergamon: Oxford, UK, **1995**.
132. LaPointe, A. M.; Schrock, R. R.; Davis, W. M. *Organometallics* **1995**, *14*, 2699–2703.
133. Huang, J. S.; Che, C. M.; Poon, C. K. *Chem. Commun.* **1992**, 161–163.
134. Li, Z. Y.; Huang, J. S.; Chan, M. C. W.; Cheung, K. K.; Che, C. M. *Inorg. Chem.* **1997**, *36*, 3064–3071.
135. Huang, J. S.; Sun, X. R.; Leung, S. K.; Cheung, K. K.; Che, C. M. *Chem. Eur. J.* **2000**, *6*, 334–344.
136. Smieja, J. A.; Omberg, K. M.; Breneman, G. L. *Inorg. Chem.* **1994**, *33*, 614–616.
137. Mansuy, D.; Mahy, J.-P.; Bedi, G.; Battioni, P. *Chem. Commun.* **1984**, 1161–1163.
138. Mahym, J.-P.; Bedi, G.; Battioni, P.; Mansuy, D. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1517–1524.
139. Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Org. Chem.* **1991**, *56*, 6744–6746.

140. Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726–728.
141. Evans, D. A.; Faul, M. M.; Bilodeau, M. T.; Anderson, B. A.; Barnes, D. M. *J. Am. Chem. Soc.* **1993**, *115*, 5328–5329.
142. Evans, D. A.; Faul, M. M.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2742–2753.
143. Li, Z.; Conser, K. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1993**, *115*, 5326–5327.
144. Li, Z.; Quan, R. W.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117*, 5889–5890.
145. Au, S. M.; Fung, W. H.; Huang, J. S.; Cheung, K. K.; Che, C. M. *Inorg. Chem.* **1998**, *37*, 6564–6567.
146. Au, S. M.; Huang, J. S.; Yu, W. Y.; Fung, W. H.; Che, C. M. *J. Am. Chem. Soc.* **1999**, *121*, 9120–9132.
147. Au, S. M.; Fung, W. H.; Cheng, M. C.; Che, C. M.; Peng, S. M. *Chem. Commun.* **1997**, 1655–1656.
148. Liang, J. L.; Huang, J. S.; Yu, X. Q.; Zhu, N. Y.; Che, CM. *Chem. Eur. J.* **2002**, *8*, 1563–1572.
149. Li, Z. Y.; Yu, W. Y.; Che, C. M.; Poon, C. K.; Wang, R. J.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1992**, 1657–1661.
150. Chiu, W. H; Cheung, K. K.; Che, C. M. *Chem. Commun.* **1995**, 441–442.
151. Anhaus, J. T.; Kee, T. P.; Schofield, M. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 1642–1643.
152. Griffith, W. P. *J. Chem. Soc.* **1965**, 3694.
153. Che, C. M.; Lam, H. W.; Mak, T. C. W. *Chem. Commun.* **1989**, 1529–1531.
154. Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Eds. *Comprehensive Organometallic Chemistry II*; Pergamon: Oxford, UK, 1995; Vol. 7, pp 372–376.
155. Che, C. M.; Lau, T. C.; Lam, H. W.; Poon, C. K. *Chem. Commun.* **1989**, 114–116.
156. Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4598–4605.
157. Ware, D. C.; Taube, H. *Inorg. Chem.* **1991**, *30*, 4605–4610.
158. Newton, C.; Edwards, K. D.; Ziller, J. W.; Doherty, N. M. *Inorg. Chem.* **1999**, *38*, 4032–4037.
159. Leung, W. H.; Wilkinson, G.; Bates, B. H.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 2791–2794.
160. Chiu, W. H.; Guo, C. X.; Cheung, K. K.; Che, C. M. *Inorg. Chem.* **1996**, *35*, 540–541.
161. Che, C. M.; Wong, K. Y.; Lam, H. W.; Chin, K. F.; Zhou, Z. Y.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1993**, 857–861.
162. Chin, K. F.; Cheung, K.-K.; Yip, H.-K.; Mak, T. C. W.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1995**, 657–663.
163. Pipes, D. W.; Bakir, M.; Vitols, S. E.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5507–5514.
164. Williams, D. S.; Coia, G. M.; Meyer, T. J. *Inorg. Chem.* **1995**, *34*, 586–592.
165. El-Samanody, El.-S.; Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **2001**, *40*, 3677–3686.
166. Crevier, T. J.; Mayer, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 5595–5596.
167. Crevier, T. J.; Bennett, B. K.; Soper, J. D.; Bowman, J. A.; Dehestani, A.; Hrovat, D. A.; Lovell, S.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 1059–1071.
168. (a) Bennett, B. K.; Lovell, S.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 4336–4337. (b) Bennett, B. K.; Crevier, T. J.; DuMez, D. D.; Matano, Y.; McNeil, W. S.; Mayer, J. M. *J. Organomet. Chem.* **1999**, *591*, 96–103.
169. Dehestani, A.; Kaminsky, W.; Mayer, J. M. *Inorg. Chem.* **2003**, *42*, 605–611.
170. Williams, D. S.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* **1995**, *117*, 823–824.
171. Shapley, R. A.; Own, Z. Y. *J. Organomet. Chem.* **1987**, *335*, 269–276.
172. Brown, S. N. *J. Am. Chem. Soc.* **1999**, *121*, 9752–9753.
173. Brown, S. N. *Inorg. Chem.* **2000**, *39*, 378–381.
174. Crevier, T. J.; Mayer, J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 1891–1893.
175. Demadis, K. D.; El-Samanody, El-S.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 838–839.
176. Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1998**, *37*, 3610–3619.
177. Huynh, M. H. V.; El-Samanody, El.-S.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **1999**, *38*, 3760–3761.
178. Huynh, M. H. V.; El-Samanody, El.-S.; Demadis, K. D.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 3075–3085.
179. Che, C. M.; Lam, H. W.; Tong, W. F.; Lai, T. F.; Lau, T. C. *Chem. Commun.* **1989**, 1883–1884.
180. Seymore, Sean, B.; Brown, S. N. *Inorg. Chem.* **2002**, *41*, 462–469.
181. Crevier, T. J.; Lovell, S.; Mayer, J. M.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 6607–6608.
182. McCarthy, M. R.; Crevier, T. J.; Bennett, B.; Dehestani, A.; Mayer, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 12391–12392.
183. Crevier, T. J.; Lovell, S.; Mayer, J. M. *Chem. Commun.* **1998**, 2371–2372.
184. Hopkins, M. D.; Miskowski, V. M.; Gray, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 6908–6911.
185. Collin, R.; Griffith, W. P.; Pawson, D. *J. Mol. Struct.* **1973**, 19 531–544.
186. Lam, H. W.; Chin, K. F.; Che, C. M.; Wang, R. J.; Mak, T. C. W. *Inorg. Chim. Acta* **1993**, *204*, 133–137.
187. Shapley, P. A.; Marshman, R. M.; Shusta, J. M.; Gebeyehu, Z.; Wilson, S. R. *Inorg. Chem.* **1994**, *33*, 498–502.
188. Leung, W. H.; Chan, E. Y. Y.; Lai, T. C. Y.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **2000**, 51–56.
189. Liang, H. C.; Shapley, P. A. *Organometallics* **1996**, *15*, 1331–1333.
190. (a) Shapley, P. A.; Reinerth, W. A. *Organometallics* **1996**, *15*, 5090–5096. (b) Shapley, P. A.; Liang, H. C.; Shusta, J. M.; Schwab, J. J.; Zhang, N.; Wilson, S. R. *Organometallics* **1994**, *13*, 3351–3359.
191. Shapley, P. A.; Liang, H. C.; Dopke, N. C. *Organometallics* **2001**, *20*, 4700–4704.
192. Leung, W. H.; Wu, M. C.; Che, C. M.; Wong, W. T.; Chin, K. F. *J. Chem. Soc., Dalton Trans.* **1994**, *17*, 2519–2521.
193. Sellmann, D.; Binkler, G. *Z. Naturforsch.* **1987**, *42*, 341–347.
194. Reinerth, W. A.; Shapley, P. A. *Inorg. Chim. Acta* **1998**, *267*, 335–340.
195. Leung, W. H.; Chim, J. L. C.; Wong, W. T. *Inorg. Chem.* **1998**, *37*, 6382–6384.
196. Sellmann, D.; Wemple, M. W.; Donaubauer, W.; Heinemann, F. W. *Inorg. Chem.* **1997**, *36*, 1397–1402.
197. Zhang, N.; Wilson, S. R.; Shapley, P. A. *Organometallics* **1988**, *7*, 1126–1131.
198. Leung, W. H.; Chim, J. L. C.; Williams, I. D.; Wong, W. T. *Inorg. Chem.* **1999**, *38*, 3000–3005.
199. Zhang, Q. F.; Lau, K. K.; Chim, J. L. C.; Wong, T. K. T.; Wong, W. T.; Williams, I. D.; Leung, W. H. *J. Chem. Soc., Dalton Trans.* **2000**, 3027–3033.
200. Lyne, P. D.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1995**, 1635–1643.
201. Griffith, W. P.; Rossetti, R. *J. Chem. Soc., Dalton Trans.* **1972**, 1449–1453.
202. Schwab, J. J.; Wilkinson, E. C.; Wilson, S. R.; Shapley, P. A. *J. Am. Chem. Soc.* **1991**, *113*, 6124–6129.
203. Chan, P. M.; Yu, W. Y.; Che, C. M.; Cheung, K. K. *J. Chem. Soc., Dalton Trans.* **1998**, 3183–3190.
204. Barner, C. J.; Collins, T. J.; Mapes, B. E.; Santarsiero, B. O. *Inorg. Chem.* **1986**, *25*, 4322–4323.

205. Wong, T. W.; Lau, T. C.; Wong, W. T. *Inorg. Chem.* **1999**, *38*, 6181–6186.
206. Chiu, S. M.; Wong, T. W.; Man, W. L.; Wong, W. T.; Peng, S. M.; Lau, T. C. *J. Am. Chem. Soc.* **2001**, *123*, 12720–12721.
207. (a) Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1980**, *102*, 198–207; Leung, S. K. Y.; Huang, J. S.; Liang, J. L.; Che, C. M.; Zhou, Z. Y. (b) Leung, S. K. Y. ; Huang, J. S.; Liang, J. L.; Che, C. M.; Zhou, Z. Y. *Angew. Chem. Int. Ed.* **2003**, *42*, 340–343.
208. Li, Z.; Che, C. M.; Poon, C. K. *J. Nat. Sci.* **1996**, *1*, 89–94.
209. Bonomo, L.; Solari, E.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2529–2531.
210. Huynh, M. H. V.; Lee, D. G.; White, P. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 10446–10447.
211. Huynh, M. H. V.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2001**, *40*, 5231–5235.
212. Huynh, M. H. V.; Lee, D. G.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2001**, *40*, 3842–3849.
213. Bernhardt, E.; Willner, H.; Jonas, V.; Thiel, W.; Aubke, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 168–171.
214. Yam, V. W. W.; Che, C. M. *Coord. Chem. Rev.* **1990**, *97*, 93–104.
215. Yam, V. W. W.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1990**, 3741–3746.
216. Yam, V. W. W.; Che, C. M. *New J. Chem.* **1989**, *13*, 707–712.
217. Yam, V. W. W. Ph.D. Thesis, University of Hong Kong, 1988.
218. Chin, K. F.; Cheng, Y. K.; Cheung, K. K.; Guo, C. X.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1995**, 2967–2973.
219. Cheng, J. Y. K.; Cheung, K. K.; Che, C. M.; Lau, T. C. *Chem. Commun.* **1997**, 1443–1444.
220. (a) Cheng, J. Y. K.; Cheung, K. K.; Che, C. M. *Chem. Commun.* **1997**, 501–502. (b) Leung, W. H.; Cheng, J. Y. K.; Hun, T. S. M.; Che, C. M.; Wong, W. T.; Cheung, K. K. *Organometallics* **1996**, *15*, 1497–1501.
221. Lau, M. K.; Chim, J. L. C.; Wong, W. T.; Williams, I. D.; Leung, W. H. *Can. J. Chem.* **2001**, *79*, 607–612.
222. Dengel, A. C.; El-Hendawy, A. M.; Griffith, W. P.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1990**, 737–742.
223. El-Hendawy, A. M.; Griffith, W. P.; Taha, F. I.; Moussa, M. N. *J. Chem. Soc., Dalton Trans.* **1989**, 901–906.
224. Lau, T. C.; Kochi, J. K. *Chem. Commun.* **1987**, 798–799.
225. Perrier, S.; Lau, T. C.; Kochi, J. K. *Inorg. Chem.* **1990**, *9*, 4190–4195.
226. Che, C. M.; Leung, W. H.; Li, C. K.; Poon, C. K. *J. Chem. Soc., Dalton Trans.* **1991**, 379–384.
227. Che, C. M.; Wong, K. Y.; Leung, W. H.; Poon, C. K. *Inorg. Chem.* **1986**, *25*, 345–348.
228. Che, C. M.; Leung, W. H.; Poon, C. K. *Chem. Commun.* **1987**, 173–175.
229. Che, C. M.; Leung, W. H. *Chem. Commun.* **1987**, 1376–1377.
230. Bailey, C. L.; Drago, R. S. *Chem. Commun.* **1987**, 179–180.
231. Goldstein, A. S.; Drago, R. S. *Chem. Commun.* **1991**, 21–22.
232. Che, C. M.; Lee, W. O. *Chem. Commun.* **1988**, 881–882.
233. Lau, T. C.; Che, C. M.; Lee, W. O.; Poon, C. K. *Chem. Commun.* **1988**, 1406–1407.
234. Wong, K. Y.; Lee, W. O.; Che, C. M.; Anson, F. C. *J. Electroanal. Chem. Interf. Chem.* **1991**, *319*, 207–216.
235. Dovletoglou, A.; Adeyemi, S. A.; Lynn, M. H.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 8989–8990.
236. Dovetoglou, A.; Meyer, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 215–223.
237. Dobson, J. C.; Takeuchi, K. J.; Pipes, D. W.; Geselowitz, D. A.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2357–2365.
238. Murmann, R. K.; Barnes, C. L. *Acta Crystallogr.* **1999**, *C55*, 2004–2007.
239. Murmann, R. K.; Barnes, C. L. *Inorg. Chem.* **2001**, *40*, 6514–6517.
240. Che, C. M.; Lai, T. F.; Wong, K. Y. *Inorg. Chem.* **1987**, *26*, 2289–2299.
241. Che, C. M.; Wong, K. Y.; Mak, T. C. W. *Chem. Commun.* **1985**, 546–548.
242. Che, C. M.; Wong, K. Y.; Mak, T. C. W. *Chem. Commun.* **1985**, 988–990.
243. Che, C. M.; Tang, W. T.; Lee, W. O.; Wong, W. T.; Lai, T. F. *J. Chem. Soc., Dalton Trans.* **1989**, 2011–2016.
244. Che, C. M.; Tang, W. T.; Li, C. K. *J. Chem. Soc., Dalton Trans.* **1990**, 3735–3739.
245. Mak, T. C. W.; Che, C. M.; Wong, K. Y. *Chem. Commun.* **1985**, 986–988.
246. Yam, V. W. W.; Che, C. M.; Tang, W. T. *Chem. Commun.* **1988**, 100–102.
247. Che, C. M.; Tang, W. T.; Wong, W. T.; Lai, T. F. *J. Am. Chem. Soc.* **1989**, *111*, 9048–9056.
248. Li, C. K.; Che, C. M.; Tong, W. F.; Lai, T. F.; Wong, K. Y. *J. Chem. Soc., Dalton Trans.* **1992**, 813–815.
249. Cheng, W. C.; Yu, W. Y.; Cheung, K. K.; Che, C. M. *Chem. Commun.* **1994**, 1063–1064.
250. Che, C. M.; Lam, M. H. W.; Wang, R. J.; Mak, T. C. W. *Chem. Commun.* **1990**, 820–821.
251. Che, C. M.; Cheng, W. K.; Yam, V. W. W. *J. Chem. Soc., Dalton Trans.* **1990**, 3095–3100.
252. Che, C. M.; Cheng, W. K. *J. Am. Chem. Soc.* **1986**, *108*, 4644–4645.
253. Kelly, C.; Szalda, D. J.; Creutz, C.; Schwarz, H. A.; Sutin, N. *Inorg. Chim. Acta* **1996**, *243*, 39–45.
254. Dobson, J. C.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 3283–3291.
255. Che, C. M.; Wong, K. Y.; Anson, F. C. *J. Electroanal. Chem. Interf. Chem.* **1987**, *226*, 211–226.
256. Che, C. M.; Lau, K.; Lau, T. C.; Poon, C. K. *J. Am. Chem. Soc.* **1990**, *112*, 5176–5181.
257. Chan, C. W.; Lai, T. F.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 895–899.
258. Collin, J. P.; Sauvage, J. P. *Inorg. Chem.* **1986**, *25*, 135–141.
259. Guadalupe, A. R.; Chen, X.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 5502–5512.
260. Li, C. K.; Che, C. M.; Tong, W. F.; Tang, W. T.; Wong, K. Y.; Lai, T. F. *J. Chem. Soc., Dalton Trans.* **1992**, 2109–2116.
261. Wong, K. Y. Ph.D. Thesis, University of Hong Kong, 1987.
262. Pipes, D. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7653–7654.
263. Che, C. M.; Tang, W. T.; Lee, W. O.; Wong, K. Y.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1551–1556.
264. Che, C. M.; Tang, W. T.; Wong, K. Y.; Li, C. K. *J. Chem. Soc., Dalton Trans.* **1991**, 3277–3280.
265. Zhao, W.; Chandler, W. D.; Lee, Donald G. *Can. J. Chem.* **1998**, *76*, 919–928.
266. Che, C. M.; Li, C. K.; Tang, W. T.; Yu, W. Y. *J. Chem. Soc., Dalton Trans.* **1992**, 3153–3158.
267. Che, C. M.; Cheng, K. W.; Chan, M. C. W.; Lau, T. C.; Mak, C. K. *J. Org. Chem.* **2000**, *65*, 7996–8000.
268. Che, C. M.; Lee, W. O.; Lau, T. C.; Poon, C. K. *Chem. Commun.* **1988**, 1406–1407.
269. Che, C. M.; Ho, C.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* **1991**, 1901–1907.

270. Che, C. M.; Yu, W. Y.; Chan, P. M.; Cheng, W. C.; Peng, S. M.; Lau, K. C.; Li, W. K. *J. Am. Chem. Soc.* **2000**, *122*, 11380–11392.
271. Lau, T. C.; Lau, K. W. C.; Lo, C. K. *Inorg. Chim. Acta* **1993**, *209*, 89–92.
272. Lau, T. C.; Lau, K W. C.; Lau, K. *J. Chem. Soc., Dalton Trans.* **1994**, 3091–3093.
273. Lau, T. C.; Chow, K. H.; Lau, K. W. C.; Tsang, W. Y. K. *J. Chem. Soc., Dalton Trans.* **1997**, 313–315.
274. Yiu, D. T. Y.; Chow, K. H.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* **2000**, 17–20.
275. Yau, S. K. Y.; Che, C. M.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* **2002**, 2697–2701.
276. Schindler, S.; Castner, E. W., Jr.; Creutz, C.; Sutin, N. *Inorg. Chem.* **1993**, *32*, 4200–4208.
277. Armstrong, J. E.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1545–1549.
278. Harbron, S. K.; Levason, W. *J. Chem. Soc., Dalton Trans.* **1987**, 633–638.
279. Nowogrocki, G.; Abraham, F.; Trehoux, J.; Thomas, D. *Acta Crystallogr.* **l976**, *B32*, 2413–2419.
280. Elout, M. O.; Haije, W. G.; Maaskant, W. J. A. *Inorg. Chem.* **1988**, *27*, 610–614.
281. Fischer, D.; Hoppe, R. *Z. Anorg. Chem.* **1991**, *601*, 41–46.
282. Griffith, W. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, UK, 1987; Vol. 4, p 519.
283. El-Hendawy, A. M.; Griffith, W. P.; Piggott, B.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1983–1988.
284. Bailey, A. J.; Griffith, W. P.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1994**, 1833–1834.
285. Bailey, A. J.; Griffith, W. P.; Savage, P. D. *J. Chem. Soc., Dalton Trans.* **1995**, 3537–3542.
286. Griffith, W. P.; Jolliffe, J. J.; Ley, S. V.; William, D. J. *Chem. Commun.* **1990**, 1219–1221.
287. Griffith, W. P.; Jolliffe, J. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3483–3488.
288. Lau, T. C.; Mak, C. K. *Chem. Commun.* **1993**, 766–767.
289. Lau, T. C.; Mak, C. K. *Chem. Commun.* **1995**, 943–944.
290. Behling, T.; Capparelli, M. V.; Skapski, A. C.; Wilkinson, G. *Polyhedron* **1982**, *1*, 840–841.
291. Arnold, J.; Wilkinson, G.; Hussain, B.; Hursthouse, M. B. *Polyhedron* **1989**, *8*, 597–602.
292. Hinckley, C. C.; Kibala, P. A. *Polyhedron* **1986**, *5*, 1119–1124.
293. Edwards, C. F.; Griffith, W. P. *Polyhedron* **1991**, *10*, 61–65.
294. Robinson, P. D.; Hinckley, C. C.; Kibala, P. A. *Acta Crystallogr.* **1988**, *C44*, 1365–1368.
295. Hinckley, C. C.; Kibala, P. A.; Robinson, P. D. *Acta Crystallogr.* **1987**, *C43*, 842–844.
296. Sivik, M. R.; Gallucci, J. C.; Paquette, L. A. *J. Org. Chem.* **1990**, *55*, 391–393.
297. Griffith, W. P.; McManus, N. T.; Skapski, A. C. *Inorg. Chim. Acta* **1985**, *103*, L5–L6.
298. Griffith, W. P.; McManus, N. T.; White, A. D. *J. Chem. Soc., Dalton Trans.* **1986**, 1035–1039.
299. Griffith, W. P.; Pumphrey, C. A.; Skapski, A. C. *Polyhedron* **1987**, *6*, 891–896.
300. Edwards, C. F.; Griffith, W. P.; Williams, D. J. *Chem. Commun.* **1990**, 1523–1524.
301. Edwards, C. F.; Griffith, W. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1992**, 145–151.
302. Harbron, S. K.; Levason, W. *J. Chem. Soc., Dalton Trans.* **1985**, 205–207.
303. Zhang, Q. F.; Lau, K. K.; Chim, J. L. C.; Wong, T. K. T.; Wong, W. T.; Williams, I. D.; Leung, W. H. *J. Chem. Soc., Dalton Trans.* **2000**, 3027–3033.
304. Perrier, S.; Kochi, J. K. *Inorg. Chem.* **1988**, *27*, 4165–4173.
305. Dengel, A. C.; Griffith, W. P.; EI-Hendawy, A. M.; Jolliffe, J. M. *Polyhedron* **1990**, *9*, 1751–1756.
306. Hagen, K.; Hobson, R. J.; Holwill, C. J.; Rice, D. A. *Inorg. Chem.* **1986**, *25*, 3659–3661.
307. Harbron, S. K.; Jewiss, H. C.; Levason, W.; Webster, M. *Acta Crystallogr.* **1987**, *C43*, 37–39.
308. Che, C. M.; Cheng, W. K.; Mak, T. C. W. *Chem. Commun.* **1986**, 200–202.
309. Lin, J. H.; Che, C. M.; Lai, T. F.; Poon, C. K.; Cui, Y. X. *Chem. Commun.* **1991**, 468–470.
310. Che, C. M.; Cheng, W. K.; Mak, T. C. W. *Inorg. Chem.* **1986**, *25*, 703–706.
311. Che, C. M.; Cheng, W. K.; Mak, T. C. W. *Inorg. Chem.* **1988**, *27*, 250–253.
312. Muller, J. G.; Takeuchi, K. J. *Inorg. Chem.* **1987**, *26*, 3634–3636.
313. Lynch, W. E.; Lintvedt, R. L.; Shui, X. Q. *Inorg. Chem.* **1991**, *30*, 1014–1019.
314. Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, T. T.; Gipson, S. L.; Keech, J. T.; Kram, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460–4472.
315. Borovik, A. S.; Bois, J. D.; Raymond, K. N. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1359–1362.
316. Bigham, W. S.; Shapley, P. A. *Inorg. Chem.* **1991**, *30*, 4093–4095.
317. Che, C. M.; Yu, W. Y. *Pure Appl. Chem.* **1999**, *71*, 281–288.
318. Leung, W. H.; Che, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 8812–8818.
319. Ho, C.; Leung, W. H.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1991**, 2933–2939.
320. Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 3844–3846.
321. Liu, C. J.; Yu, W. Y.; Peng, S. M.; Mak, T. C. W.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1998**, 1805–1812.
322. Liu, C. J.; Yu, W. Y.; Che, C. M.; Yeung, C. H. *J. Org. Chem.* **1999**, *64*, 7365–7374.
323. Maux, P. L.; Bahri, H.; Simonneaux, G. *Chem. Commun.* **1994**, 1287–1288.
324. Gross, Z.; Ini, S.; Moshe, K.; Shmuel, C. *Tetrahedron Lett.* **1996**, *37*, 7325–7328.
325. Zhang, R. Yu, W. Y.; Lai, T. S.; Che, C. M. *Chem. Commun.* **1999**, 409–410.
326. Lai, T. S.; Kwong, H. L.; Zhang, R.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1998**, 3559–3564.
327. Lai, T. S.; Zhang, R.; Cheung, K. K.; Kwong, H. L.; Che, C. M. *Chem. Commun.* **1998**, 1583–1584.
328. Zhang, J. L.; Zhou, H. B.; Huang, J. S.; Che, C. M. *Chem. Eur. J.* **2002**, *8*, 1554–1562.
329. Tokita, Y.; Yamaguchi, K.; Watanabe, Y.; Morishima, I. *Inorg. Chem.* **1993**, *32*, 329–333.
330. Zhang, R.; Yu, W. Y.; Lai, T. S.; Che, C. M. *Chem. Commun.* **1999**, 1791–1792.
331. Groves, J. T.; Ahn, K. H. *Inorg. Chem.* **1987**, *26*, 3831–3833.
332. Groves, J. T.; Quinn, R. *J. Am. Chem. Soc.* **1985**, *107*, 5790–5792.
333. Marchon, J. C.; Ramasseul, R. *Chem. Commun.* **1988**, 298–299.
334. Groves, J. T.; Quinn, R. *Inorg. Chem.* **1984**, *23*, 3844–3846.
335. Scharbert, B.; Zeisberger, E.; Paulus, E. *J. Organomet. Chem.* **1995**, *493*, 143–147.
336. Groves, J. T.; Roman, J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5594–5595.
337. Groves, John, T.; Bonchio, M.; Carofiglio, T.; Shalyaev, K. *J. Am. Chem. Soc.* **1996**, *118*, 8961–8962.
338. Gross, Z.; Ini, S. *Inorg. Chem.* **1999**, *38*, 1446–1449.
339. Gross, Z.; Ini, S. *Org. Lett.* **1999**, *1*, 2077–2080.

340. Chen, C. Y.; Cheng, S. H.; Su, Y. O. *J. Electroanal. Chem.* **2000**, *487*, 51–56.
341. Zhang, J. L.; Che, C. M. *Org. Lett.* **2002**, *4*, 1991–1914.
342. Liu, C. J.; Li, S. G.; Peng, W. Q.; Che, C. M. *Chem Commun.* **1997**, 65–66.
343. Liu, C. J.; Yu, W. Y.; Li, S. G.; Che, C. M. *J. Org. Chem.* **1998**, *63*, 7364–7369.
344. Zhang, J. L.; Liu, Y. L.; Che, C. M. *Chem. Commun.* **2002**, 2906–2907.
345. Yu, X. Q.; Huang, J. S.; Yu, W. Y.; Che, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 5337–5342.
346. Maux, P. L.; Bahri, H.; Simonneaux, G.; Toupet, L. *Inorg. Chem.* **1995**, *34*, 4691–4697.
347. Cheng, S. Y. S.; James, B. R. *J. Mol. Catal. A: Chem.* **1997**, *117*, 91–102.
348. Rajapakse, N.; James, B. R.; Dolphin, D. *Catal. Lett.* **1989**, *2*, 219–225.
349. Che, C. M.; Chung, W. C.; Lai, T. F. *Inorg. Chem.* **1988**, *27*, 2801–2804.
350. Buchler, J. W.; Smith, P. D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 341.
351. Gross, Z.; Mahammed, A. *J. Mol. Catal. A: Chem.* **1999**, *142*, 367–372.
352. Che, C. M.; Lai, T. F.; Chung, W. C.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1987**, *26*, 3907–3911.
353. Antipas, A.; Buchler, J. W.; Gouterman, M.; Smith, P. D. *J. Am. Chem. Soc.* **1978**, *100*, 3015–3024.
354. Brisdon, A. K.; Jones, P. J.; Levason, W.; Ogden, J. S.; Holloway, J. H.; Hope, E. G.; Stanger, G. *J. Chem. Soc., Dalton Trans.* **1990**, 715–718.
355. Brisdon, A. K.; Holloway, J. H.; Hope, E. G.; Levason, W.; Ogden, J. S.; Saad, A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 447–449.
356. Burns, R. C.; O'Donnell, T. A. *Inorg. Synth.* **1986**, *24*, 79–81.
357. Brisdon, A. K.; Holloway, J. H.; Hope, E. G.; Levason, W.; Ogden, J. S.; Saad, A. K. *J. Chem. Soc., Dalton Trans.* **1992**, 139–143.
358. Marx, R.; Seppelt, K.; Ibberson, R. M. *J. Chem. Phys.* **1996**, *104*, 7658–7664.
359. Richardson, A. D.; Hedberg, K.; Lucier, G. M. *Inorg. Chem.* **2000**, *39*, 2787–2793.
360. Rotger, M.; Boudon, V.; Selig, H. *Spectrochim. Acta A* **1997**, *53A*, 991–994.
361. Holloway, J. H.; Rook, J. *J. Chem. Soc., Dalton Trans.* **1987**, 2285–2287.
362. Douglas, P. G.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 334–338.
363. Mann, B. E.; Masters, C.; Shaw, B. L. *Chem. Commun.* **1970**, 1401.
364. Frost, P. W.; Howard, J. A. K.; Spencer, J. L. *Chem. Commun.* **1984**, 1362–1363.
365. Connelly, N. G.; Howard, J. A. K.; Spencer, J. L.; Woodley, P. K. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2003–2009.
366. Aracama, M.; Esteruelas, M. A.; Lahoz, F. J.; Lopez, J. A.; Meyer, U.; Oro, L. A.; Werner, H. *Inorg. Chem.* **1991**, *30*, 288–293.
367. Howard, J. A. K.; Johnson, O.; Koetzle, T. F.; Spencer, J. L. *Inorg. Chem.* **1987**, *26*, 2930–2933.
368. Danopoulos, A. A.; Wong, A. C. C.; Wilkinson, G.; Hursthouse, M. B.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1990**, 315–331.
369. Redshaw, C.; Clegg, W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1992**, 2059–2062.
370. Wong, K. Y.; Che, C. M.; Li, C. K.; Chiu, W. H.; Zhou, Z. Y.; Mak, T. C. W. *Chem. Commun.* **1992**, 754–756.
371. Leung, W.-H.; Hun, T. S. M.; Hou, H.-W.; Wong, K.-Y. *J. Chem. Soc., Dalton Trans* **1997**, 237–243.
372. Tooze, R. P.; Wilkinson, G.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 2711–2720.
373. Huynh, M. H. V.; White, P. S.; John, K. D.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4049–4051.
374. Buhr, J. D.; Taube, H. *Inorg. Chem.* **1979**, *18*, 2208–2212.
375. Lam, H. W.; Che, C. M.; Wong, K. Y. *J. Chem. Soc., Dalton Trans.* **1992**, 1411–1416.
376. Demadis, K. D.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1997**, *36*, 5678–5679.
377. Coia, G. M.; Devenney, M.; White, P. S.; Meyer, T. J.; Wink, D. A. *Inorg. Chem.* **1997**, *36*, 2341–2351.
378. Huynh, M. H. V.; Meyer, T. J.; White, P. S. *J. Am. Chem. Soc.* **1999**, *121*, 4530–4531.
379. Demadis, K. D.; Bakir, M.; Klesczewski, B. G.; Williams, D. S.; White, P. S.; Meyer, T. J. *Inorg. Chim. Acta* **1998**, *270*, 511–526.
380. Huynh, M. H. V.; Jameson, D. L.; Meyer, T. J. *Inorg. Chem.* **2001**, *40*, 5062–5063.
381. Grasset, F.; Dussarrat, C.; Darriet, J. *J. Mater. Chem.* **1997**, *7*, 1911–1915.
382. Stitzer, K. E.; Smith, M. D.; Gemmill, W. R.; zur Loye, H. C. *J. Am. Chem. Soc.* **2002**, *124*, 13877–13885.
383. Wong, K. Y.; Che, C. M.; Anson, F. C. *Inorg. Chem.* **1987**, *26*, 737–741.
384. Lee, W. O.; Che, C. M.; Wong, K. Y. *J. Mol. Catal.* **1994**, *89*, 57–62.
385. Li, C. K.; Tang, W. T.; Che, C. M.; Wong, K. Y.; Wang, R.-J.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1991**, 1909–1914.
386. Lai, Y. K.; Wong, K. Y. *Electrochim. Acta* **1993**, *38*, 1015–1021.
387. Che, C. M; Ho, C.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* **1991**, 1259–1263.
388. Wong, K. Y.; Yam, V. W. W.; Lee, W. W. S. *Electrochim. Acta* **1992**, *37*, 2645.
389. (a) Fackler, N. L. P.; Zhang, S.; O'Halloran, T. V. *J. Am. Chem. Soc.* **1996**, *118*, 481–482. (b) Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 5070–5076.
390. Khan, M. M. T.; Sreelatha, C. H.; Mirza, S. A.; Ramachendraiah, G.; Abdi, S. H. R. *Inorg. Chim. Acta* **1988**, *154*, 103–108.
391. Khan, M. M. T.; Shukla, R. S.; Rao, A. P. *Inorg. Chem.* **1989**, *28*, 452–458.
392. Che, C. M.; Wong, K. Y.; Lee, W. O.; Anson, F. C. *J. Electroanal. Chem.* **1991**, *309*, 303–311.
393. Che, C. M.; Wong, K. Y. *Chem. Commun.* **1986**, 229–230.
394. Li, C. K. Ph.D. Thesis, University of Hong Kong, 1991.
395. Dengel, A. C.; Griffith, W. P.; O'Mahoney, C. A.; Williams, D. J. *Chem. Commun.* **1989**, 1720–1721.
396. Dengel, A. C.; Griffith, W. P. *Inorg. Chem.* **1991**, *30*, 869–871.
397. Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932–2938.
398. Gilbert, J. A.; Eggleston, D. S.; Murphy, W. R., Jr.; Geselowitz, D. A.; Gersten, S. W.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 3855–3864.
399. Chronister, C. W.; Binstead, R. A.; Ni, J.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 3814–3815.
400. Binstead, R. A.; Chronister, C. W.; Ni, J.; Hartshorn, C. M.; Meyer, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 8464–8473.
401. Hurst, J. K.; Zhou, J.; Lei, Y. *Inorg. Chem.* **1992**, *31*, 1010–1017.
402. Lei, Y.; Hurst, J. K. *Inorg. Chem.* **1994**, *33*, 4460–4467.

403. Lei, Y.; Hurst, J. K. *Inorg. Chim. Acta* **1994**, *226*, 179–185.
404. Yamada, H.; Hurst, J. K. *J. Am. Chem. Soc.* **2000**, *122*, 5303–5311.
405. Rotzinger, F. P.; Munavalli, S.; Comte, P.; Hurst, J. K.; Gratzel, M.; Pern, F.; Frank, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 6619–6626.
406. Lebeau, E. L.; Adeyemi S. A.; Meyer, T. J. *Inorg. Chem.* **1998**, *37*, 6476–6484.
407. Lai, Y. K.; Wong, K. Y. *J. Electroanal. Chem.* **1995**, *380*, 193–200.
408. Raven, S. J.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 4478–4483.
409. Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 2027–2034.
410. Roecker, L.; Meyer, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 746–754.
411. Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4106–4115.
412. Bailey, A. J.; Griffith, W. P.; Marsden, S. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1998**, 3673–3677.
413. Power, J. M.; Evertz, K.; Henling, L.; Marsh, R.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **1990**, *29*, 5058–5065.
414. Che, C. M.; Leung W. H.; Chung, W. C. *Inorg. Chem.* **1990**, *29*, 1841–1846.
415. Cheng, W. K.; Wong, K. Y.; Tong, W. F.; Lai, T. F.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1992**, 91–96.
416. Casteel, W. J., Jr.; Wilkinson, A. P.; Borrmann, H.; Serfass, R. E.; Bartlett, N. *Inorg. Chem.* **1992**, *31*, 3124–3131.
417. Hope, E. G. *Polyhedron* **1993**, *12*, 2977–2980.
418. Chiu, W. H.; Peng, S. M.; Che, C. M. *Inorg. Chem.* **1996**, *35*, 3369–3374.
419. Lay, P. A.; Sargeson, A. M. *Inorg. Chim. Acta* **1992**, 198–200.
420. Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161–6164.
421. Chin, K. F.; Wong, K. Y.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1993**, 197–198.
422. Bernhard, P.; Sargeson, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 597–606.
423. Soper, J. D.; Bennett, B. K.; Lovell, S.; Mayer, J. M. *Inorg. Chem.* **2001**, *40*, 1888–1893.
424. Soper, J. D.; Kaminsky, W.; Mayer, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 5594–5595.
425. Maestri, A. G.; Cherry, K. S.; Toboni, J. J.; Brown, S. N. *J. Am. Chem. Soc.* **2001**, *123*, 7459–7460.
426. Che, C. M.; Cheng, W. K.; Leung, W. H.; Mak, T. C. W. *Chem. Commun.* **1987**, 418–419.
427. Huang, J. S.; Che, C. M.; Li, Z. Y.; Poon, C. K. *Inorg. Chem.* **1992**, *31*, 1313–1315.
428. Danopoulos, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1992**, *11*, 2961–2964.
429. Stershic, M. T.; Keefer, L. K.; Sullivan, B. P.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 6884–6885.
430. Griffith, W. P.; McManus, N. T.; Skapski, A. C. *Chem. Commun.* **1984**, 434–435.
431. Haukka, M.; Venäläinen, T.; Ahlgrén, M.; Pakkanen, T. A. *Inorg. Chem.* **1995**, *34*, 2931–2936.
432. Sellmann, D.; Gottschalk-Gaudig, T.; Heinemann, F. W. *Inorg. Chim. Acta* **1998**, *269*, 63–72.
433. Rossi, G.; Gardini, M.; Pennesi, G.; Ercolani, C.; Goedken, V. L. *J. Chem. Soc., Dalton Trans.* **1989**, 193–195.
434. Jüstel, T.; Bendix, J.; Metzler-Nolte, N.; Weyhermueller, T.; Nuber, B.; Wieghardt, K. *Inorg. Chem.* **1998**, *37*, 35–43.
435. Kim, S.-H.; Moyer, B. A.; Azan, S.; Brown, G. M.; Olins, A. L.; Allison, D. P. *Inorg. Chem.* **1989**, *28*, 4648–4650.
436. Lay, P. A.; Taube, H. *Inorg. Chem.* **1989**, *28*, 3561–3564.
437. Hall, J. P.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2410–2414.
438. Adcock, P. A.; Keene, F. R.; Smythe, R. S.; Snow, M. R. *Inorg. Chem.* **1984**, *23*, 2336–2343.
439. Huang, J. S.; Leung, S. K. Y.; Cheung, K. K.; Che, C.-M. *Chem. Eur. J.* **2000**, *6*, 2971–2981.
440. Huynh, M. H. V.; Baker, R. T.; Jameson, D. L.; Labouriau, A.; Meyer, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 4580–4582.
441. Stifel, E. I.; Coucouvanis, D.; Newton, W. E., Eds. *Molybdenum Enzymes, Cofactors and Model Systems*; ACS Symposium Series 535; American Chemical Society: Washington, DC, 1993; Chapters 10–23.
442. Leigh, G. I. *Acc. Chem. Res.* **1992**, *25*, 177.
443. Coucouvanis, D.; Demadis, K. D.; Malinak, S. M.; Mosier, P. E.; Tyson, M. A.; Laughlin, L. J. In *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; Stiefel, E. I.; Matsumoto, K., Eds.; ACS Symposium Series 653; American Chemical Society: Washington, DC, 1996; Chapter 7, p 117.
444. Sun, X. R.; Huang, J. S.; Cheung, K. K.; Che, C. M. *Inorg. Chem.* **2000**, *39*, 820–826.
445. Huynh, M. H. V.; White, P. S.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 4101–4104.
446. Huynh, M. H. V.; White, P. S.; Meyer, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 9170–9171.
447. Huynh, M. H. V.; Morris, D. E.; White, P. S.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2330–2333.
448. Peter, J. W.; Lanzilotta, W. N.; Lemon, B. J.; Seefeldt, L. C. *Science* **1998**, *282*, 1853–1858.
449. Jin, X.; Kazuhito, I.; Carl, B. E. *Proc. Natl. Acad. Sci. USA* **1998**, *95*, 14851–14856.
450. Gyula, K.; Peter, C.; Corinna, P.; Roland, L. *J. Eur. Mol. Biol. Organ.* **1999**, *18*, 3981–3989.
451. Elisabeth, D.; Maria, V. V.; Tomoko, O.; Fevzi, D. *J. Bioenerg. Biomembr.* **1999**, *31*, 275–288.
452. William, L. N.; Jason, C.; Dennis, D. R.; Lance, S. C. *Biochemistry* **1998**, *37*, 11376–11384.
453. Zhaolei, Z.; Lishar, H.; Vladimir, S. M.; Young-In, C.; Kyu, K. K.; Li-Wei, H.; Antony, C. R.; Edward, B. A.; Sung-Hou, K. *Nature* **1998**, *392*, 677–684.
454. Birgit, S.; Roswitha, W.; Martin, E. *Biochemistry* **1997**, *36*, 4471–4479.
455. Bakir, M.; White, P. S.; Dovletoglou, A.; Meyer, T. J. *Inorg. Chem.* **1991**, *30*, 2835–2836.
456. Huynh, M. H. V.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 1395–1398.
457. El-Samanody, El-S.; Demadis, K. D.; Gallagher, L. A.; Meyer, T. J.; White, P. S. *Inorg. Chem.* **1999**, *38*, 3329–3336.
458. Leung, W. H.; Hun, T. S. M.; Wong, K. Y.; Wong, W. T. *J. Chem. Soc., Dalton Trans.* **1994**, 2713–2718.
459. Smieja, J. A.; Omberg, K. M.; Busuego, L. N.; Breneman, G. L. *Polyhedron* **1994**, *13*, 339–343.
460. Gross, Z.; Mahammed, A. *Inorg. Chem.* **1996**, *35*, 7260–7263.
461. Gross, Z.; Barzilay, C. M. *Chem. Commun.* **1995**, 1287–1288.
462. Ke, M.; Sishta, C.; James, B. R.; Dolphin, D.; Sparapany, J. W.; Ibers, J. A. *Inorg. Chem.* **1991**, *30*, 4766–4771.
463. Zhang, R.; Yu, W. Y.; Wong, K. Y.; Che, C. M. *J. Org. Chem.* **2001**, *66*, 8145–8153.
464. Champness, N. R.; Frampton, C. S.; Levason, W.; Preece, S. R. *Inorg. Chim. Acta* **1995**, *233*, 43–50.
465. Champness, N. R.; Levason, W.; Mould, R. A. S.; Pletcher, D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2777–2783.

466. Champness, N. R.; Levason, W.; Pletcher, D.; Spicer, M. D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2201–2207.
467. Cipriano, R. A.; Levason, W.; Mould, R. A. S.; Pletcher, D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1990**, 2609–2616.
468. Cipriano, R. A.; Levason, W.; Mould, R. A. S.; Pletcher, D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1990**, 339–347.
469. Hinckley, C. C.; Matusz, M.; Robinson, P. D. *Acta Crystallogr.* **1988**, *C44*, 371–372.
470. Hinckley, C. C.; Ali, I. A.; Robinson, P. D. *Acta Crystallogr.* **1990**, *C46*, 697–699.
471. Meyer, T. J. *J. Electrochem. Soc.* **1984**, *131*, 221C–228C.
472. Meyer, T. J. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1988; p 33.
473. Moyer, B. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3601–3603.
474. Moyer, B. A.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 436–444.
475. Kubow, S. A.; Marmion, M. E.; Takeuchi, K. J. *Inorg. Chem.* **1988**, *27*, 2761–2767.
476. Ho, C.; Che, C. M.; Lau, T. C. *J. Chem. Soc., Dalton Trans.* **1990**, 967–970.
477. Groves, J. T.; Ahn, K.-H. *Inorg. Chem.* **1987**, *26*, 3831–3833.
478. Dobson, J. C.; Helms, J. H.; Doppelt, P.; Sullivan, B. P.; Hatfield, W. E.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 2200–2204.
479. Roecker, L.; Kutner, W.; Gilbert, J. A.; Simmons, M.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* **1985**, *24*, 3784–3791.
480. Hua, X.; Lappin, A. G. *Inorg. Chem.* **1995**, *34*, 992–994.
481. Takeuchi, K. J.; Thompson, M. S.; Pipes, D. W.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 1845–1851.
482. Farrer, B. T.; Thorp, H. H. *Inorg. Chem.* **2000**, *39*, 44–49.
483. Llobet, A.; Doppelt, P.; Meyer, T. J. *Inorg. Chem.* **1988**, *27*, 514–520.
484. Cheng, W. C.; Yu, W. Y.; Zhu, J.; Cheung, K. K.; Peng, S. M.; Poon, C. K.; Che, C. M. *Inorg. Chim. Acta* **1996**, *242*, 105–113.
485. Szczepura, L. F.; Maricich, S. M.; See, R. F.; Churchill, M. R.; Takeuchi, K. J. *Inorg. Chem.* **1995**, *34*, 4198–4205.
486. Nagao, H.; Shibayama, M.; Kitanaka, Y.; Howell, F. S.; Shimizu, K.; Mukaida, M.; Kakihana, H. *Inorg. Chim. Acta* **1991**, *185*, 75–81.
487. Nagao, H.; Nishimura, H.; Kitanaka, Y.; Howell, F. S.; Mukaida, M.; Kakihana, H. *Inorg. Chem.* **1990**, *29*, 1693–1700.
488. Aoyagi, K.; Yukawa, Y.; Shimizu, K.; Mukaida, M.; Takeuchi, T.; Kakihana, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1493–1499.
489. Marmion, M. E.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1988**, *110*, 1472–1480.
490. Marmion, M. E.; Leising, R. A.; Takeuchi, K. J. *J. Coord. Chem.* **1988**, *19*, 1–16.
491. Che, C. M.; Yu, W. Y. unpublished data.
492. Che, C. M.; Yam, V. W. W; Mak, T. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2284–2291.
493. Philips, F. L.; Skapski, A. C. *Acta Crystallogr.* **1975**, *B31*, 1814–1818.
494. Barthazy, P.; Wörle, M.; Rüegger, H.; Mezzetti, A. *Inorg. Chem.* **2000**, *39*, 4903–4912.
495. Neumann, R.; Dahan, M. *J. Am. Chem. Soc.* **1998**, 120, 11969–11976.
496. Flower, K. R.; Lightfoot, A. P.; Wan, H.; Whiting, A. *Chem. Commun.* **2001**, 1812–1813.
497. Wong, K. Y.; Che, C. M.; Yip, W.-H.; Wang, R.-J.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1992**, 1417–1421.
498. Cheng, W. C.; Yu, W. Y.; Cheung, K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1994**, 57–62.
499. Leung, W. H. Ph.D. Thesis, University of Hong Kong, 1989.
500. McHatton, R. C.; Anson, F. C. *Inorg. Chem.* **1984**, *23*, 3935–3942.
501. Cabaniss, G. E.; Diamantis, A. A.; Murphy, W. R., Jr.; Linton, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 1845–1853.
502. Thompson, M. S.; DeGiovani, W. F. G.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.* **1984**, *49*, 4972–4977.
503. Abruna, H. D.; Denisevich, P.; Umana, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1–5.
504. Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13, p 60.
505. Moyer, B. A.; Sipe, B. K.; Meyer, T. J. *Inorg. Chem.* **1981**, *20*, 1475–1480.
506. Roecker, L.; Dobson, J. C.; Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 779–781.
507. Acquaye, J. H.; Muller, J. G.; Takeuchi, K. J. *Inorg. Chem.* **1993**, *32*, 160–165.
508. (a) Huynh, M. H. V.; Witham, L. M.; Lasker, J. M.; Wetzler, M.; Mort, B.; Jameson, D. L.; White, P. S.; Takeuchi, K. J. *J.Am. Chem. Soc.* **2003**, *125*, 308–309. (b) Roecker, L.; Meyer, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 4066–4073.
509. Marmion, M. E.; Takeuchi, K. J. *J. Chem. Soc., Dalton Trans.* **1988**, 2385–2391.
510. Marmion, M. E.; Takeuchi, K. J. *Chem. Commun.* **1987**, 1396–1397.
511. Muller, J. G.; Acquaye, J. H.; Takeuchi, K. J. *Inorg. Chem.* **1992**, *31*, 4552–4557.
512. Cundari, T. R.; Drago, R. S. *Inorg. Chem.* **1990**, *29*, 3904–3907.
513. Dobson, J. C.; Seok, W. K.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 1513–1514.
514. Fung, W. H.; Yu, W. Y.; Che, C. M. *J. Org. Chem.* **1998**, *63*, 7715–7726.
515. Fung, W. H.; Cheng, W. C.; Yu, W. Y.; Che, C. M.; Mak, T. C. W. *Chem. Commun.* **1995**, 2007–2008.
516. Murahashi, S.-I.; Komiya N.; Oda, Y.; Kuwabara, T.; Naota, T. *J. Org. Chem.* **2000**, *65*, 9186–9193.
517. Seok, W. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7358–7367.
518. Binstead, R. A.; McGuire, M. E.; Dovletoglou, A.; Seok, W. K.; Roecker, L. E.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 173–186.
519. Gallagher, L. A.; Meyer, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 5308–5312.
520. Grover, N.; Thorp, H. H. *J. Am. Chem. Soc.* **1991**, *113*, 7030–7031.
521. Grover, N.; Gupta, N.; Singh, P.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 2014–2020.
522. Gupta, N.; Grover, N.; Neyhart, G. A.; Singh, P.; Thorp, H. H. *Inorg. Chem.* **1993**, *32*, 310–316.
523. Neyhart, G. A.; Grover, N.; Smith, S. R.; Kalsbeck, W. A.; Fairley, T. A.; Cory, M.; Thorp, H. H. *J. Am. Chem. Soc.* **1993**, *115*, 4423–4428.
524. Welch, T. W.; Neyhart, G. A.; Goll, J. G.; Ciftan, S. A.; Thorp, H. H. *J. Am. Chem. Soc.* **1993**, *115*, 9311–9312.

525. Cheng, C. C.; Goll, J. G.; Neyhart, G. A.; Welch, T. W.; Singh, P.; Thorp, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 2970–2980.
526. Neyhart, G. A.; Cheng, C.-C.; Thorp, H. H. *J. Am. Chem. Soc.* **1995**, *117*, 1463–1471.
527. Farrer, B. T.; Pickett, J. S.; Thorp, H. H. *J. Am. Chem. Soc.* **2000**, *122*, 549–553.
528. Gilbert, J. A.; Gersten, S. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 6872–6873.
529. Gilbert, J.; Roecker, L.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1126–1132.
530. Farrer, B. T.; Thorp, H. H. *Inorg. Chem.* **1999**, *38*, 2497–2502.
531. Lebeau, E. L.; Binstead, R. A.; Meyer, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10535–10544.
532. Li, C. K.; Che, C. M.; Tong, W. F.; Lai, T. F. *J. Chem. Soc., Dalton Trans.* **1992**, 813–818.
533. Schoonover, J. R.; Ni, J.; Roecker, L.; White, P. Meyer T. J. *Inorg. Chem.* **1996**, *35*, 5885–5892.
534. Nazeeruddin, M. K.; Rotzinger, F. P.; Comte, P.; Grätzel, M. *J. Chem. Soc., Chem Commun.* **1988**, 872–873.
535. Neubold, P.; Della Vedova, B. S. P. C.; Wieghardt, K.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *28*, 763.
536. Geselowitz, D. A.; Kutner, W.; Meyer, T. J. *Inorg. Chem.* **1986**, *25*, 2015–2023.
537. Ying, W. L.; Emerson, J.; Clarke, M. J.; Sanadi, D. R. *Biochemistry* **1991**, *30*, 4949–4952.
538. Emerson, J.; Clarke, M. J.; Ting, W. L.; Sanadi, D. R. *J. Am. Chem. Soc.* **1993**, *115*, 11799–11805.
539. Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M.; Ogoshi, H. *J. Am. Chem. Soc.* **1981**, *103*, 2199–2203.
540. Collman, J. P.; Barnes, C. E.; Collins, T. J.; Brothers, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 7030–7032.
541. Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151–5163.
542. Berry, K. J.; Moubaraki, B.; Murray, K. S.; Nichols, P. J.; Schulz, L. D.; West, B. O. *Inorg. Chem.* **1995**, *34*, 4123–4133.
543. Vernik, I.; Stynes, D. V. *Inorg. Chem.* **1998**, *37*, 10–17.
544. Gilbert, J. A.; Geselowitz, D.; Meyer, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 1493–1501.
545. Christie, J. A.; Collins, T. J.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *Chem. Commun.* **1984**, 198–199.
546. Armstrong, J. E.; Robinson, W. R.; Walton, R. A. *Inorg. Chem.* **1983**, *22*, 1301–1306.
547. Imbe, Y.; Umakoshi, K.; Matsunami, C.; Sasaki, Y. *Inorg. Chem.* **1995**, *34*, 813–820.
548. Chakravarty, A. R.; Cotton, F. A.; Schwotzer, W. *Inorg. Chem.* **1984**, *23*, 99–103.
549. Sugimoto, H.; Higashi, T.; Mori, M.; Nagano, M.; Yoshida, Z. I.; Ogoshi, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 822–828.
550. Masuda, H.; Taga, T.; Osaki, K.; Sugimoto, H.; Mori, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2345–2351.
551. Patel, A.; Richens, D. T. *Inorg. Chem.* **1991**, *30*, 3789–3792.
552. Osman, J. R.; Crayston, J. A.; Richens, D. T. *Inorg. Chem.* **1998**, *37*, 1665–1668.
553. Bear, R. B.; Anson, F. C. *J. Electroanal. Chem. Interf. Chem.* **1985**, *187*, 265–282.
554. Zhou, J.; Xi, W.; Hurst, J. K. *Inorg. Chem.* **1990**, *29*, 160–167.
555. (a) Kläui, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 627–637. (b) Che, C. M.; Huang, J. S.; Li, Z. Y.; Poon, C. K.; Tong, W. F.; Lai, T. F.; Cheng, M. C.; Wang, C. C.; Wang, Y. *Inorg. Chem.* **1992**, *31*, 5220–5225.
556. Paes, L. W.; Faria, R. B.; Machuca-Herrera, J. O.; Machado, S. d. P. *Inorg. Chim. Acta* **2001**, *321*, 22–26.
557. Mezzetti, A.; Zangrando, E.; Zotto, A. D.; Rigo, P. *Chem. Commun.* **1994**, 1597–1598.
558. Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **1993**, *115*, 9794–9795.
559. Kirchner, K.; Mauthner, K.; Mereiter, K.; Schmid, R. *Chem. Commun.* **1993**, 892–894.
560. Shen, J. Y.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1997**, *16*, 2754–2756.
561. Pramanik, K.; Ghosh, P.; Chakravorty, A. *Inorg. Chem.* **1998**, *37*, 5678–5680.
562. Wheeler, S. H.; Pignolet, L. H. *Inorg. Chem.* **1980**, *19*, 972–979.
563. Collman, J. P.; Bohle, D. S.; Powell, A. K. *Inorg. Chem.* **1993**, *32*, 4004–4011.
564. Dilworth, J. R.; Hu, J. *Adv. Inorg. Chem.* **1994**, *40*, 411–459.
565. Soong, S. L.; Hain, J. H.; Millar, M., Jr.; Koch, S. A. *Organometallics* **1988**, *7*, 556–557.
566. Koch, S. A.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 3362–3363.
567. Satsangee, S. P.; Hain, J. H., Jr.; Cooper, P. T.; Koch, S. A. *Inorg. Chem.* **1992**, *31*, 5160–5161.
568. Zhang, Q. F.; Lai, C. Y.; Wong, W. Y.; Leung, W. H. *Organometallics* **2002**, *21*, 4017–4020.
569. Torrens, H. *Coord. Chem. Rev.* **2000**, *196*, 331–352.
570. Hills, A.; Hughes, D. L.; Richards, R. L.; Arroyo, M.; Cruz-Garritz, D.; Torrens, H. *J. Chem. Soc., Dalton Trans.* **1991**, 1281–1284.
571. Arroyo, M.; Chamizo, J. A.; Hughes, D. L.; Richards, R. L.; Roman, P.; Sosa, P.; Torrens, H. *J. Chem. Soc., Dalton Trans.* **1994**, 1819–1824.
572. Abasq, M.-L.; Pickett, C. J.; Richards, R. L.; Arroyo, M.; Chamizo, J. A.; Calderon, A.; Sosa, P.; Torrens, H. *Polyhedron* **1996**, *15*, 3623–3629.
573. Kawano, M.; Uemura, H.; Watanabe, T.; Matsumoto, K. *J. Am. Chem. Soc.* **1993**, *115*, 2068–2070.
574. Sellmann, D.; Ruf, R.; Knoch, F.; Moll, M. *Inorg. Chem.* **1995**, *34*, 4745–4755.
575. Mochizuki, K.; Kesting, F.; Weyhermüller, T.; Wieghardt, K.; Butzlaff, C.; Trautwein, A. X. *Chem. Commun.* **1994**, 909–911.
576. Khan, M. M. T.; Siddiqui, M. R. H. *Inorg. Chem.* **1991**, *30*, 1157–1159.
577. Matsumoto, K.; Sano, Y.; Kawano, M.; Uemura, H.; Matsunami, J.; Sato, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1239–1244.
578. Li, C. K.; Tang, W. T.; Che, C. M.; Wong, K. Y.; Wang, R. J.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1991**, 1909–1914.
579. Maiti, R.; Shang, M.; Lappin, A. G. *Chem. Commun.* **1999**, 2349–2350.
580. Casteel, W. J.; Lohmann, D. H.; Bartlett, N. *J. Fluorine Chem.* **2001**, *112*, 165–171.
581. Zemva, B.; Lutar, K.; Jesih, A.; Casteel, W. J. Jr.; Bartlett, N. *Chem. Commun.* **1989**, 346–347.
582. Bruhn, C.; Preetz, W. *Acta Crystallogr.* **1995**, *C51*, 865–867.
583. Preetz, W.; Ruf, D.; Tensfeldt, D. *Z. Naturforsch. B* **1984**, *39B*, 1100–1109.
584. Bruhn, C.; Preetz, W. *Acta Crystallogr.* **1994**, *C50*, 1555–1557.
585. Schmidtke, H.-H.; Lehnert, N. *Inorg. Chem.* **1998**, *37*, 6373–6381.

586. Strand, D.; Linder, R.; Schmidtke, H. H. *Inorg. Chim. Acta* **1991**, *182*, 205–211.
587. Preetz, W.; Semrau, M. *Z. Anorg. Allg. Chem.* **1995**, *621*, 725–731.
588. Maiboroda, A.; Rheinwald, G.; Lang, H. *Inorg. Chem.* **2000**, *39*, 5725–5730.
589. Gheller, S. F.; Heath, G. A.; Raptis, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 7924–7926.
590. Thiele, G.; Wochner, H.; Wagner, H. *Z. Anorg. Allg. Chem.* **1985**, *530*, 178–186.
591. Krebs, B.; Henkel, G.; Dartmann, M. Z.; Preetz, W.; Bruns, M. *Naturforsch. B* **1984**, *39B*, 843–849.
592. Burns, M.; Preetz, W. *Z. Anorg. Allg. Chem.* **1986**, *537*, 88–96.
593. Cotton, F. A.; Duraj, S. A.; Hinckley, C. C.; Matusz, A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 3080–3083.
594. Crochet, P.; Esteruelas, M. A.; López, A. M.; Martínez, M.; Oliván, M.; Oñate, E.; Ruiz, N. *Organometallics* **1998**, *17*, 4500–4509.
595. Buil, M. L.; Eisenstein, O.; Esteruelas, M. A.; García-Yebra, C.; Gutiérrez-Puebla, E.; Oliván, M.; Oñate, E.; Ruiz, N.; Tajada, M. A. *Organometallics* **1999**, *18*, 4949–4959.
596. Tenorio, M. J.; Puerta, M. C.; Salcedo, I.; Valerga P. *J. Organomet. Chem.* **1998**, *564*, 21–28.
597. Johnson, T. J.; Albinati, A.; Koetzle, T. F.; Ricci, J.; Eisenstein, O.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 4966–4976.
598. Esteruelas, M. A.; Lledós, A.; Martín, M.; Maseras, F.; Osés, R.; Ruiz, N.; Tomàs, J. *Organometallics* **2001**, *20*, 5297–5309.
599. Li, Z. W.; Yeh, A.; Taube, H. *J. Am. Chem. Soc.* **1993**, *115*, 10384–10385.
600. Li, Z. W.; Yeh, A.; Taube, H. *Inorg. Chem.* **1994**, *33*, 2874–2881.
601. Belmonte, P. A.; Own, Z. Y. *J. Am. Chem. Soc.* **1984**, *106*, 7493–7496.
602. Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, *5*, 417–423.
603. Koch, J. L.; Shapley, P. A. *Organometallics* **1997**, *16*, 4071–4076.
604. Huynh, M. H. V.; White, P. S.; Meyer, T. J. *Inorg. Chem.* **2000**, *39*, 2825–2830.
605. Huynh, M. H. V.; White, P. S.; Carter, C. A.; Meyer, T. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 3037–3039.
606. Lee, D. G.; van den Engh, M. *Can. J. Chem.* **1972**, *50*, 3129.
607. Purcell, W.; Roodt, A.; Basson, S. S.; Leipoldt, J. G. *Transition Met. Chem.* **1991**, *16*, 60.
608. Jayaprakash, K. N.; Gillepsie, A. M.; Gunnoe, T. B.; White, D. P. *Chem. Commun.* **2002**, 372–373.
609. Meublat, L.; Lance, M.; Bougon, R. *Can J. Chem.* **1989**, *67*, 1729–1731.

Comprehensive Coordination Chemistry II
ISBN (set): 0-08-0437486

Volume 5, (ISBN 0-08-0443273); pp 733–847