ADVANCES IN INORGANIC CHEMISTRY, VOL. 37

RECENT ADVANCES IN OSMIUM CHEMISTRY

PETER A. LAY* and W. DEAN HARMAN†

* Department of Inorganic Chemistry, University of Sydney, New South Wales, 2006 Australia and † Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901

I. Introduction

A. History

Osmium was first discovered in 1803 by Tennant (*1*), who also isolated the first coordination complex [OsO_4]. Although the discovery of Os preceded that of Ru by 41 years (*2*), the known chemistry of Ru is

more extensive than that of Os. The reasons for this are that, compared with Ru, Os chemistry is considerably more expensive, and second, most Os complexes are prepared via more difficult routes starting from the hazardous (*3*) [OsO_4]. In spite of this, there are now literally thousands of Os coordination complexes, not to mention a quite extensive organometallic chemistry (*4*). In recent years, the number of complexes has expanded rapidly because of the development of more convenient synthetic methods. This review is aimed at describing these recent developments.

B. Scope of This Review

1. Reviews on Osmium Chemistry

A summary of the reviews published on Os chemistry up until 1986 is given in Griffith's 1987 article (*2*). More extensive reviews of the literature up until 1980 are found in Gmelin (*5, 6*), and brief annual surveys of publications during 1986–1988 have appeared (*7*).

In the area of Os organometallic chemistry, a comprehensive review of the literature up until 1982 has been produced (*4*). More recent reviews include the annual surveys on the organometallic chemistry of Ru and Os (*8–10*), organometallic arene chemistry of Ru and Os (*11*), and terminal methylene complexes (*12*).

A 1987 review surveys the methods available for the determination of Os and other platinum group metals (*13*), with a more recent review examining the use of thiourea complexes in the determination of Os (*14*). In the following text, reviews on more specific topics will be referred to where appropriate.

2. Scope

This review on the synthesis, properties, and chemistry of coordination complexes will concentrate on the literature since the end of 1985, referring to earlier literature only where relevant. It includes a general survey of recent publications, with more detailed discussions of interesting developments in the latter sections. Analogous Ru chemistry will also be included in particular sections, to show the similarities and differences in the chemistry of these elements. Appropriate literature dealing with organometallic chemistry will be referred to where relevant to the discussion of the coordination chemistry, because Os chemistry often transcends these traditional boundaries. However, no attempt has been made to review recent developments in Os organo-

metallic chemistry; therefore, this review is confined largely to the chemistry of Os in oxidation states II or higher.

II. Survey of Coordination Complexes

A. Oxidation States

1. General Comments

Osmium complexes exist in every oxidation state from II− to VIII, but generally the coordination chemistry is restricted to oxidation states II through VIII (*2, 5, 6*). The low-oxidation-state chemistry is dominated by ligands that are good σ donors (e.g., amine ligands) and π acceptors (e.g., N heterocycles). By contrast, higher oxidation states are stabilized by the addition of ligands that are both strong σ and π donors, e.g., O^{2-} and N^{3-}. The strengths of π bonding and π backbonding are so great with Os that changing one ligand in the coordination sphere can have a dramatic effect on the stability of an oxidation state. This has an important influence on both the physical properties and the reactivities of Os complexes, and as such, will be discussed in detail where appropriate.

2. Osmium(0)

This oxidation state is rare for nonorganometallic complexes, being found only in the trigonal-bipyramidal $[Os(PR_3)_5]$ complexes and in reactive intermediates such as $[Os(PR_3)_4]$ and $[Os(PR_3)_3]$ (*15*).

3. Osmium(I)

Os(I) is confined to complexes containing ligands that are very good at stabilizing low oxidation states, such as those with the cyano ligand (*2, 5, 6, 16*).

4. Osmium(II)

An extensive pentaammine chemistry has emerged in recent years, but most Os(II) complexes are stronger reductants than are their Ru(II) analogs and are sensitive to aerial oxidation. Many air-stable Os(II) complexes with N-heterocyclic, phosphine, cyano, and CO ligands are known. In general, Os(II) is octahedral and low spin (*2, 5, 6*). However,

$[Os(PPh_3)_3Cl_2]$ (*17*) and $[Os(PPr^i_3)_2(CO)(H)(Cl)]$ (*18*) are five coordinate, and $[Os(bpy)(PPh_3)_2(CO)(H)_2]$ is seven coordinate (*19*).

5. Osmium(III)

This oxidation state is dominated by amine complexes, and a large variety of complexes with N, O, S, and P donors. Complexes with N-heterocyclic ligands tend to be strong oxidants. Invariably, Os(III) complexes are low spin and octahedral (*2, 5, 6*).

6. Osmium(IV)

In order to stabilize Os(IV), it is necessary to have either several ligands that are good π bases (e.g., Cl^- or Br^-), or one ligand that is a strong π base (e.g., O^{2-}) (*2, 5, 6*). Many Os(IV) complexes contain one or more halo ligands. There is also a growing number of oxo- and nitrido-bridged complexes.

Most Os(IV) complexes are low spin and octahedral. Although they have two unpaired electrons, they often have anomalous magnetic properties at room temperature. This is due to quenching of the electron spin by the orbital spin, as a consequence of the large spin-orbit coupling constant (*20*). Recently, low-spin, diamagnetic, tetrahedral complexes have been characterized that contain four sterically hindered alkyl or aryl groups (*21*), and the square-planar $[Os(NAr)_2(PMe_2Ph)_2]$ (Ar = 2,3-$Pr^i_2C_6H_3$) is also known (*22*).

7. Osmium(V)

Os(V) complexes are relatively rare and generally unstable toward disproportionation or other reactions. Authentic complexes that have been isolated include $[OsF_5]_4$, $[Os_2Cl_{10}]$, salts of $[OsX_6]^-$ (X = F^- or Cl^-), and mixed halo/aqua or halo/oxo complexes, all of which are octahedral (*2, 5, 6*). Recently, the tetrahedral $[Os(2\text{-}MeC_6H_4)_4]^+$ and five-coordinate $[Os(O)(ehba)_2]^-$ complexes have been isolated and characterized (*23*).

8. Osmium(VI)

Generally, two strong π bases are required to stabilize Os(VI), hence its chemistry is dominated by octahedral complexes with the *trans*-dioxo moiety. However, a complex containing three doubly deprotonated 2-aminobenzenethiol ligands, $[Os(abt)_3]$, has been characterized (*24*). In addition, a growing number of five-coordinate complexes

that have either an oxo, nitrido, or imido ligand, together with four good σ and π-donor ligands, have been reported. Examples include [Os-O(Ctmen-2H)(Ctmen-H)]ClO_4 (*25*), similar complexes with four alkyl groups (*26*) or two diolato(2−) ligands (*27*), and $[Os(N)(R)_4]^-$ and [Os-(NMe)$(R)_4$] (*28*). Five-coordinate complexes with two oxo ligands are also known (*29, 30*) and the diamagnetic tetrahedral complexes [Os-$(O)_2(R)_2$] (R = 2,6-xylyl or 2,4,6-mesityl), $[Os(O)(NBu^t)(mes)_2]$, and $[Os(O)_2(SSO_3)_2]^{2-}$ have been characterized recently (*31–33*). The isolation and characterization of the air-stable trigonal-planar complex, $[Os(NAr)_3]$ (Ar = 2,3-$Pr^i{}_2C_6H_3$) (*22*), is even more remarkable given that most complexes are octahedral (*2, 5, 6*).

9. *Osmium(VII)*

The few isolated complexes of Os(VII) contain at least four ligands that are both strong π and σ donors, e.g., the tetrahedral $[OsO_4]^-$ ion, the octahedral $[OsOF_5]$ complex, and the pentagonal-bipyramidal $[OsF_7]$ (*2, 5, 6*).

10. *Osmium(VIII)*

Tetrahedral $[OsO_4]$ is quite stable and forms five-coordinate adducts with a number of ligands. It also adds two OH^- ligands to form *trans*-$[Os(O)_4(OH)_2]^{2-}$, or substitutes one or more oxo groups for other strong ligands, such as N^{3-} or NR^{2-} (*2, 5, 6*). The unusual six-coordinate Os(VIII) complexes, *trans*-$[Os(O)_2(OSiMe_3)_2(NP(Ph)_2CH_2P(Ph)_2N)]$ (*34*) and *trans*-$[Os(O)_2(pda)_2]$ (*24*), have been synthesized recently.

B. General Synthetic Methods

1. *Overview*

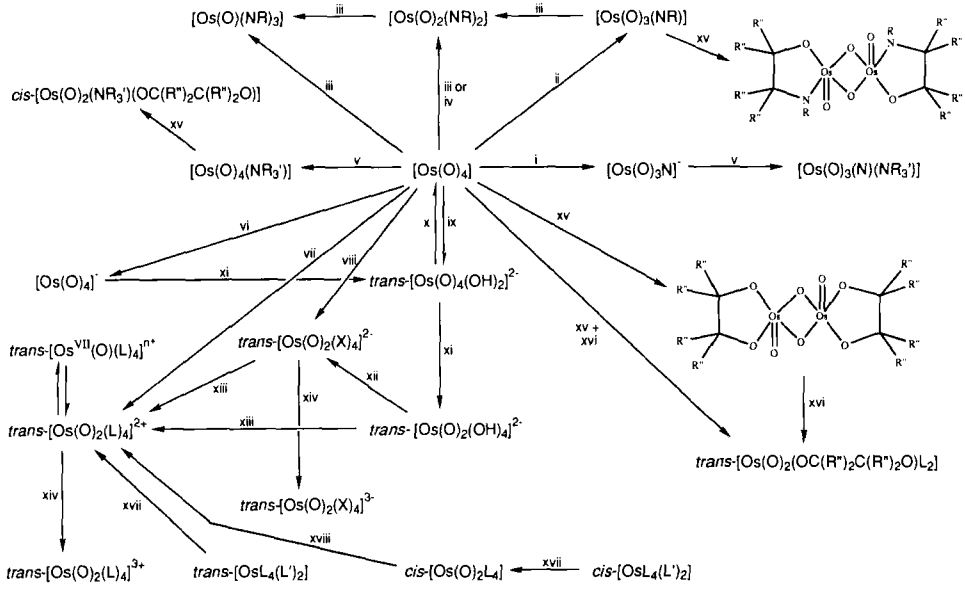
With the exception of the neutral halo complexes, which are prepared by direct reaction of the halogen with the metal, and a number of complexes generated by the direct reaction of the metal with a strong acid, coordination complexes of Os are prepared directly or indirectly from $[OsO_4]$ (*2*). The latter is a toxic, volatile solid, normally purchased in 1-g ampuls and opened within the reaction mixture contained in a fume hood to prevent escape of the toxic vapor (*3*) and loss of the reactant. It is also available as an aqueous solution of "osmic acid," which is suitable for some reactions.

General routes for the syntheses of complexes with oxo and N-donor

ligands are presented. More extensive compilations of synthetic methods are given elsewhere (*2, 5, 6*).

2. *Complexes with Oxo Ligands*

Five-coordinate Os(VIII) complexes of the type $[Os(O)_4L]$ contain a weak Os—L bond and are prepared by the addition of the ligand to $[OsO_4]$ (*2*). The *trans*-dioxoOs(VI) complexes are prepared in a number of ways, including the reduction of $[OsO_4]$ by an alkene or alkyne to form an osmyl diester with the oxidized ligand (*2*), the reduction of $[OsO_4]$ in the presence of excess ligand (*2, 35, 36*), and the ligand substitution reactions of *trans*-$[Os^{VI}O_2X_4]^{2-}$ complexes (*2, 5, 6*). The *cis*- and *trans*-dioxoOs(VI) complexes are also prepared from the oxidations of Os(II) or Os(III) complexes or geometric isomerizations of cis complexes (*2, 37–40*). This chemistry is summarized in Scheme 1.



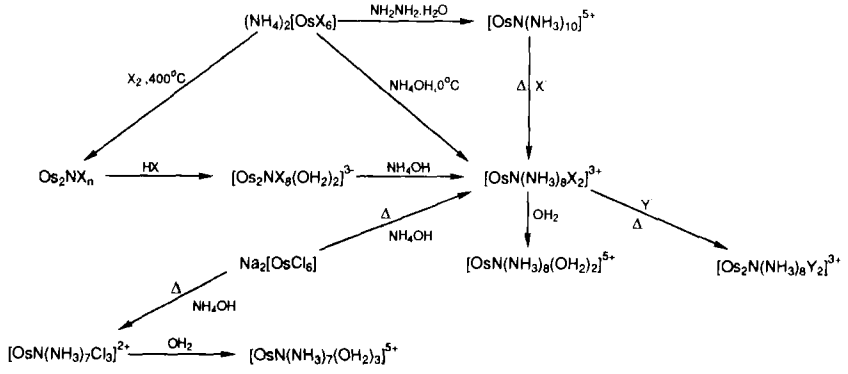
SCHEME 1. Preparation of oxo complexes. Reagents: (i) NH_3, (ii) RNH_2 (R = tertiary alkyl group), (iii) $RN{=}PPh_3$, (iv) $RNH{-}SiMe_3$, (v) NR'_3, (vi) reductant, nonaqueous solvent (vii) excess L, (viii) excess HX, (ix) OH^-, (x) nonreducing acid, (xi) reductant, (xii) excess HX or X^-, (xiii) L, (xiv) $h\nu$ plus reductant or electrochemical reduction, (xv) $R''_2C{=}CR''_2$, (xvi) L = py, etc., (xvii) oxidation of Os(II), Os(III), or Os(IV) complexes, and (xviii) Δ

3. *Nitrido and Nitrido-Bridged Complexes*

a. Mononuclear Complexes. $[Os^{VIII}(O)_3(N)]^-$ is best prepared from the reaction of NH_3 with $[OsO_4]$ in strongly basic media (*2, 5, 6*). It is the only known Os(VIII) complex with the N^{3-} ligand, and reacts with HX to form the Os(VI) complexes $[Os(N)X_5]^{2-}$, $[Os(N)X_4]^-$, and *trans*-$[Os(N)X_4(OH_2)]^-$. These, in turn, undergo ligand exchange reactions to produce a large range of other Os(VI) nitrido complexes (*2, 5, 6*).

Alternative methods for the synthesis of mononuclear Os(VI) nitrido complexes are the chemical or electrochemical oxidation of Os(II) or Os(III) ammine complexes (*41–43*) and the oxidation of Os(IV) complexes by organic azides (*44*).

b. Dinuclear Complexes. The original syntheses of dinuclear Os(IV)$_2$ μ-nitrido complexes involved heating $(NH_4)_2[OsX_6]$ in the presence of HX or NH_3 to yield *trans,trans*-$[(H_2O)X_4OsNOsX_4(OH_2)]^{3-}$ and $[X(NH_3)_4OsNOs(NH_3)_4X]^{3+}$, respectively. Heating *trans,trans*-$[(H_2O)X_4OsNOsX_4(OH_2)]^{3-}$ in excess ammonia also produces *trans,trans*-$[X(NH_3)_4OsNOs(NH_3)_4X]^{3+}$ complexes. The X^- ligands can be substituted to prepare a range of complexes (*45*), whereas the octaammine complex ($X = Cl^-$) and $[Os_2N(NH_3)_7Cl_3]Cl_2$ are also obtained from heating $Na_2[OsCl_6]$ in aqueous NH_3 (*46*). Recently, the reaction of $NH_2NH_2 \cdot H_2O$ with solid $(NH_4)_2[OsCl_6]$ was found to yield the decaammine complex, $[(NH_3)_5OsNOs(NH_3)_5]^{5+}$ (*47*). This complex undergoes trans substitution reactions, resulting in a high-yielding and simple entry into the aforementioned series (*47*). The μ-N^{3-} chemistry is summarized in Scheme 2.



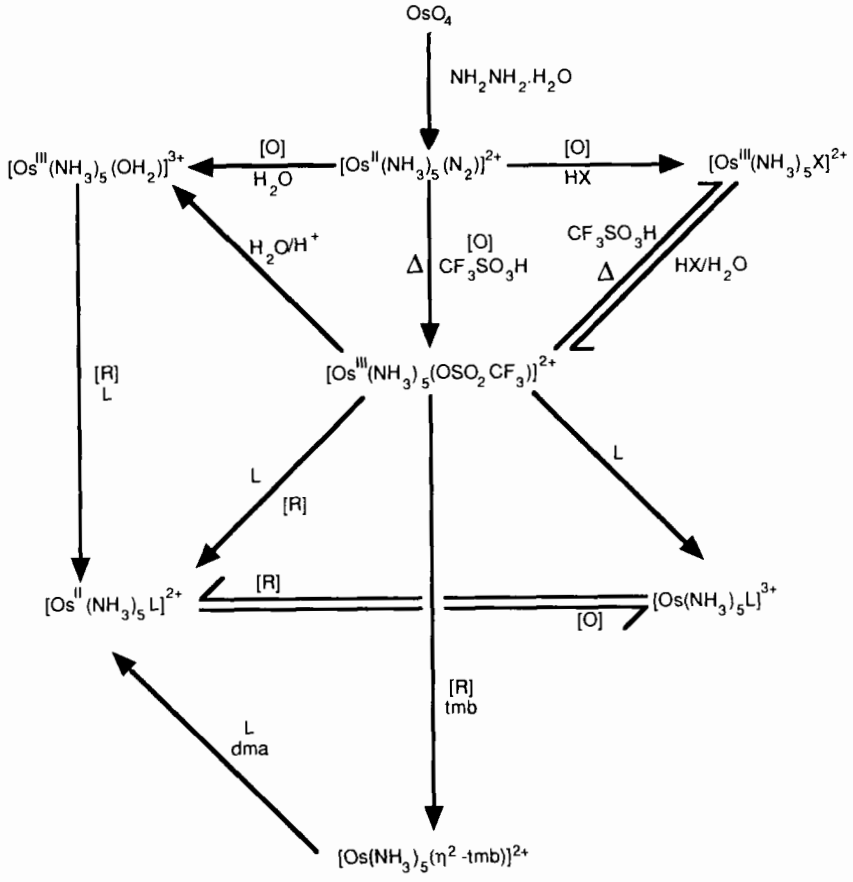
SCHEME 2. Preparation of μ-nitrido complexes.

4. Osmium Ammine Complexes

a. Pentaammineosmium(III) and -osmium(II) Complexes. Though original methods for preparing these complexes involved heating $[OsX_6]^{2-}$ (X = Cl or Br) with excess NH_3 (*48–53*), all modern synthetic methods use $[Os(NH_3)_5(N_2)]^{2+}$ as an intermediate. This complex is generated from the reaction of $[OsCl_6]^{2-}$ with excess $NH_2NH_2 \cdot H_2O$, and because of its synthetic importance, the reaction conditions have been improved to give overall yields of ≥90% (*47, 54–59*). The lability of the N_2 ligand in the Os(III) oxidation state, following oxidation of the Os(II) precursor, is utilized in preparative procedures that rely on this intermediate (*56, 58, 60, 61*). However, such *in situ* reactions are limited in their applications, and prior to the early 1980s this prevented the development of $[Os(NH_3)_5L]^{n+}$ chemistry that paralleled the extensive $[Ru(NH_3)_5L]^{n+}$ chemistry (*62, 63*). More recently, pentaammineosmium chemistry has been opened up by the synthesis of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. Unlike triflato complexes of the other inert metal ions, which are normally prepared from reactions of the neat solvent with chloro complexes (*64, 65*), the Os(III) complex is prepared in quantitative yield by the oxidation of $[Os(NH_3)_5(N_2)]Cl_2$ in neat CF_3SO_3H (*59, 66, 67*). The triflato complex has the synthetic advantages of being readily substituted by many ligands and being soluble in most polar organic solvents. However, the use of this complex as a synthetic intermediate is still limited to ligands that are better σ donors to Os(III) than $CF_3SO_3^-$. Moreover, the ligands must not be sufficiently basic so as to bring about competition between substitution and base-catalyzed disproportionation of Os(III) amine complexes to Os(II) and Os(IV). The latter leads to multiple substitution and is a particular problem with the preparation of N-heterocyclic complexes (*68*). Unlike pentaammineruthenium chemistry, wherein these problems are overcome by the use of labile $[Ru(NH_3)_5(OH_2)]^{2+}$ or other Ru(II) solvent complexes (*62, 63*), the analogous complexes in Os chemistry are not of general synthetic utility. This is because of the propensity of $[Os(NH_3)_5(OH_2)]^{2+}$ to reduce water (*68, 69*) and of the other solvent complexes to be either substitutionally inert or to undergo chemical reactions to produce inert complexes. Nevertheless, the $[Os(NH_3)_5(OH_2)]^{2+}$ ion has been used as a synthetic intermediate on a number of occasions (*70–72*). The claim, however, that the Os(II) aqua complex is in equilibrium with η^2-heterocyclic complexes (*72*) has been shown to be incorrect (*73*).

In order to overcome the difficulties of coordinating weak σ donors, several methods have been developed by Harman and Taube for the

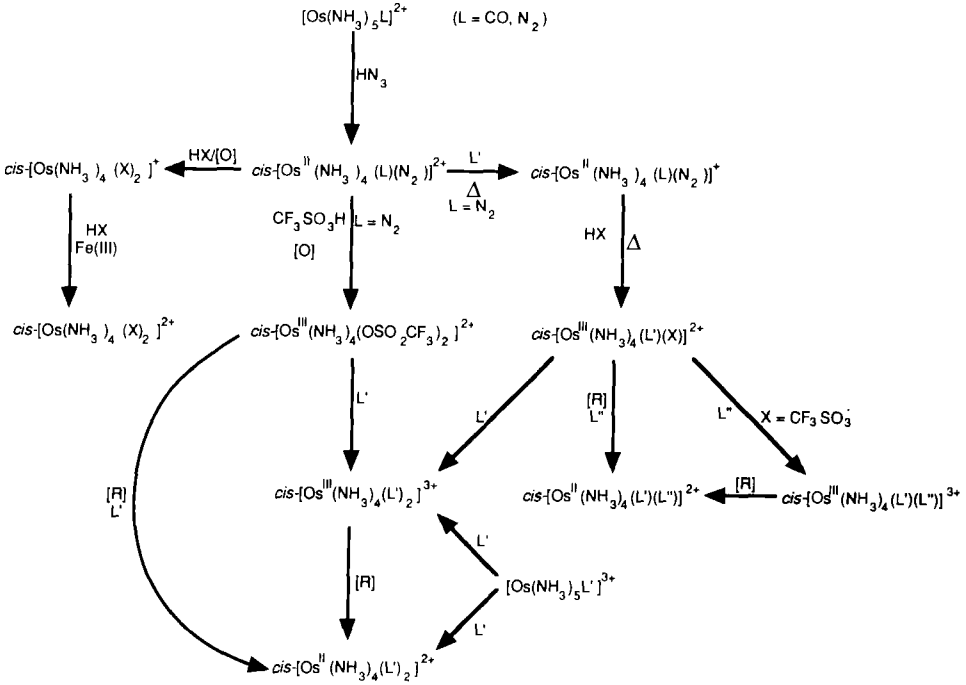
preparations of labile Os(II) synthetic intermediates (*74, 75*). Together with the triflato complex, such methods have resulted in an explosion of our knowledge of pentaammineosmium chemistry. These synthetic methods involve the *in situ* reduction of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ in dma/dme (see the list of abbreviations at the end of this article) to form a labile solvent complex (*75*), or the use of $[Os^{II}(NH_3)_5(1,2,3,4\text{-tetramethylbenzene})]^{2+}$ as an intermediate (*74*). An array of dinuclear decaamminediosmium and heterodinuclear complexes have been prepared using such intermediates (see Section II,D). Current synthetic methods for pentaammine and decaammine complexes are summarized in Scheme 3.



SCHEME 3. Preparation of pentaammine and decaammine complexes.

b. Tetraammineosmium(II), -osmium(III), and -osmium(IV). The conventional routes to the synthesis of *cis*-tetraammine complexes involve diazotization of $[Os(NH_3)_5(N_2)]^{2+}$ to form *cis*-$[Os(NH_3)_4(N_2)_2]^{2+}$ (*76, 77*). One of the N_2 ligands is readily replaced with other ligands by gentle warming (*77–80*). Heating in aqueous HX solutions result in the loss of both N_2 ligands with concomitant oxidation to form *cis*-$[Os(NH_3)_4X_2]^+$ (*61*). *cis*-$[Os(NH_3)_4(OSO_2CF_3)_2](CF_3SO_3)$ is prepared most conveniently from oxidation of *cis*-$[Os(NH_3)_4(N_2)_2]Cl_2$ in neat CF_3SO_3H (*81*) and undergoes substitution chemistry similar to that of the pentaammine analog. Mixed-ligand complexes are prepared by treating *cis*-$[Os(NH_3)_4(N_2)_2]^+$ with an excess of the appropriate ligand to give *cis*-$[Os(NH_3)_4(N_2)L]^{2+}$ (L = PR_3, N heterocycle, etc.), which are used to generate the corresponding Os(III) monotriflato complex. Although such chemistry is in its infancy, it is likely to lead to the synthesis of a large number of *cis*-tetraammine complexes. An alternative method is to use complexes such as *cis*-$[Os^{III}(NH_3)_4(pz)Cl]^{2+}$, generated as previously described (*77, 79*), to synthesize triflato intermediates. *cis*-$[Os(NH_3)_4(heterocycle)_2]^{3+/2+}$ also result from reactions of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ with excess ligand (*68*). In addition, dinuclear nonaammine- and octaamminediosmium complexes are prepared using triflato or dinitrogen intermediates in the manner just described. The chemistry of the *cis*-tetraammine complexes is summarized in Scheme 4.

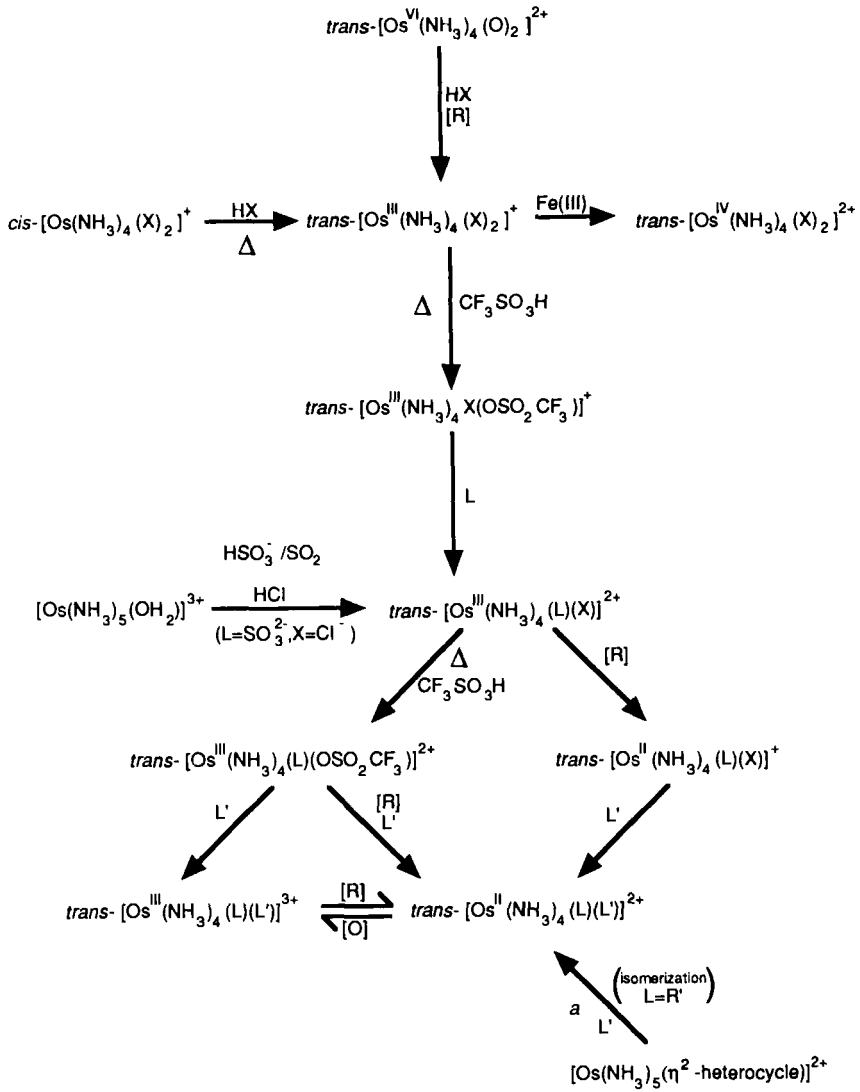
Apart from the nitrosyl complexes, which are discussed in detail elsewhere (*2, 82*), the *trans*-tetraammineOs(III) complexes and related complexes with chelating amine ligands are prepared by geometric isomerization of the cis complexes. This requires refluxing for several days in the presence of HX (*61*). An alternative route is the reduction of the *trans*-$[Os^{VI}(NH_3)_4(O)_2]^{2+}$ precursor in HX (*83*). The substitution chemistry of the triflato group is used to synthesize a variety of complexes starting from the halo complexes (*81, 84*) and requires further exploration. As is the case for the *trans*-$[MA_4Cl_2]^+$ complexes of Rh(III), Ir(III), and Ru(III) (*65, 81*), only one of the chloro ligands is replaced to produce *trans*-$[Os(NH_3)_4Cl(OSO_2CF_3)]^+$, even after prolonged heating in neat CF_3SO_3H (*81*). This is synthetically useful because it enables the sequential displacement of the chloro ligands. Other synthetic routes into the *trans*-tetraammine series include the activation of the *trans*-NH_3 group toward substitution by the formation of either the Os(II)–ylide complex of 2,6-lutidine (and other N heterocycles in which the ligand is bound to Os via the para carbon) (*85*), or the formation of an Os(III)—SO_3^{2-} bond (*86*). *cis*- and *trans*-$[Os^{IV}(NH_3)_4X_2]^{2+}$ are prepared from the Fe(III) oxidation of Os(III) complexes (*83*). The synthesis of the *trans*-tetraammine complexes is summarized in Scheme 5.



SCHEME 4. Preparation of *cis*-tetraammine complexes.

c. Triammineosmium(II), -osmium(III), and -osmium(IV). The mer complexes are prepared by the diazotization of the appropriate *trans*-tetraammine complex to form *mer*-$[Os^{II}(NH_3)_3(N_2)X_2]$, which is oxidized in HX to *mer*-$[Os(NH_3)_3X_3]$ (*87*). These complexes are readily oxidized further to their Os(IV) analogs, *mer*-$[Os(NH_3)_3X_3]^+$ (*83*).

The fac isomers are probably among the products formed from the diazotization of the *cis*-tetraammine complexes, but have yet to be obtained pure (*87*). When *cis*-$[Os(NH_3)_4(OSO_2CF_3)_2]^+$ is reduced in the presence of an arene ligand, an ammine and two triflato ligands are displaced to form $[Os^{II}(NH_3)_3(\eta^6\text{-arene})]^{2+}$. The benzene complex is also a product of the prolonged heating of $[(NH_3)_5Os(\mu\text{-}\eta^2{:}\eta^2\text{-benzene})Os(NH_{35}]^{4+}$ along with $[(NH_3)_5Os(\mu\text{-}\eta^2{:}\eta^6\text{-benzene})Os(NH_3)_3]^{4+}$, which has a triammine unit (*88*). The naphthalene ligand is readily substituted for other ligands to form *fac*-$[Os^{II}(NH_3)_3L_3]^{2+}$ complexes (*81, 89*), which provides a convenient synthetic route for the preparation of the fac isomers. Imidazole activates ligands to substitution and the reaction of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ with excess ligand results in *fac*-$[Os(NH_3)_3(im)_3]^{2+}$ (*90*). The chemistry of the triammine

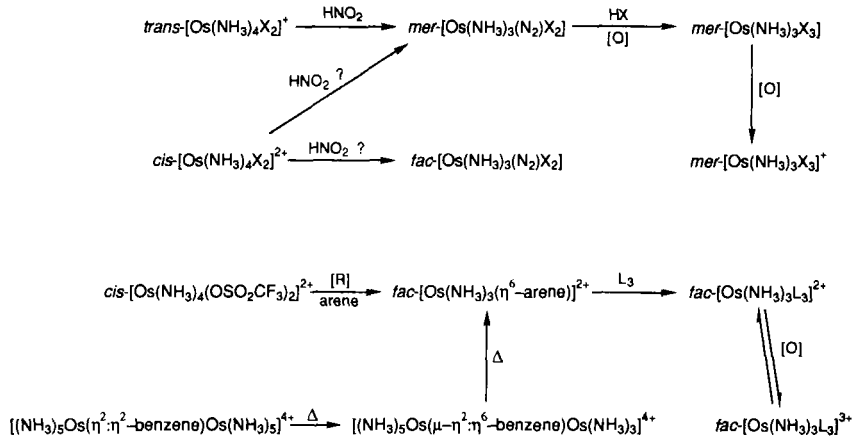


SCHEME 5. Preparation of *trans*-tetraammine complexes.

complexes, apart from the nitrosyl complexes that are discussed in detail elsewhere (*2, 82*), is summarized in Scheme 6.

5. *N-Macrocyclic Complexes*

At the time of Griffith's review (2), no macrocyclic complexes of Os had been reported except for the porphyrin and phthalocyanine com-

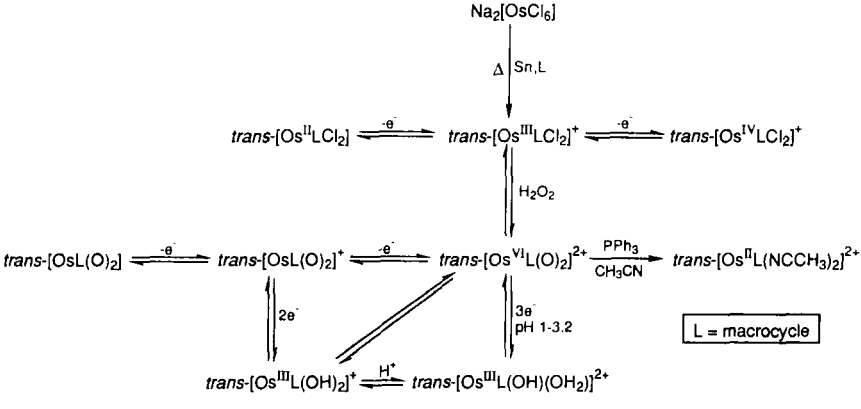


SCHEME 6. Preparation of triammine complexes.

plexes, which are reviewed in Section II,C,4,d and elsewhere (*2, 91, 92*). In recent times, methods have been devised for the synthesis of the macrocyclic complexes of Os. This chemistry has been reviewed (*39, 93*) and is summarized in Scheme 7.

6. *Complexes With bpy, trpy, phen, and Related Ligands*

General methods for the preparation of N-heterocyclic complexes have been well summarized previously (*2*). One of the new synthetic procedures involves the use of triflato complexes, e.g., *cis-*



SCHEME 7. Preparation of macrocyclic complexes.

$[Os(bpy)_2(OSO_2CF_3)_2]^+$ and $[Os(trpy)(bpy)(OSO_2CF_3)]^{2+/+}$, as intermediates (*94–96*).[1] Although such complexes provide convenient entries into the aqua/hydroxo/oxo chemistry and they are also useful intermediates for the preparation of other complexes (*42*), their synthetic utility has only just begun to be explored. Other recently developed synthetic routes utilize intermediates that contain bidentate carbonato ligands, for synthesizing *cis*-$[Os(bpy)_2L_2]^{n+}$ and *cis*-$[Os(bpy)(dppe)L_2]^{n+}$ complexes (*97, 98*). This new chemistry is summarized in Scheme 8.

7. Osmium(III) Complexes

Most Os(III) complexes are prepared by either the direct reduction of $[OsO_4]$ or $[OsX_6]^{2-}$ ($X = Cl^-$ or Br^-) with an excess of the ligand (*2, 5, 6*). The latter is made from the reduction of $[OsO_4]$ in the presence of HCl or HBr (*99*). Other reactions include those of $OsCl_3$ with the ligands and the reduction of Os(VI) or Os(IV) complexes (*2, 5, 6*).

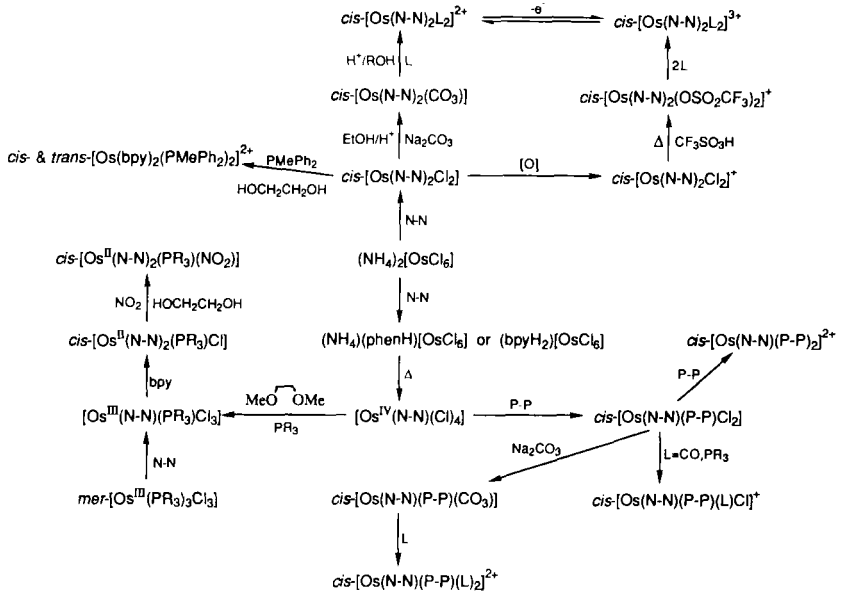
C. Mononuclear Complexes

Because of the sheer volume of work published over the last 5 years, only certain specialist topics will be discussed in any depth (Sections III–V). Whereas this survey covers many areas in a cursory fashion, it amply illustrates the rapid growth of knowledge in Os chemistry. It also serves to indicate where future advances are likely to occur, especially in the "organometallic" chemistry of $[Os(NH_3)_nL_m]^{x+}$ complexes, which often mimics or surpasses the extensive chemistry normally associated with phosphine ligands. Examples wherein novel organometallic chemistry has occurred are the η^2-ketone and η^2-arene complexes of pentaammineosmium.

1. Boron Ligands

Osmaboranes and Osmacarboranes. The first osmaboranes were reported in 1983 from the reactions of $[Os(CO)(Cl)(H)(PPh_3)_3]$ with *arachno*-$[B_3H_8]^-$ or *nido*-$[B_5H_8]^-$, to yield *arachno*-$[(HOsB_3H_8)(CO)(PPh_3)_2]$ (**I**) and *nido*-$[(OsB_5H_9)(CO)(PPh_3)_2]$ (**II**), respectively. Both complexes have two hydride and one or more boron atoms bound to

[1] Although some aspects of the preparation and reactivity of $[Os(trpy)(bpy)(OSO_2CF_3)]^{2+}$ appeared in the literature in 1984 (*96*), this paper was actually submitted after our paper dealing with $[Os(trpy)(bpy)(OSO_2CF_3)]^{2+/+}$ (*95*). The preparation of these complexes was communicated to the authors of Ref. *96* in 1982.

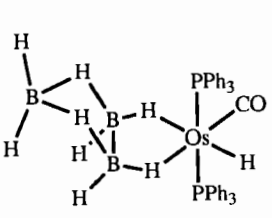


SCHEME 8. New methods for the synthesis of complexes with bidentate N-heterocyclic ligands.

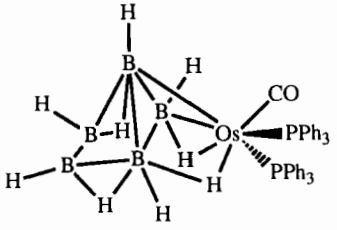
Os (*100*). Treatment of the nido complex with NaH yields Na-[$(Ph_3P)_3(CO)Os(B_5H_8)$] (**III**), which reacts with $[PtCl_2(PMe_2Ph)_2]$ to give $[(Ph_3P)_2(CO)Os(PhMe_2P)(Cl)(H)Pt(B_5H_7)]$ (**IV**). X-Ray crystallography shows that the borane and hydride ligands act as bridges (*101*). Similarly, *mer*-$[OsCl_3(PMe_2Ph)_3]$ reacts with $[NBu_4][B_9H_{14}]$ (*102*) or *closo*-$[B_{10}H_{10}]^{2-}$ in EtOH (*103*) to yield [6,6,6-$(PMe_2Ph)_3$-*nido*-6-OsB_9H_{13}] (**V**) and $[(PMe_2Ph)_2OsB_{10}H_8(OEt)_2]$ (**VI**), respectively. The structure of the former has been determined by X-ray crystallography (*102*). $[OsCl_2(PPh_3)_3]$ and *closo*-$[B_{10}H_{10}]^{2-}$ yield $[(PPh_3)(Ph_2PC_6H_4)OsB_{10}H_7(OEt)_2]$ (**VII**), for which the X-ray structure shows that one of the PPh_3 ligands has orthometalated to a boron atom (*103*). Similarly, $[(\eta^6\text{-}C_6Me_6)OsCl_2]_2$ reacts with *closo*-$[B_{10}H_{10}]^{2-}$ to form [1-$(\eta^6\text{-}C_6Me_6)OsB_{10}H_{10}$] (**VIII**), with Tl[*arachno*-B_3H_8] to form [2-$(\eta^6\text{-}C_6Me_6)ClOsB_3H_8$] (**IX**), or with *arachno*-$[B_9H_{14}]^-$ to form [6-$(\eta^6\text{-}C_6Me_6)OsB_9H_{13}$] (**X**) (*104*).

closo-[1-$Os(CO)_3$-2,3-$\{(CH_3)_3Si\}_2$-2,3-$C_2B_4H_4$] (**XI**) is made from $[Os_3(CO)_{12}]$ and *closo*-$[Sn\{(CH_3)_3Si\}_2C_2B_4H_4]$ or *nido*-$[\{(CH_3)_3Si\}_2C_2B_4H_6]$ and has been characterized by ^1H, ^{11}B, ^{13}C, and ^{29}Si NMR and mass spectroscopies (*105*). More recently, *nido*-[9,9,9-$(CO)(PPh_3)_2$-9,6-

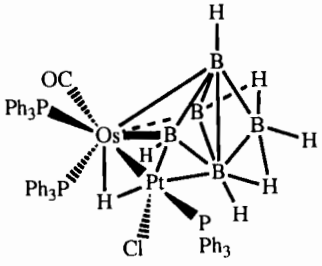
$OsCB_8H_{10}$-5-PPh_3] (**XII**) was prepared from [Os(Cl)(CO)(H)$(PPh_3)_3$] and *arachno*-$[CB_8H_{13}]^-$, and its X-ray structure was determined (*106*). The structures of the osmaboranes and osmacarboranes are given in Fig. 1.



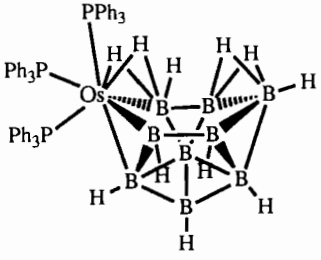
I



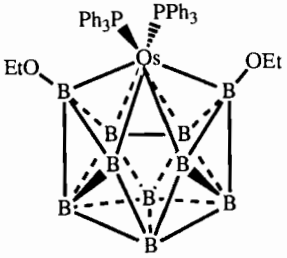
II



IV

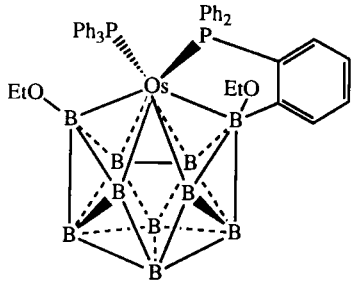


V

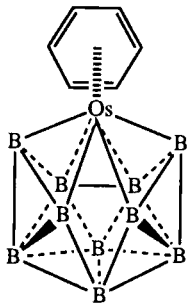


VI*

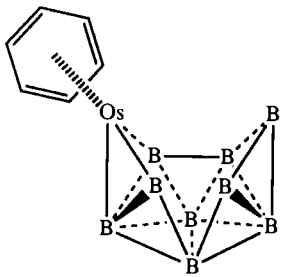
FIG. 1. Structures of the osmaboranes and osmacarboranes. Structure **III** (not shown) is the same as **II**, except a hydride is removed; only borons of the borohydrides are shown in structures **VI–X** and **XII** (asterisks).



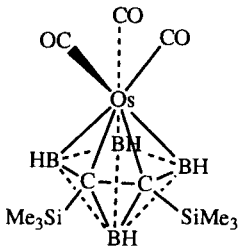
VII*



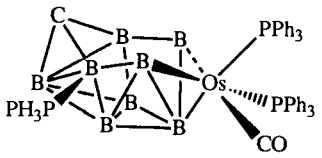
X=H VIII*
X=Cl IX*



X*



XI



XII*

FIG. 1. (*Continued*)

2. *Carbon Ligands*

a. Cyano Complexes. $[Os^{I}(CN)_5Cl]^{5-}$ and *trans*-$[Os^{I}(CN)_4Cl_2]^{5-}$ are produced by X-radiation of $K_4[Os(CN)_6]$ in a KCl matrix. These complexes are stable at room temperature and have been characterized by the hyperfine and superhyperfine coupling observed with EPR spectroscopy (*16*).

trans-$[Os(CN)_4(NCCH_3)_2]^{2-}$ is prepared by irradiating *trans*-$[Os^{VI}(O)_2(CN)_4]^{2-}$ in an acetonitrile solution containing an alkene or other substrate (*107*) and $[Os(CN)_2\{CNCH(Ph)CH_2OH\}_4]$ is prepared from the reaction of $[Os(CN)_2(CNH)_4]$ with an epoxide (*108*). $[Os(N)(CN)_5]^{2-}$, *trans*-$[Os(N)(CN)_4(OH)]^-$, *trans*-$[Os(NH)(CN)_4(OCOCF_3)]$, and *trans*-$[Os\{N(COCF_3)\}(CN)_4(OCOCF_3)]^-$ are discussed in Sections II,C,4,q and II,C,6,o. The well-known complexes *cis*-$[Os(LL)_2(CN)_2]$ (LL = bpy or phen) have been studied by X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry (*109*). Lattice dynamics of $K_4[Os(CN)_6] \cdot 3H_2O$ have been evaluated by NMR spectroscopy at temperatures near its phase transition and the dynamics have been compared with the isostructural Fe(II) and Ru(II) complexes (*110*). The nonmagnetic $Th[Os(CN)_6] \cdot 5H_2O$ has been prepared and its structure characterized by X-ray powder diffraction and thermogravimetric analysis (*110a*). X-ray crystal structures of the isomorphous series $Na_4[M(CN)_6] \cdot 10\ H_2O$ (M = Fe, Ru, Os) have also been reported and the IR spectra of the three complexes compared (*110b*). The heterogeneous electron transfer rate of the $[Os(CN)_6]^{3-/4-}$ couple has been measured at a carbon fiber electrode using very fast cyclic voltammetry (*111*). An outer-sphere charge-transfer complex, $\{[Pt(NH_3)_5Cl]^{3+} \cdot [Os(CN)_6]^{4-}\}^-$, has been prepared and its spectroscopy studied (*111a*).

The *trans*-dioxoOs(VI) complexes that contain two trans or cis cyano ligands are obtained from the reactions of *trans*-$[Os(O)_2(OH)_4]^{2-}$ and CN^- in a 1:2 molar ratio in the presence of a carboxylic acid. If oxalic acid is used, the product is *trans-O,O-cis*-$[Os(O)_2(CN)_2(ox)]^{2-}$; however, if acetic acid is used, the produce is *trans,trans,trans*-$[Os(O)_2(CN)_2(OH)_2]^{2-}$. A brief report on the latter complex appeared some time ago (*2, 112*), but its substitution reactions were not explored. The OH^- ligands are substituted by other ligands to produce *trans,-trans,trans*-$[Os(O)_2(CN)_2X_2]^{2-}$ (X^- = NCO^-, NCS^-, MeO^-, and $SeCN^-$), *trans,trans,trans*-$[Os(O)_2(CN)_2(py)_2]$, and *trans-O,O*-$[Os(O)_2(CN)_2(bpy)]$. All complexes were characterized by infrared (IR), Raman, and UV/Vis spectroscopies, the latter being strongly vibronically coupled (*113*). *trans*-$[Os(O)_2(CN)_4]^{2-}$ undergoes photochemical or electrochemical reduction to the Os(V) analog (*107, 114*), and the ^{13}C and ^{18}O derivatives of the Os(VI) complex have been prepared to study the vibrational fine structure that occurs within the charge-transfer transitions in the UV/Vis spectrum (*115*).

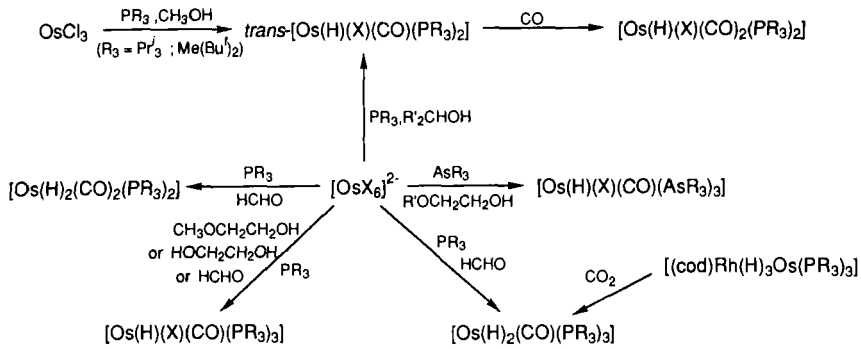
b. Carbonyl Complexes. A very large number of carbonyl complexes of Os have been prepared and characterized, most of which have been reviewed elsewhere (*6, 8–12, 116*). The only CO complexes discussed

here are those with ligands that are normally associated with classical coordination chemistry, e.g., $[Os(NH_3)_5(CO)]^{2+}$. Most carbonyl complexes in oxidation states of Os(II) or higher contain halide and/or hydride ligands, and complexes with halides have been reviewed recently (*116*). The unusual Os(IV) CO complex, $[OsCl_5(CO)]^-$, is prepared from Cl_2 oxidation of *trans*-$[OsCl_4(CO)_2]^-$. The former is reduced reversibly to the Os(III) complex and both have been studied by near-infrared (NIR), IR, Raman, and UV/Vis spectroscopies and electrochemistry (*117*).

The synthesis of carbonyl complexes is achieved in several ways. Although, the direct reaction of CO with an Os complex is a general route, preparation is also via oxidative dehydrogenation of coordinated methanol (Section V,E,2,b), dehydration of coordinated formate (Section V,E,4,g), and elimination of RH or $(CH_3)_2NH$ from coordinated aldehydes (RCH = O) or dmf, respectively (Section V,E,4,h). The direct reactions of CO with $[Os(NH_3)_5L]^{2+}$ complexes have not as yet yielded the CO complex, but all of the above reactions of coordinated ligands can be used in the synthesis of $[Os(NH_3)_5(CO)]^{2+}$ (*55, 118–120*). $[Os(NH_3)_5(CO)]^{2+}$ is oxidized to the Os(III) complex by $[IrCl_6]^{2-}$, isolated as $[Os^{III}(NH_3)_5CO][Ir^{III}Cl_6]$ (*58*). The Os(III) complex is quite acidic, with the first pK_a value of the ammine ligands being ~2.5 (*87*). It undergoes base-catalyzed disproportionation to give $[Os^{II}(NH_3)_5CO]^{2+}$ and Os(IV) and/or Os(V) nitride carbonyl complexes. The latter are intermediates in the coupling reaction to form *cis,cis*-$[(CO)(NH_3)_4Os(N_2)Os(NH_3)_4(CO)]^{4+}$ (Section V,E,1,c) (*58*). $[Os(NH_3)_5(CO)]^{2+}$ is diazotized to form *cis*-$[Os(NH_3)_4(N_2)(CO)]^{2+}$ (*55, 87*).

Reactions of coordinated ligands are also standard preparative methods for the synthesis of Os hydride/carbonyl/phosphine or arsine complexes, which in turn are the starting materials for a large range of organometallic or coordination complexes (*116*). The general synthetic methods are summarized in Scheme 9 (*18, 19, 106, 121–137*). The five-coordinate $[Os(H)(X)(CO)(PR_3)_2]$ complexes are coordinatively unsaturated and very effective hydrogenation catalysts (*125, 135, 137*). $[Os(H)_2(CO)(PMe_2Ph)_3]$ is also prepared by the reduction of CO_2 by the hydride ligands in $[(cod)Rh(H)_3Os(PMe_2Ph)_3]$ (*138*).

Oxidation of 2-methoxyethanol or 1,2-ethanediol by $[OsO_4]$, in the presence of a porphyrin, is used to prepare $[Os^{II}(P)(CO)(X)]$ complexes [P is a porphyrinato(2−) ligand] (*139*). Recently, more convenient preparations of porphyrinato complexes were developed using the reactions of $[Os_3(CO)_{12}]$ with the appropriate porphyrin (Section II,C,4,d) (*38, 40, 140, 141*). Electrochemical studies show that both the Os(III) and Os(III)/porphyrin–cation–radical complexes are moderately stable



SCHEME 9. Preparation of osmium carbonyl/hydride/phosphine or arsine synthetic intermediates via the reactions of coordinated ligands.

with respect to CO dissociation (*142*). Despite this, the CO ligand is sufficiently labile on Os(III) for oxidation of the CO complexes to be useful routes in the synthesis of Os porphyrin complexes of oxidation state III and higher. Recently, the use of [Os(oep)(PBu_3)(CO)] (*143*), [Os(tpp)(PBu_3)(CO)] (*143*), [Os(*p*-Xtpp)(CO)(EtOH)] (X = Cl, H, OMe, or Me) (*40*), and [Os(tmp)(CO)(EtOH)] (*40*) in such reactions has been reported. [Os(mix)(CO)(EtOH)] has also been prepared and reconstituted into Ru-modified and native sperm whale myoglobins to form carbonyl osmoglobin ([Os^{II}(CO)][Mb]) (*144*).

Complexes prepared by the direct reaction of CO with a complex include *trans*-[$OsCl_2$(CO)(PMe_2Ph)$_3$] from *trans*-[$OsCl_2$(PMe_2Ph)$_3$] (*145*), *trans-P,P-cis-C,C*-[Os(H)(Cl)(CO)$_2$($PMeBu^t_2$)$_2$] from [Os(H)-(Cl)(CO)($PMeBu^t_2$)$_2$] (*124*), and *cis*-[OsL(CO)(PPh_3)] from *trans*-[OsL(PPh_3)$_2$] (L = hba-b or chba-dcb) (*146*). The latter is a remarkable reaction because it involves the direct coordination of CO to an Os(IV) center to form a stable complex. *trans*-[$OsCl_2$(CO)(PMe_2Ph)$_3$] undergoes isomerization to form *cis*-[$OsCl_2$(CO)(PMe_2Ph)$_3$] (*145*).

Two series of complexes, [Os(bpy)$_2$(CO)(R)] (R = H^- or alkyl) and [Os(bpy)(phen)(CO)X], have been characterized and their excited states studied (*147, 148*). The former are also used in the autocatalytic reduction of CO_2 (*149*).

c. Complexes with Thiocarbonyl, Selenocarbonyl, and Tellurocarbonyl Ligands. The syntheses of [$OsCl_2$(CS)(PPh_3)$_3$], [OsH(H_2O)(C-S)(PPh_3)$_3$]$^+$, [OsH(CO)(CS)(PPh_3)$_3$]$^+$, and [Os(CO)(CS)(PPh_3)$_3$] have been described (*17*); [$OsCl_2$(CS)(PPh_3)$_3$] reacts with bsd to give [Os-Cl_2(CS)(PPh_3)$_2$(bsd)] (Section II,C,7,h) (*150*). *trans-P,P-cis-Cl,-*

Cl-[$OsCl_2(CO)(CE)(PPh_3)_2$] (E = O, S, Se, or Te) have been prepared from reactions of HE^- or H_2E with [$OsCl_2(CCl_2)(CO)(PPh_3)_2$]. X-Ray crystallography has shown that the trans influences of the chalcocarbonyl ligands increase in the order CO < CS ≤ CSe < CTe. Six-coordinate [$OsCl_2(CCl_2)(CS)(PPh_3)_2$], [$OsCl_2(CS)_2(PPh_3)_2$], [$OsCl_2$(CS)(CSe)$(PPh_3)_2$], and [$OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2]^+$ (*151*) and five-coordinate *trans*-[$OsX(NO)(CS)(PPh_3)_2$] (X^- = Cl^- or I^-), *trans*-[$Os(NO)(CS)(PPh_3)_2L]^+$ (L = CO or PPh_3), *trans-P,P-cis-I,I*-[$Os(I)_2$(NO)(CS)$(PPh_3)_2]I_3$, and *trans*-[Os(HSe)(NO)(CS)$(PPh_3)_2$] have also been prepared (*152*). [Os(CS)(Cl)(4-MeC_6H_4)$(PPh_3)_2$] reacts with SNN-Me_2 to give [Os(CS)(Cl)(4-MeC_6H_4)(*S*-$SNNMe_2$)$(PPh_3)_2$] (*153*).

d. Carbon Dioxide Complexes. No stable mononuclear carbon dioxide complexes have been reported, but a CO_2 complex is likely to be an intermediate in the formation of [$Os(H)_2(CO)(PMe_2Ph)_3$] from [(cod)$Rh(H)_3Os(PMe_2Ph)_3$] and CO_2 (Section II,C,2,b). When [Os-$(NH_3)_5(OSO_2CF_3)]^{2+}$ is reduced in dme in the presence of CO_2, [Os-$(NH_3)_5(CO)]^{2+}$ is recovered in ~ 40% yield. Presumably, this arises from the formation of an [$Os(NH_3)_5(CO_2)]^{2+}$ intermediate, although such an intermediate has not been characterized (*120*).

e. Carbon Disulfide and Related Complexes. [$OsX(NO)(CS_2)$-$(PPh_3)_2$] (X = Cl^- or I^-), which have an η^2-(*C,S*) binding mode for the CS_2 ligand, are methylated to form [$OsX(NO)\{\eta^2$-(*C,S*)-S = CSMe}-$(PPh_3)_2$]. The CS_2 complex (X = Cl^-) is also converted into [OsCl(NO)(CSSe)$(PPh_3)_2$], which exists as both the η^2-*C,S* and η^2-*C,Se* linkage isomers (Section V,D,2), and evidence has been obtained for the existence of a transient [$OsCl(NO)\{\eta^2$-(*C,S*)-CSTe}$(PPh_3)_2$] intermediate. The η^2-(*C,S*)-S = $CSMe^-$ ligand undergoes a linkage isomerization reaction on the addition of donor ligands to form η^1-(*C*)-C(S)SMe^- complexes, *trans*-[$OsI(X)\{\eta^1$-C(S)SMe}$(NO)(PPh_3)_2$], (X = Cl^- or SCN-Me_2^-), [$OsI(CNBu^t)\{\eta^1$-C(S)Me}$(NO)(PPh_3)_2]^+$, and *trans-P,P-cis-H,H*-[$Os(H)_2(NO)\{\eta^1$-C(S)SMe}$(PPh_3)_2$]. These complexes were characterized by NMR (^1H and ^{31}P) and IR spectroscopies (*152*).

f. Alkyl and Aryl Complexes. Though complexes with alkyl and aryl ligands are organometallic complexes, by definition, there are many examples of alkyl and aryl complexes that fit comfortably within the classes of complexes discussed in this review. Others contain only alkyl or aryl groups but exhibit many of the properties traditionally associated with coordination complexes. Where appropriate, these two types of alkyl and aryl complexes are discussed, but for more comprehen-

sive treatments of this chemistry other reviews should be consulted (*4, 8–10*).

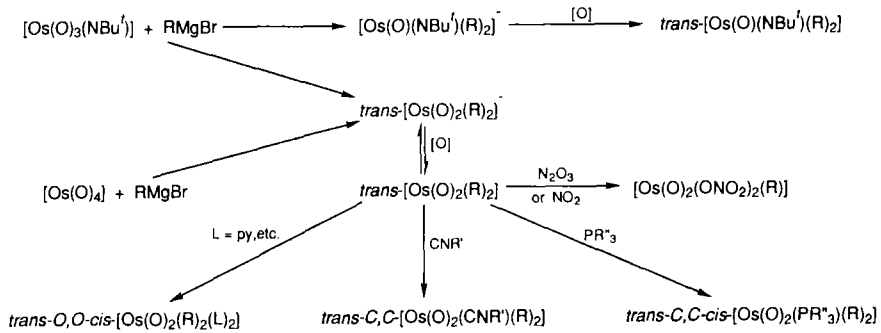
Alkyl ligands are isoelectronic with amines, but because they carry a negative charge they are much stronger σ donors than are amines, and hence stabilize higher oxidation states. Os(VI) chemistry of the air and thermally stable alkyl complexes $[OsO(CH_2SiMe_3)_4]$, $[OsN(R)_4]^-$ (R = CH_3, CH_2Ph, or CH_2SiMe_3), $[Os(NR')(R)_4]$ (R = Me, CH_2Ph, or CH_2SiMe_3, R' = Me; R = CH_2SiMe_3, R' = Et or $SiMe_3$), *cis*-$[OsN(CH_2SiMe_3)_2X_2]^-$ [X^- = Cl^-, NCS^-, ReO_4^-, $\frac{1}{2}CO_3^{2-}$, $\frac{1}{2}CrO_4^{2-}$, $\frac{1}{2}SO_4^{2-}$, or $\frac{1}{2}(CH_2S^-)_2$], *cis*-$[OsN(CH_2SiMe_3)_2(NCS)(SCN)]^-$, and $[Os(Y)(COR)_n(R)_{4-n}]$ (Y = CH_3N^{2-} and O^{2-}; R = CH_2SiMe_3, R = CH_3; n = 1 or 2) is growing rapidly (*26, 28, 154–159*). The much greater σ-donor capacity of an alkyl group as compared to an amine group is illustrated by the fact that with amine ligands a *trans*-dioxo arrangement is required to stabilize Os(VI), whereas four alkyl groups will stabilize Os(VI) with one oxo ligand.

Recently, the tetrahedral oxo/aryl complexes $[Os(O)_2(R)_2]$ [R = 2,6-xylyl (*31*) or 2,4,6-mesityl (*32*)] were prepared via the reaction of $[OsO_4]$ with RMgBr and subsequent oxidation of the red complexes [believed to be the Os(V) complexes $[Os(O)_2(R)_2]^-$] to give the deep-green Os(VI) complexes. A similar reaction of $[Os(O)_3(NBu^t)]$ with mesMgBr results in a mixture of $[Os(O)_2(mes)_2]$ and $[Os(O)(NBu^t)(mes)_2]$ (*30*). These new complexes were characterized by mass, IR, ^1H, and ^{13}C NMR spectroscopies, conductivity, cyclic voltammetry, and X-ray crystallography. The Os — C bond lengths in $[Os(O)_2(xylyl)_2]$ [2.058(6) and 2.060(6) Å (*31*)] and $[Os(O)_2(mes)_2]$ [2.053(8) and 2.047(8) Å (*32*)] are significantly shorter than those in $[Os(O)(NBu^t)(mes)_2]$ [2.119(13) and 2.161(14) Å (*30*)], which is probably an indication of the better donor properties of Bu^tN^{2-} compared with O^{2-}. This is consistent with the electrochemistry, because it is more difficult to reduce $[Os(O)(NBu^t)(mes)_2]$ than the dioxo analog, and the Os(V) complex that is produced is less stable. By contrast, $[Os(O)(NBu^t)(mes)_2]$ is oxidized reversibly to its Os(VII) counterpart, although its dioxo analog undergoes an irreversible multielectron oxidation in acetonitrile at more positive potentials. $[Os(O)_2(mes)_2]$ reacts with pyridine ligands to form octahedral, *trans-O,O-cis*-$[Os(O)_2(mes)_2(L)_2]$ (L = py, 4-Bu^tpy, or $\frac{1}{2}$bpy), with 2,6-$Me_2C_6H_3NC$ to give the trigonal-bipyramidal $[Os(O)_2(xylylNC)(mes)_2]$ (in which the mes ligands occupy the axial positions), and with tertiary phosphines to form *trans-C,C-cis*-$[Os(O)_2(PR_3)_2(mes)_2]$ (PR_3 = PMe_3, PMe_2Ph, or $PMePh_2$), which are rare examples of *cis*-dioxoOs(VI) complexes. All of these complexes were characterized by mass, IR, and ^1H NMR spectroscopies. The tetrahedral bis-dioxo starting material undergoes a com-

plex series of redox reactions with N_2O_3 or NO_2 to give [mesN_2]-[$Os^{VI}(O)_2(ONO_2)_2$(mes)], which was characterized by IR and ^1H NMR spectroscopies and an X-ray structural analysis. It is a distorted trigonal bipyramid in which the nitrato ligands occupy axial positions and the Os — C bond length of 2.053(13) Å is comparable to that of the parent complex (*30*). This chemistry is summarized in Scheme 10.

Again, the ability of the alkyl and aryl groups to stabilize oxidation states higher than those of their isoelectronic amine and N-heterocyclic counterparts is evidenced by the isolation and characterization of remarkable stable peralkylated and perarylated Os(IV) and Os(V) complexes, $[Os(R)_4]^{0/1+}$ [R = cyclohexyl, phenyl, or 2-tolyl) (*21, 23, 160–162*)]. Both oxidation states have distorted tetrahedral geometries as shown by single-crystal X-ray diffraction. The Os(IV) complexes decompose in the presence of strong π acids such as RNC, CO, and PMe_3 to give a variety of products with alkyl ligands, viz. [Os{η^6-2-(2-MeC_6H_4)}2-$MeC_6H_4)_2$L] (L = CO or PMe_3), *cis*-[Os(2-$MeC_6H_4)_2(CNR)_4$] (R = Me_3C or 2,6-$Me_2C_6H_3$), *fac*-[Os{*C,N*-3-Me[2-C(2-$MeC_6H_4NCMe_3$]C_6H_3}(2-MeC_6H_4)(CNR)] (R = CH_3 or 2,6-$Me_2C_6H_3$), and *cis,fac*-[Os(2-$MeC_6H_4)_2(CNCMe_3)_3$(CO)] (*160*). In addition to the reversible oxidation of [Os(2-tolyl)$_4$] to the Os(V) complex, two reversible reductions to the Os(III) and Os(II) complexes are observed in the CV. The Os(V) complex has been characterized by IR and electron paramagnetic resonance (EPR) spectroscopies (*162*).

There are a large number of alkyl Os(II) complexes. These are not discussed in detail, but recent examples are given below. The structure has been determined of the osmacycle, [Os{$CH_2CH_2S(NSO_2C_6H_4$Me-4)O}Cl(NO)$(PPh_3)_2$] (Fig. 2), which is prepared from the reaction of $OSNSO_2C_6H_4$Me-4 with [OsCl(NO)$(C_2H_4)(PPh_3)_2$] (*163, 164*). The



SCHEME 10. Chemistry of oxo/alkyl and oxo/aryl complexes.

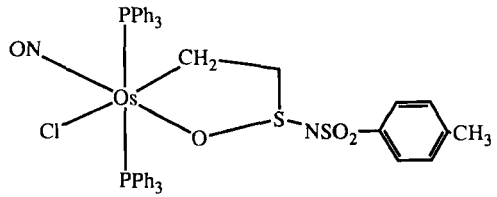


FIG. 2. Structure of $[Os\{CH_2CH_2S(NSO_2C_6H_4Me\text{-}4)O\}Cl(NO)(PPh_3)_2]$.

structure of *cis*-$[Os(PMe_3)_4(H)(neopentyl)]$ has also been determined and its reactions with N_3^-, CO, CH_4, 2-xylyl isocyanide, and Me_3CNC have been studied (*165*). With CH_4, it yields a cyclometalated product and *cis*-$[Os(PMe_3)_4(H)(CH_3)]$ (*165*). The orthometalated complex $[Os(PPh_3)(Ph_2PC_6H_4)(B_{10}H_7(OEt)_2)]$ (Fig. 1) is mentioned in Section II,C,1 (*103*). *trans,cis-X,Y*-$[Os(NO)(X)(Y)(CF_3)(PPh_3)_2]$ ($X = Y = Cl^-$; $X = Cl^-$, $Y = I^-$; $X = Y = I^-$) have been obtained by X_2 oxidation of $[Os(NO)(Cl)(=CF_2)(PPh_3)_2]$ in the presence of F^- and the complexes were characterized by X-ray diffraction and IR spectroscopy (*166*). The alkenyl complexes $[Os\{(E)\text{-}CH=CHPh\}(Cl)(CO)(PMeBu^t_2)_2]$ and $[Os(CO)\{(E)\text{-}CH=CHPh\}\{\eta^2\text{-}(N,O)\text{-}N(O)=CRR'\}(PMeBu^t_2)_2)]$ have also been reported (*124*). The *cis*- and *trans*-$[Os(bpy)_2(CO)R]^+$ complexes are discussed in Section II,C,2,b.

Os(II) aryl complexes, $[Os^{II}(NH_3)_5(aryl)]^{n+}$ and *trans*-$[Os^{II}(NH_3)_4L(aryl)]^{n+}$, have been prepared with pyridinium, *N*-methylpyridinium, *N*-methyl-4-picolinium, 2,6-lutidinium, and 2,6-lutidine bound through the para carbon (Section V,D,3) (*85, 90, 167*). Similarly, a complex containing a 2-C-bound *N,N'*-dimethylimidazolium ligand, $[Os^{III}(NH_3)_5(2\text{-}C\text{-}diMeim)]^{2+}$, is formed via Mg^0 reduction of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ in the presence of an excess of the iodide salt of the ligand in neat nmp or dma. Surprisingly, a similar reduction in dme using the triflate salt of the ligand resulted in the η^2-C,C linkage isomer. The two linkage isomers have not been interconverted, as yet (*90*). All of the C-bound N heterocycles reported above undergo reversible oxidations to their Os(III) counterparts (*90*).

g. Carbene Complexes. *trans*-$[Os(NO)(Cl)(=CF_2)(PPh_3)_2]$ is prepared by the reaction of $[OsCl(NO)(PPh_3)_3]$ with $Cd(CF_3)_2$ (*166*). Carbene ether and alcohol complexes have also been reported (Section II,C,2,o).

h. Alkene Complexes. Like Ru(II), Os(II) has a high affinity for olefins and stable $[Os(NH_3)_5(alkene)]^{2+}$ complexes that have been pre-

pared from either reactions of olefins with labile $[Os^{II}(NH_3)_5(solvent)]^{2+}$ complexes (*70, 71, 120, 168*), the partial hydrogenation of η^2-bound arenes (Section V,E,4,c) (*120, 169*), or other reactions of coordinated ligands (Section V,E,4) (*70, 120, 168*), including those with ethene, propene, *iso*-butylene, 1,3-butadiene, 1,5-hexadiene, *cis*-2-methoxy-2-butene, *trans*-2-methoxy-2-butene, *cis*-2-hydroxy-2-butene, *trans*-2-hydroxy-2-butene, 3,4-dibromo-1-butene, styrene, cyclohexene, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, 3-methoxycyclohexene, 3,6-dimethoxycyclohexene, 2-cyclohexen-1-one, and 1,3-cyclohexadiene; $[Os(NH_3)_5(\eta^2\text{-}(C,C)\text{-3-methoxycyclohexene})]^{2+}$ has been characterized by X-ray crystallography (*169*). All complexes show reversible Os(III/II) redox couples, and the Os(III) complexes are much more kinetically stable than are their Ru(III) congenors. Generally, the olefin bound to Os(III) is released over a matter of hours under ambient conditions (*120, 169*).

An Os(II) complex with a chelating diene, norbornadiene, is prepared from $[Os(bpy)_2(CO_3)]$ and the ligand in the presence of acid (*97*), whereas $[Os(tpp)(\eta^2\text{-}C_2H_4)]$ is formed from the reductive elimination reaction of 1,2-dibromoethane with $[Os(tpp)]^{2-}$ (*170*). Similar complexes are formed from the reactions between alkenes and Os(II) phosphines, e.g., *trans*-$[OsCl_2(PR_3)_3(\eta^2\text{-}CH_2{=}CHR')]$ [$R_3 = Me_2Ph$; $R' = H$ (*145*)], $[Os(H)(Cl)(CO)(PPr^i_3)_2(\eta^2\text{-}CH_2CHR)]$ [R = H, CO_2Me, CN, or COMe (*18*), in which the alkene is trans to the hydrido ligand], and *trans*-$[OsCl(NO)(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (*163*).

i. Alkyne Ligands. $[Os(NH_3)_5(alkyne)]^{3+/2+}$ (alkyne = ethyne, 2-butyne, and diphenylacetylene) have been isolated and characterized (*71, 120, 168, 171*). The thermodynamically stable linkage isomers of both the Os(III) and Os(II) oxidation states of $[Os(NH_3)_5(diphenylacetylene)]^{3+/2+}$ are the η^2-alkyne complexes, which have been characterized by NMR spectroscopy and electrochemistry (*171*). The alkyne complexes exhibit reversible electrochemical oxidations to Os(III) analogs.

j. η^2-Bound Arene and Heterocyclic Ligands. A recent interesting development has been the synthesis and characterization of a variety of η^2-arene complexes of the type $[Os(NH_3)_5(\eta^2\text{-arene})]^{2+}$. They have been characterized by NMR spectroscopy and electrochemistry. These Os(II) complexes are much more stable than their Ru(II) analogs, none of which has been isolated, although it is possible that an η^2 Ru(II)/benzene complex is the reactive intermediate in the hydrogenation of benzene by $[Ru(NH_3)_5]^{2+}$ (*172*). $[Ru(NH_3)_5(\eta^2\text{-arene})]^{2+}$ coordination has only to date been observed in heterodinuclear Os(II)–Ru(II) dimers,

where the coordination of osmium has enhanced the donor abilities of the arene (Section II,D,2,c) (*172*). The ligands that bind in this fashion to Os include benzene (*172, 173*), toluene (*75*), *p*-xylene (*75*), *tert*-butylbenzene (*75*), cumene (*75*), α,α,α-trifluorotoluene [(trifluoromethyl)benzene] (*75*), 1,2,3,4-tetramethylbenzene (*74*), biphenyl (*75*), diphenylacetylene (*171*), naphthalene (*172*), anthracene (*174*), phenanthrene (*174*), pyrene (*174*), aniline (*175*), *N,N*-dimethylaniline (*175*), benzonitrile (*176*), benzophenone (*177*), 2,2-dimethylpropiophenone (*177*), phenol (*178*), methoxybenzene (*169*), and 1,4-dimethoxybenzene (*169*). There is also evidence for the existence of small amounts of the η^2-arene linkage isomer of $[Os(NH_3)_5(styrene)]^{2+}$ from CV data reported for the oxidation of the Os(II) complex (Section III,B), although no mention of this possibility was made in the original paper (*71*).

N-, O-, and S-heterocyclic ligands also form $[Os(NH_3)_5\{\eta^2\text{-}(C,C)\text{-}L\}]^{2+}$ complexes [L = 2,6-lutidine, 2,6-lutidinium, pyridinium, *N*-methylpyridinium, and *N*-methyl-4-picolinium (*85, 167*), *N,N'*-dimethylimidazolium (*90*), pyrrole (*90, 179*), *N*-methylpyrrole (*90, 179*), thiophene (*90, 179*), furan (*90, 179*), and 1,3-dimethyluracil (*72, 73*)]. On oxidation to Os(III), arene ligands are rapidly lost from the coordination sphere, or in the case of the substituted arene ligands with good σ donors, rapid linkage isomerization reactions occur (Section V,D).

k. η^6-Arene Ligands. $[Os(NH_3)_3(\eta^6\text{-arene})]^{2+}$ (arene = benzene or naphthalene) are prepared by either the thermal degradation of $[(NH_3)_5Os(\eta^2{:}\eta^2\text{-arene})Os(NH_3)_5]^{4+}$ or the reaction of the appropriate arene with *cis*-$[Os(NH_3)_4(solvent)_2]^{2+}$ (*88, 89*) (see Section II,B,4,c).

l. Allyl Complexes. The Os(IV) η^3-aryl complexes, $[Os(NH_3)_5(\eta^3\text{-}CH_2CRCH)]^{3+}$, have been reported (*180*) (Section V,E,2,a) and show reactivity typical of complexes with phosphine ligands, e.g., $[Os(H)(CO)(\eta^3\text{-}CH_2CRCH_2)(PPh_3)_2]$ (R = Me or H) (*133*).

m. η^2-(C,O)-Ketones and -Aldehydes. $[Os(NH_3)_5]^{2+}$ has a remarkable ability to stabilize η^2-aldehyde and ketone complexes, which are prepared by the reduction of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ in a solution of the appropriate ligand. Not only are these complexes very inert toward ligand substitution, but they are also moderately air stable in the solid state (*120, 168, 169, 177, 181*). Complexes that bind in this η^2 fashion are acetaldehyde, acetone, 2-butanone, cyclopentanone, cyclobutanone, 2-cyclohexen-1-one, 2,2-dimethylpropiophenone, and benzophenone. The Os(III) analogs are very unstable toward linkage isomerization

reactions (Sections V,D,1). The X-ray structure of $[Os(NH_3)_5\{\eta^2\text{-}(C,O)\text{-acetone}\}]^{2+}$ indicates a considerable contribution from the Os(IV) metallocycle resonance structure (Fig. 3). Thus, the C—O bond length is intermediate between a C—O single bond and double bond, and the coordinated C has an sp^3 tetrahedral geometry (*181*).

Recently, $[Os(H)Cl(CO)(PPr^i_3)_2\{\eta^2\text{-}(CD_3)_2CO\}]$ has been postulated to be in rapid equilibrium with $[Os(H)Cl(CO)(PPr^i_3)_2]$ and $[OsCl\{OCH(CD_3)_2\}(CO)(PPr^i_3)_2]$ in d_6-acetone (*181a*), but there does not appear to be any examples of stable η^2-ketone or aldehyde complexes of Os with phosphine ligands.

As is the case for the η^2-arene complexes, the chemistry of Ru and Os differs markedly. Thus, whereas $[Ru(NH_3)_5\{\eta^2\text{-}(C,O)\text{-}O{=}CR_2\}]^{2+}$ complexes have been isolated, they are sensitive to moisture, oxygen, and nitrogen and are thermally unstable, unlike their substitutionally inert Os(II) counterparts (*182–184*).

n. Isonitrile Complexes. *cis*-$[Os(2\text{-}MeC_6H_4)_2(CNR)_4]$ (R = Me_3C or 2,6-$Me_2C_6H_3$) and *cis,fac*-$[Os(2\text{-}MeC_6H_4)_2(Me_3CNC)_3(CO)]$ are prepared from $[Os(2\text{-}MeC_6H_4)_4]$ (*160*). $[Os(CNR)(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SNNMe_2)]$ (R = 2-xylyl and Me_3C) (*185*), [Os(hba-b)(CO)($CNBu^t$)] and [Os(chba-dcb)($CNBu^t$)$_2$] (*146,*) [Os(pc)($CNBu^t$)$_2$] (*187*), $[Os(H)(CNR)L_4]^+$ [L = $P(OMe)_3$, $P(OEt)_3$, or $PPh(OEt)_2$; R = 4-$MeOC_6H_4$ or 4-MeC_6H_4] (*187*), $[OsL_4(4\text{-}MeC_6H_4NC)(4\text{-}MeC_6H_4N{=}NH)]^+$ [L = $P(OEt)_3$ or $PPh(OEt)_2$] (*188*), $[Os(O)_2(CNxylyl)(mes)_2]$ (*30*), and $[OsI\{\eta^1\text{-}C(S)SMe\}(NO)(CNBu^t)(PPh_3)_2]^+$ (*152*) are discussed in Sections II,C,7,j, II,C,4,x, II,C,4,d, II,C,5,b, II,C,4,m, II,C,2,f, and II,C,2,e, respectively.

cis-$[Os(bpy)_2(CNR)_2]^{2+}$ (R = Me or Ph; Section V,E,4,b) undergo reversible oxidations to the Os(III) analogs and two reversible one-electron reductions that are probably bpy-ligand centered. The electronic absorption and emission spectra of the Os(II) complexes have also been reported (*97*).

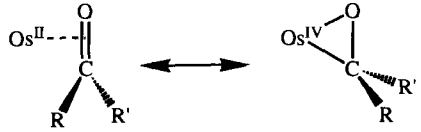


FIG. 3. Resonance forms of Os^{II}-η^2-O=CR_2 complexes.

o. C-Bound Aldehyde and Ketone Complexes. The reactivity of the C-bound formyl complexes *trans*-[Os(CHO)(CO)(P-P)$_2$](SbF$_6$) [P-P = $Ph_2PCH_2CH_2PPh_2$ or *o*-$(Ph_2P)_2C_6H_4$] with electrophiles is discussed. CF_3SO_3R (R = Me or H) attack the oxygen atom at −30°C to form the carbene ether and alcohol complexes, *trans*-[M(CHOR)(CO)(P-P)$_2$]$SbF_6 \cdot CF_3SO_3$, which were characterized by NMR (^{1}H and ^{31}P) and IR spectroscopies and extended Hückel calculations (*189*). [Os(Y)(COR)$_n$(R)$_{4-n}$] (Y = CH_3N^{2-} or O^{2-}; R = CH_2SiMe_3, R = CH_3; n = 1 or 2) were prepared from CO insertion reactions with [Os(Y)(R)$_4$] and characterized by NMR and IR spectroscopies (*159*).

3. *Silyl Complexes*

The reaction between [Os(Ph)(Cl)(CO)(PPh_3)$_2$] and R_3SiH, (R = Et or Cl) leads to the elimination of C_6H_6 to form [Os(SiR_3)(Cl)(CO)(P-Ph_3)$_2$]. The $SiCl_3^-$ complex undergoes substitution reactions at Si to produce other silyl complexes, e.g., the complex with R = Me. The reaction of [Os(H)Cl(CO)(PPh_3)$_2$] with $Hg(SiMe_3)_2$ results in the same complex as a minor product, but the major product isolated was [Os(CO) {η^2-(*C*^{2},*P*)-$Ph_2PC_6H_4$} {η^2-(*P*,*Si*)-*o*-$Ph_2PC_6H_4SiMe_2$} (PPh_3)] (Fig. 4). These complexes were characterized by NMR (^{1}H and ^{31}P) and IR spectroscopies, and the latter two, by X-ray crystallography (*190*). [Os($PPh_2CH_2CH_2SiR^1R^2$)$_2$(CO)$_2$] (R^1 = R^2 = Me or Ph; R^1 = Me, R^2 = Ph) are prepared from [$Os_3(CO)_{12}$] and $Ph_2PCH_2CH_2SiR^1R^2H$ at 140°C. The crystal structure of the complex, where R^1 = R^2 = CH_3, has been determined (*191*). *mer*-[Os(CO)$_3$(PR_3)($SiMeCl_2$)$_2$] [PR_3 = PPh_3 or $P(OCH_2)_3CEt$] has also been prepared and characterized by IR, ^{1}H NMR, and mass spectroscopies (*192*).

The reaction of [Os(H)Cl(CO)(PPr^i_3)$_2$] with triethylsilane produces

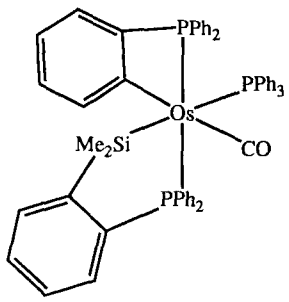


FIG. 4. Structure of [Os(CO){η^2-(*C*^{2},*P*)-$C_6H_4PPh_2$}{η^2-(*P*,*Si*)-*o*-$Ph_2PC_6H_4SiMe_2$}-(PPh_3)].

the dihydrogen complex $[Os(SiEt_3)Cl(\eta^2\text{-}H_2)(CO)(PPr^i{}_3)_2]$ which acts as a catalyst for the addition of triethylsilane to phenylacetylene. The Os(II) dihydrogen complex is in equilibrium with a small amount of the Os(IV) hydrido complex $[Os(H)_2(SiEt_3)Cl(CO)(PPr^i{}_3)_2]$, as shown by ^1H NMR spectroscopy (*192a*).

4. Nitrogen Ligands

a. Ammine Complexes. An improved synthesis of $[Os(NH_3)_6]^{3+}$ involves the reaction of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ in anhydrous liquid ammonia (*59, 67*). This complex has been recrystallized as the mixed salt $[Os(NH_3)_6](ClO_4)_2Cl\cdot KCl$ (*193*), which has had its structure determined by X-ray crystallography.

A large variety of pentaammine, tetraammine, and triammine complexes have been prepared and characterized in recent years using the synthetic procedures outlined in Section II,B,4. The various classes of pentaammine complexes that have been prepared are summarized in the appropriate sections (Table I) (*2, 47, 54–60, 66–71, 74, 75, 80, 85, 90, 118–120, 167–169, 171–181, 194–201*). Dimeric and polymeric complexes are described in Section II,D.

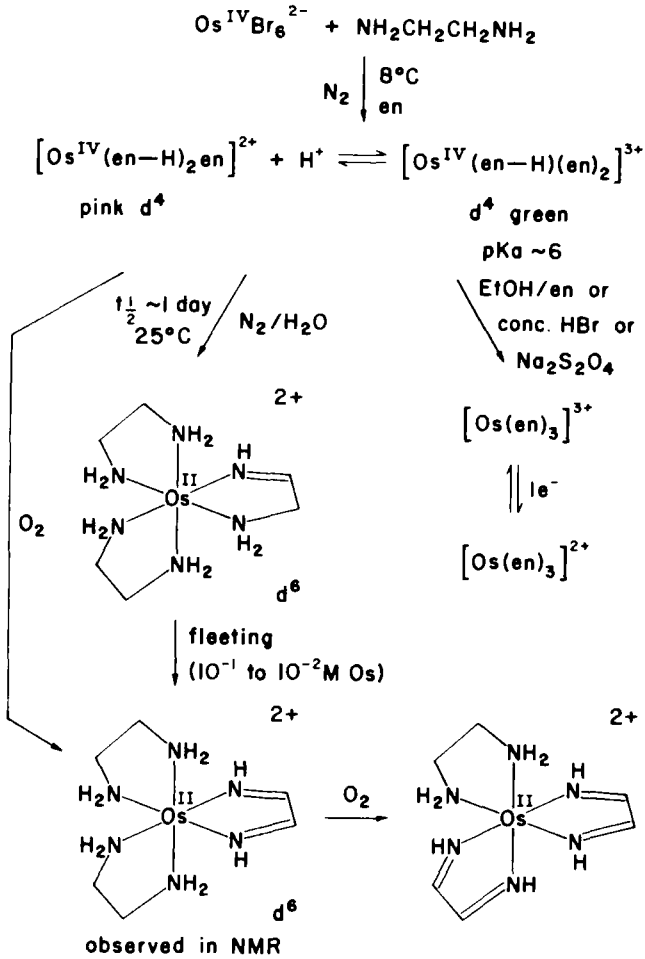
b. Amine Complexes. Many amine adducts of $[OsO_4]$ have been studied and are discussed in Sections II,C,6,b, V,A, and V,E,1,b. The aniline complexes $[Os(NH_3)_5(NH_2Ph)]^{3+/2+}$ and $[Os(NH_3)_5(NMe_2\text{-}Ph)]^{3+/2+}$ were characterized by spectroscopic and electrochemical techniques (Section V,D,3) (*175*). Other $[Os(NH_3)_5(NH_2R)]^{3+}$ complexes are intermediates in the oxidative dehydrogenation reactions of coordinated amines (Section V,E,2,b).

The doubly deprotonated Os(IV) complex $[Os(en)(en\text{-}H)_2]^{2+}$, produced from the reaction of $[OsBr_6]^{2-}$ with neat 1,2-ethanediamine, was partially characterized in the 1950s (*202, 203*) and recently its structure was confirmed by X-ray crystallography (*204, 205*). It is reduced to $[Os(en)_3]^{3+}$ by a number of reductants, and the structure of *rac*-$[Os(en)_3](CF_3SO_3)_3$ has been published (*205*). The Os(III) complex is reversibly reduced to its Os(II) analog, but this complex has not been structurally characterized (*204, 205*). All complexes are oxidized by air to form ethanediimine complexes, i.e., $[Os^{II}(en)_2(diim)]^{2+}$ and $[Os^{II}(en)(diim)_2]^{2+}$, and have been characterized by NMR (^1H and ^{13}C) and UV/Vis spectroscopies (Scheme 11). Recently, $[Os^{IV}(Ctmen)(Ctmen\text{-}H)_2]^{2+}$ has been prepared and found to be very stable because the Ctmen ligand cannot undergo oxidation without breaking a C—C bond (*206*). It has been characterized by X-ray crystallography (*206*) and has

TABLE I

PENTAAMMINEOSMIUM COMPLEXES $[Os(NH_3)_5L]^{n+}$

Ligand	Section	Ref.
Os(II) and Os(III)		
NH_3	II,C,4,a	*59, 67, 193*
CO	II,C,2,b	*55, 58, 118–120*
C-imidazolium	II,C,2,f	*90*
C-(*N*-heterocyclic)	II,C,2,f	*85, 90, 167*
η^2-alkene	II,C,2,h	*70, 71, 120, 168, 169*
η^2-alkynes	II,C,2,i	*71, 120, 168, 171*
η^2-(*C,C*)-arenes	II,B,4,a and II,C,2,j	*71, 74, 75, 169, 172–178*
η^2-(*C,C*)-*N*-heterocycles	II,C,2,j	*90*
η^2-(*C,C*)-*O*-heterocycles	II,C,2,j	*90*
η^2-(*C,C*)-*S*-heterocycles	II,C,2,j	*90*
η^2-(*C,O*)-aldehydes	II,C,2,m	*177*
η^2-(*C,O*)-ketones	II,C,2,m	*120, 168, 169, 177, 181*
Alkyl- and arylamines	II,C,4,b, V,D,3, and V,E,2,b	*118, 175*
N-imidazoles	II,C,4,e	*90*
N-pyridines	II,C,4,e	*60, 66, 68*
N-pyrazine	II,C,4,e	*60, 66, 68*
N-pyrimidine	II,C,4,e	*60, 66, 68*
N-pyridazine	II,C,4,e	*60, 66, 68*
N-4,4′-bipyridine	II,C,4,e	*68*
NO	II,C,4,f	*2*
N_2	II,B,4,a and II,C,4,j	*47, 54–59*
N-imines	II,C,4,k	*194*
N-oximes	II,C,4,l and V,E,5,g	*195*
N-nitriles	II,C,4,n	*67, 176, 196*
N-NCS^-	II,C,4,t	*197, 198*
N-$NCSe^-$	II,C,4,u	*198*
OH_2	II,B,4,a and II,C,6,a	*69, 199*
OH^-	II,C,6,a	*69*
Alcohols	II,C,6,c	*118*
O-dmso	II,C,4,k and V,D, 4	*67, 120, 200*
Ethers	II,C,6,l	*120*
O-amides	II,C,6,g and V,E,5,h	*67, 120*
O-aldehydes	II,C,6,j	*177*
O-ketones	II,C,6,j, V,D,1, and V,E,3	*67, 120, 168, 169, 177, 181*
Trialkyl phosphates	II,C,6,e and V,E,3	*67, 68, 80*
Carboxylates	II,C,6,o and V,E,5,g	*119*
Triflate	II,B,4,a and II,C,6,q	*59, 66, 67*
S-SO_2	II,C,7,j	*60*
S-SO_3^{2-}	II,C,7,s	*60*
S-dmso	II,C,7,l and V,D,4	*67, 120, 200*
S-thiophene	II,C,7,c	*90, 179*
Cl^-, Br^-, and I^-	II,C,8,c	*68*
η^2-H_2	II,C,9,a	*201*
H^-	II,C,9,c	*201*
Os(IV)		
Allyl	II,C,2,1	*180*



SCHEME 11. Chemistry of the Os/en system. Reprinted with permission from the *Journal of the American Chemical Society*, Ref. *204*. Copyright 1982, American Chemical Society.

Os—N bond lengths similar to those observed in the en analog (*204*). $[Os(Ctmen)_3]^{3+/2+}$ have been isolated and characterized (*206*) and *trans*$[Os(Ctmen)_2Cl_2]Cl$ has been prepared by the Sn reduction of $Na_2[OsCl_6]$ in an ethanolic solution of the ligand. It is oxidized to *trans*-$[Os^{VI}(O)_2(Ctmen)_2]^{2+}$ by aqueous H_2O_2 and the dioxo complex has been characterized by IR and UV/Vis spectroscopies. The five-coordinate $[Os^{VI}(O)(Ctmen\text{-}2H)(Ctmen\text{-}H)]^+$ is prepared by either the reaction of the six-coordinate complex with collidine in acetonitrile, or

the reaction of $K[Os(O)_3(NBu^t)]$ in methanol. It was characterized by X-ray crystallography and IR spectroscopy and adopts a square-pyramidal geometry (*24*). The equilibrium between $[Os(O)(Ctmen\text{-}2H)(Ctmen\text{-}H)]^+$ and *trans*-$[Os(O)_2(Ctmen)_2]^{2+}$ in basic media (*24*) provides a mechanism for the previously observed (*207*) rapid ^{18}O exchange of *trans*-$[Os^{VI}(en)_2(O)_2]^{2+}$.

1,2-Phenylenediamine ($pdaH_2$) reacts with $[OsO_4]$ to form *trans*-$[Os^{VIII}(O)_2(pda)_2]$, which is an unusual example of an Os(VIII) complex. It has been characterized by IR and NMR spectroscopies (*24*). Four-coordinate diaminato–Os(VI) complexes of the type $[Os(O)(NAr)(ArNCHRCHRNAr)]$ (Ar = 2,6-$Pr^i_2C_6H_3$; R = H; R + R = cyclopentane or norbornane) have been prepared from the reactions of $[Os(O)(NAr)_3]$ with alkenes and characterized by NMR (^1H and ^{13}C) and IR spectroscopies, and an X-ray structure was determined for R = H) (*22*). Similarly, $[Os(O)_2(NBu^t)_2]$ and fumaronitrile give $[Os(O)_2\{Bu^tN(CHCN)_2NBu^t\}]$, in which the ligand is bound via the deprotonated amines, as deduced from IR, Raman, and ^1H NMR spectroscopies (*208*). The reactions of $[OsO_4]$ with Ntmen and HX yield *trans*-$[Os(O)_2X_2(Ntmen)]$ (X = Cl^- or Br^-), which have been characterized by UV/Vis, IR, and ^1H NMR spectroscopies (*209*).

c. Macrocyclic Complexes. Since the first report of an Os macrocyclic complex in 1986 (*210*), many complexes have been prepared. *trans*-$[Os^{VI}(14\text{-tmc})(O)_2]^{2+}$, which is obtained from *trans*-$[Os^{III}(14\text{-tmc})Cl_2]^+$ (Scheme 7), undergoes a reversible three-electron reduction to form *trans*-$[Os^{III}(14\text{-tmc})(OH)(OH_2)]^{2+}$ at pH values of 1–3.2. In the pH range 3.2–6.5, the reduction product is $[Os^{III}(14\text{-tmc})(OH)_2]^+$, whereas at pH values >7, the reversible reduction to $[Os^{V}(14\text{-tmc})(O)_2]^+$ and the subsequent two-electron reduction to *trans*-$[Os(14\text{-tmc})(OH)_2]^+$ are observed (*210, 211*). This contrasts with analogous Ru chemistry, wherein the Ru(IV) complex is also a stable intermediate. Like most other *trans*-dioxo Os(VI) complexes, $[Os(14\text{-tmc})(O)_2]^{2+}$ exhibits considerable vibrational structure in its UV/Vis spectrum (*210*). Electrochemistry in acetonitrile exhibits two one-electron reversible reductions to form $[Os^{V}(14\text{-tmc})(O)_2]^+$ and $[Os^{IV}(14\text{-tmc})(O)_2]$, respectively. The Os(V) complex was isolated by this method and has been characterized by IR and electronic absorption spectroscopies. It also exhibits vibronic coupling in its UV/Vis bands (*212*).

The preparation of the macrocyclic complexes has been extended to include *trans*-$[Os(L)Cl_2]^+$ complexes (L = 15-tmc, 16-tmc, [14]$aneN_4$, [15]$aneN_4$, [16]$aneN_4$, $crMe_3$, and tet*a*) (*39, 114, 213*), and the crystal structure of *trans*-$[Os(16\text{-tmc})Cl_2)]ClO_4$ has been determined (*213*).

The complexes exhibit reversible reductions to their Os(II) analogs, but oxidations to their Os(IV) analogs are irreversible for the secondary amine macrocycles. This is probably due to oxidative dehydrogenation of the ligand (Section V,E,2,b). By contrast, the macrocycle 16-tmc cannot undergo oxidative dehydrogenation reactions and a reversible Os(IV/III) redox couple is observed to form *trans*-$[Os^{IV}(16\text{-tmc})(Cl)_2]^{2+}$. This complex is moderately stable and its UV/Vis spectrum and reduction back to Os(III) by ascorbate have been reported (*213*). All of the complexes, $[Os(n\text{-tmc})(O)_2]^{2+}$ and $[Os(crMe_3)(O)_2]^{2+}$, have been prepared by the method described above (*114, 213*) and are weak oxidants, with no reaction occurring with benzyl alcohol or styrene even at 70°C. Refluxing an acetonitrile solution of *trans*-$[Os(14\text{-tmc})(O)_2]^{2+}$ with PPh_3 results in the formation of *trans*-$[Os(14\text{-tmc})(NCCH_3)_2]^{2+}$ and $OPPh_3$ (*39*). The redox chemistry is summarized in two recent reviews (*39, 93*), and the electrochemistry of $[Os(14\text{-tmc})(O)_2]^{2+}$ has been studied in detail (*211*). *trans*-$[Os(n\text{-tmc})(O)_2]^{2+}$ and $[Os(crMe_3)(O)_2]^{2+}$ are also powerful photooxidants and the rate constants for their excited-state quenching with arenes in acetonitrile to form the corresponding cation radicals and dioxo Os(V) complexes, are reported (*107, 211a*). The excited states also undergo oxo transfer reactions with trialkylphosphines, dialkylsulfides, and alkenes (*114*).

d. Porphyrin and Phthalocyanine Complexes. Osmium porphyrin complexes were first prepared from the reaction of $[OsO_4]$ with the porphyrin at 200°C in $Me(OCH_2CH_2)_2OH$ to give $[Os^{II}(P)(CO)X]$ complexes (P = porphyrin) (*139*). More recently, a less hazardous method which involves refluxing the porphyrin with $[Os_3(CO)_{12}]$ was developed (*140*). This is used to prepare [Os(P)(CO)] [P = oep (*38, 140*), mix-dme (*140*), tpp (*38, 40*), mix (*144*), and *p*-Xtpp; X = Me, Cl, or OMe (*40*)], which react readily with nucleophiles to form six-coordinate complexes such as [Os(P)(CO)(ROH)] (P = oep, mix-dme, tpp, or *p*-Xtpp; X = Cl, OMe, or Me; R = Me, Et, Pr^i, or Ph) (*38, 40, 140, 144, 214*), $[Os^{II}(P)(CO)(PBu^n_3)]$ (P = oep or tpp), and [Os(P)(CO)(py)] (*140*). The latter are oxidized by Br_2 to form $[Os^{III}(P)(PBu^n_3)(Br)]$, which undergo reversible oxidations to $[Os^{IV}(P)(PBu^n_3)(Br)]^+$ (*143*). $[Os^{II}(P)(CO)]$ (P = oep or tpp) are also oxidized by air in CH_2Cl_2 to give $[Os^{III}(P)(CO)(Cl)]$, which are reversibly reduced by $SnCl_2$ to reform the starting material (*38*).

Oxidations of [Os(P)(CO)] with *tert*-butyl hydroperoxide or 3-chloroperoxybenzoic acid give *trans*-$[Os(P)(O)_2]$ (*38, 40, 140, 214*) (P = mix-dme, oep, tpp, or *p*-Xtpp; X = Cl, Me, or MeO), and the crystal structures of $[Os(p\text{-Metpp})(O)_2]\cdot thf$ (*40*) and $[Os(oep)(O)_2]$ (*215*) have

been reported. Reductions of $[Os(P)(O)_2]$ with ascorbate produce $[Os^{IV}(P)(OH)_2]$ (P = tpp or *p*-Xtpp; X = Cl, Me, or MeO), which are unstable toward aerial oxidation back to the *trans*-dioxoOs(VI) complexes (*40*). Os(IV) complexes containing alcoholate ligands $[Os^{IV}(P)(OR)_2]$ are also prepared via the reduction of $[Os(P)(O)_2]$ in the presence of the appropriate alcohol. The reductants used include N_2H_4 (*216*), PPh_3 (*140*), $SnCl_2$ (*38*), and ascorbate (*214*). These Os(IV) complexes are also intermediates in the oxidation of $[Os^{II}(P)(CO)(EtOH)]$ complexes to $[Os^{VI}(P)(O)_2]$ in ethanol (*40*). The complexes prepared by these methods include those in which P = mix-dme, oep, tpp, or *p*-Xtpp (X = Cl, Me, or MeO), and in which R = Me, Et, Pr^i, and Ph. Most of these Os(IV) complexes exhibit reversible one-electron oxidations to form $[Os^{V}(P)(OR)_2]^+$ and reductions to form $[Os^{III}(P)(OR)_2]^-$. The Os(V) complexes are unstable on the slower bulk electrolysis time scale and disproportionate to form $[Os(P)(O)_2]$ and other products (*214*). $[Os^{IV}(P)(OPr^i)_2]$ is also prepared by the γ-radiolysis of [Os(P)(CO)] in $CCl_4/Pr^iOH/H_2O$ (*38*). The 2-propanol complex undergoes reversible protonation to form $[Os^{IV}(P)(HOR)_2]^{2+}$ and reduction to form $[Os(P)(HOR)_2]$ (*38*). The crystal structures of $[Os^{IV}(tpp)(OPr^i)_2]$, $[Os^{IV}(tpp)(OPh)_2]$, and $[Os(oep)(OEt)_2]$ have been mentioned (*214, 217*), but no details were given.

$[Os(P)(O)_2]$ is also reduced by PhSH to give $[Os^{IV}(P)(SPh)_2]$ (P = oep or tpp) (*214*); by Br_2, to give $[Os^{IV}(oep)Br_2]$ (*214*); and by PPh_3, to give $[Os^{IV}(P)(O)(OPPh_3)]$ intermediates en route to $[Os^{II}(P)(OPPh_3)_2]$ (*218*). All of the Os(IV) complexes are paramagnetic except $[Os(P)(SPh)_2]$, which is diamagnetic (*214*). Unlike the alcoholate complexes, $[Os(oep)(Br)_2]$ is oxidized at the porphyrin ring. Both $[Os(oep)(Br)_2]$ and $[Os(oep)(SPh)_2]$ are reversibly reduced to their Os(III) analogs (*214*).

In the presence of excess PPh_3, $[Os^{VI}(oep)(O)_2]$ and $[Os^{VI}(tpp)(O)_2]$ are converted to $[Os^{II}(oep)(OPPh_3)_2]$ and $[Os^{II}(tpp)(PPh_3)_2]$, respectively. The structures of the Os(II) complexes were determined by X-ray crystallography. The $OPPh_3$ complex is converted to $[Os^{II}(oep)(PPh_3)_2]$ by refluxing in benzene with excess PPh_3 (*218*). Dioxo complexes are also reported to be useful epoxidation catalysts (*219*). $[Os^{III}(P)(PBu^n_3)Br]$ (P = oep or tpp) reacts with cyclohexene in the presence of PhIO to form the corresponding epoxide and enone. The active catalysts are not $[Os(P)(O)_2]$ complexes, because they do not oxidize styrene to styrene oxide, whereas this catalytic system does. Turnovers for the oxidation of cyclohexene ($\geq$120), are much higher than for the Ru analogs (*143*).

$[Os(oep)(pz)_2]$ is prepared from the reaction of $[Os(oep)]_2$ with excess

pz (*220*), and resonance Raman spectroscopy has been used as a probe for π backbonding in the series [Os(oep)(L)(L′)] (L = CO, L′ = py; L = L′ = py; L = L′ = NH_3) (*221*). K_2[Os(tpp)] reacts with dibromoethane to produce [Os(tpp)(η^2-C_2H_4)] and with water to yield K[Os^{II}(tpp)(H)] (*170*). The latter reacts with benzoic acid or benzoic acid-d_1 to produce the η^2-dihydrogen complexes [Os^{II}(tpp)(H_2)] and [Os^{II}(tpp)(HD)], in which the H—H and H—D bonds are very weak (*140*).

Mononuclear complexes of the dimeric dpb (Fig. 5) ligand are prepared from [Zn(H_2dpb)] and [$Os_3(CO)_{12}$] to form [(CO)(OH_2)Os(dpb)Zn], and then [Os(H_2dpb)(CO)($HOCH_3$)]. Pyridine displaces CH_3OH to give [Os(H_2dpb)(CO)(py)], or, under irradiation [Os(H_2dpb)(py)$_2$]. [Os(H_2dpb)(CO)($HOCH_3$)] and [Os(H_2dpb)(CO)(py)] exist as two geometric isomers in which the CO ligand points toward the second porphyrin ring or is on the opposite side (*141*).

[Os^{II}(mix)(CO)(EtOH)] and [Os^{II}(mix)(dmf)$_2$] have been inserted into native and ruthenated myoglobin to form carbonyl myoglobin [Os^{II}(CO)(Mb)] and the oxidized myoglobins [Os^{III}][Mb] and [Os^{III}][Ru_3Mb]. The ascorbate reduction of O_2 to water is catalyzed by [Os^{III}][Ru_3Mb] (*144*).

Although some phthalocyanato(2−) complexes have been reported (*2*), pure [Os(Pc)] has been prepared for the first time by reacting 2-cyanobenzamide with $OsCl_3$ in molten naphthalene with subsequent heating of the crude [Os(pc)L_x] in a stream of N_2 at less than 400°C. The pure complex was characterized by its IR and FD mass spectra. It reacts with excess ligand to produce [Os(pc)L_2] (L = py, dmso, pz, and Me_3CNC), which were characterized by electronic, IR, mass, and NMR (^{1}H and ^{13}C) spectroscopies (*186*).

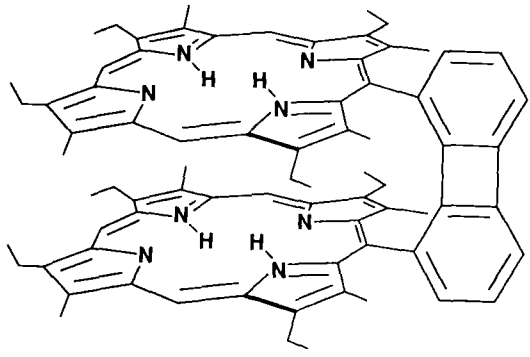


FIG. 5. Structure of the dinuclear porphyrin ligand dpbH_4.

e. Complexes with N Heterocycles. Much of the extensive literature on N-heterocyclic complexes has been reviewed elsewhere, particularly those involving bpy, phen, trpy, and related ligands (*2, 222–225*). Table II (*41, 42, 60, 66, 68, 90, 226–236*) summarizes some of the more recent work performed on N-heterocyclic complexes and several of these complexes are discussed in other parts of this review (*94–98*). Their spectroscopy is discussed in Section IV,A,2.

f. Nitrosyl and Nitrosonium Complexes. Os and Ru nitrosyl chemistries have been discussed in recent reviews (*2, 82*). Though Os chemistry is not as extensive as that of Ru, it is expected that with further research, many new Os–NO compounds will be found. As with nitrosyl complexes of other elements, there is considerable debate about whether the ligand is best considered as an NO^-, NO^0, or NO^+ for a particular complex. This will not be discussed here, as it is well covered in other reviews (*2, 82*). Recent publications on nitrosyl complexes are collected in Table III (*2, 43, 153, 163, 166, 237–248a*). They are arranged according to the formalism that the ligand is in the NO^+ oxidation state, with the superscript denoting the number of d electrons (*2*), i.e., $[Os(NO)]^6$ represents an Os(II) nitrosyl complex under this formalism.

g. Nitrosoarene and Nitrosoamine Complexes. $[Os(Cl)(NO(PPh_3)_2(L)]$ (L = C_2H_4 or PPh_3) reacts with nitrosobenzene to form $[Os(Cl)(NO)\{\eta^2\text{-}(N,O)\text{-}ONPh\}(PPh_3)_2]$, which was characterized by IR and ^{31}P NMR spectroscopies. Unlike its Ru analog, this complex is quite air and thermally stable (*248*).

The six-electron electrochemical oxidation of $[Os^{II}(trpy)(bpy)(NH_3)](PF_6)_2$ in the presence of Et_2NH or morpholine gives $[Os^{II}(trpy)(bpy)\{N(O)NR_2\}]^{2+}$. The same complexes are produced in low yields from the reaction between $[Os^{II}(trpy)(bpy)(NO)]^{3+}$ and excess amine. This appears to be the only example of coordination of nitrosoamines through the central (nitroso) N atom. The complexes have been characterized by IR (including ^{15}N labeling) and ^1H NMR spectroscopies. The latter shows that though there is limited rotation about the N=N double bond, the barriers to rotation are reduced to 57 kJ mol^{-1} (R = Et) and 63–67 kJ mol^{-1} (R_2 = morpholine) from the free ligand values of ~96 kJ mol^{-1} (*249*).

h. Hydroxylamine and Hydrazine Complexes. $[Os(Cl)(NO)\{\eta^2\text{-}(N,O)\text{-}ONPh\}(PPh_3)_2]$ reacts reversibly with HCl to give the deprotonated hydroxylamine complex, $[Os(Cl)_2\{N(OH)Ph\}(NO)(PPh_3)_2]$, which has been characterized by IR and NMR (^1H and ^{31}P) spectroscopies (*248*).

TABLE II

RECENT EXAMPLES OF COMPLEXES WITH *N*-HETEROCYCLIC LIGANDS

Complex	Studies and references
$[Os(NH_3)_5L]^{n+}$, L = py, pz, pd, pyr, 4,4′-bpy, isn, Mepz Etpz, pzH, Phpy, im, or pyrrole	Preparation, electrochem. UV/Vis/NIR, IR (*60, 66, 68*)
cis-$[Os(NH_3)_4L_2]^{n+}$, L = pz or Phpy	Preparation, electrochem., UV/Vis/NIR, IR (*68*)
trans-$[Os(NH_3)_4(L)X]^{n+}$	Section II,B,4,b
fac-$[Os(NH_3)_3(im)_3]^{3+/2+}$	Preparation, IR, UV/Vis (*90*)
$[Os(trpy)(NH_3)Cl_2]^+$	Preparation, UV/Vis, IR, electrochem. (*41, 42, 226*)
$[Os(L\text{-}L)(NH_3)Cl_3]$, L-L = 2py or 4,4′-$Me_2$bpy	Preparation, UV/Vis, IR, electrochem. (*42, 226*)
mer-$[OsCl_3(pic)_2(NCCH_3)]$	Preparation, X-ray, UV/Vis, ^{1}H NMR, IR (*42, 226*)
$[Os(H)(CO)(Hbim)(PPh_3)_2]$	Preparation, IR, ^{1}H and ^{31}P NMR (*227*)
$[(H)(CO)(PPh_3)_2Os(bim)Ir(cod)]$	Preparation, IR, ^{1}H and ^{31}P NMR (*227*)
$[Os(trpy)(bpy)(4,4'\text{-}bpy)]^{2+}$	Preparation, (*228*)
$[Os(tterpy)(X\text{-}tterpy)]^{n+}$, X = H, mv^{2+}, or ptz	CV, emission, intramolecular e^- transfer (*229*)
$[Os(Me\text{-}tterpy)(X\text{-}tterpy)]^{n+}$, X = Me, MeO, Br, mv^{2+}, ptz, or diaa	CV, UV/Vis, ^{1}H NMR, mass spectrosc. (*230*)
cis-$[Os(4,4'\text{-}X_2\text{-}5,5'\text{-}Y_2bpy)_2(CO)Cl]^+$, X = H, Me, Cl, NEt_2, or OMe, Y = H; X = Me, Y = H or Me	^{1}H NMR, UV/Vis absorption and emission, IR (*231*)
cis-$[Os(4,4'\text{-}X_2\text{-}5,5'\text{-}Y_2bpy)_2Cl_2]$, X = H, Me, Cl, NEt_2, or OMe, Y = H; X = Me, Y = H or Me)	^{1}H NMR, UV/Vis, IR (*231*)
$[Os(bpy)_2(dpq)]^{2+}$	Preparation, CV (*232*)
$[Os(dpp)_3]^{2+}$	Preparation, emission (*233*)
$[Os(4,4'\text{-}dcbpy)_3]^{4-}$	Preparation, emission (*233*)
fac-$[Os(py)_3X_3]^{0/1+}$, X = Cl^-, or Br^-	Preparation, CV, UV/Vis, IR, mag., cond. (*234*)
mer-$[Os(py)_3X_3]^{0/1+}$, X = Cl^- or Br^-	Preparation, CV, UV/Vis, IR, mag., cond. (*234*)
mer-$[Os(py)_3X_3]^{0/1+}$, X = Cl^-	X-ray (*234*)
trans-$[Os(O)_2(py)_3(OH_2)]^{2+}$	Preparation, CV, ^{1}H NMR, UV/Vis, IR, Raman (*235*)
trans-$[Os(O)_2(py)_2X_2]^{2+}$, X = Cl^- or Br^-	Preparation, CV, ^{1}H NMR, UV/Vis, IR, Raman (*235*)
$[Os(Me\text{-}tterpy)(O)_2(OH)]^+$	Preparation, ^{1}H NMR, mass spectrosc., CV (*230*)
trans-$[Os(O)_2(5\text{-}SO_3^-\text{-}bpy)(chd)]$	Preparation, ^{1}H NMR, IR (*236*)
trans-$[Os(N)(trpy)X_2]^+$, X = Cl^- or Br^-	CV, ^{1}H NMR, UV/Vis (*41, 42, 226*)
trans-$[Os(N)(trpy)X_2]^+$, X = Cl^-	X-Ray (*41*)
trans-$[Os(N)(L)_2Cl_3]$, L = py, pic, or Bu^{t}py	Preparation ^{1}H NMR, UV/Vis, IR (*42, 226*)
mer-$[Os(N)(L\text{-}L)Cl_3]$, L-L = bpy, 4,4′-Me_2bpy, η^2-trpy, or η^2-$HC(py)_3$	Preparation, UV/Vis, ^{1}H NMR, IR (*42, 226*)

TABLE III

NITROSYL COMPLEXES

Complex	Studies and references
[Os(NO)]^4	
cis-[Os(NO)(NSCl)Cl$_4$]$^-$	Preparation, IR, X-ray (indicates an $NSCl^{2-}$ ligand) (*237*)
[Os(NO)]^5	
[Os(NO)F$_5$]$^-$	X-Ray, XPS, EPR, electrochem. (*238*)
[Os(NO)]^6	
[Os(NH$_3$)$_5$(NO)]$^{3+}$	(*2*)
[Os(NO)Cl$_3$]	Reaction with trithiazyl chloride (*237*)
[Os(NO)F$_5$]$^{2-}$	Variable-temp. IR and Raman, including assignments and normal coordinate analyses; X-ray (*239*)
[Os(NO)Cl$_5$]$^{2-}$	CNDO/2 calculations of atomic charges and orbital populations (*240, 241*); variable-temp. IR and Raman, including assignments and normal coordinate analyses; X-ray (*239*); synthesis (*237*); reaction with pycaH (*242*)
[Os(NO)Br$_5$]$^{2-}$	Variable-temp. IR and Raman, including assignments and normal coordinate analyses; X-ray (*239*)
[Os(NO)I$_5$]$^{2-}$	Variable-temp. IR and Raman, including assignments and normal coordinate analyses; X-ray (*239*)
trans-[Os(NO)Cl$_4$(OH$_2$)]$^-$	Calculation of atomic charges and core binding energies (*241*)
mer,trans-NO,O-[Os(NO)Cl$_3$(η^2-*N,O*-pyca)]$^-$	Preparation, IR (*242*)
trans-[Os(NO)(NH$_3$)$_4$X]$^{2+}$, X = F$^-$, Cl$^-$, Br$^-$, I$^-$, OH$^-$, or NO$_3^-$	Variable-temp. IR and Raman, including assignments and normal coordinate analyses (*243–245*)
trans-[Os(NO)(NH$_3$)$_4$L]$^{3+}$	Variable temp. IR and Raman, including assignments, normal coordinate analyses (L = OH$_2$, NH$_3$), and hydrogen bonding between OH$_2$ ligand and Cl$^-$ anions (*243, 244*)
trans-NO,OH$_2$-[Os(NO)(NH$_3$)$_3$X(OH$_2$)]Y$_2$, X = Cl$^-$, Y = Cl$^-$, Br$^-$, or I$^-$, X = Y = Br$^-$ or I$^-$	Hydrogen bonding between the OH$_2$ ligand and Y$^-$ counterions as studied by variable-temp. IR and Raman (*244*)
trans,trans-Cl,C-[OsCl(NO)(L-L)(PPh$_3$)$_2$], L = η^2-*C,O*-	Preparation from *trans*-[OsCl(NO)(C$_2$H$_4$)(PPh$_3$)$_2$] and

TABLE III (*Continued*)

Complex	Studies and references
$CH_2CH_2S(NSO_2C_6H_4Me\text{-}4)O^{2-}$	O=S=$NSO_2C_6H_4$Me-4 and characterization by ^1H and ^{31}P NMR, IR, and single-crystal X-ray diffraction (*163*)
trans-[Os(NO)X_3L_2], L = PPh_3 or $AsPh_3$; X_3 = Cl_3, $Cl_2(Br)$, $Cl(Br)_2$, or Br_3	Preparation and characterization by IR and m.p. (*246*) (L = PPh_3; X = Cl^-); byproduct (*166*); atomic charges and core binding energies (*241*)
[Os(NO)$Cl_2(S_2CNR_2)(PPh_3)$]	Synthesis and characterization by IR, UV/Vis, and m.p. (R = Me or Et) (*246*)
trans,trans-NO,X-[Os(NO)Cl(X)(CF_2)-$(PPh_3)_2$]X	Intermediates in the reactions of *trans*-[Os(NO)Cl$(CF_2)(PPh_3)_2$] with X_2 (X = Cl or I) (*166*)
trans,trans-NO,X-[Os(NO)Cl(X)(CO)-$(PPh_3)_2$]X	Intermediates in the reactions of *trans,trans-NO,X*-[Os(NO)Cl(X)$(CF_2)(PPh_3)_2$]X with OH_2 (X = Cl or I) (*166*)
trans,cis-X,X-[Os(NO)$Cl(X)_2(PPh_3)_2$]	Decomposition product of *trans,trans-NO,X*-[Os(NO)Cl(X)(CO)$(PPh_3)_2$]X (X = Cl^- or I^-) (*166*)
trans,trans-NO,X-[Os(NO)Cl(X)$(CF_3)(PPh_3)_2$]	Preparation, IR spectra (X = Cl^- or I^-) and X-ray structure (X = Cl^-) (*166*)
{*trans,trans-NO,I*-[Os(NO)ClI$(CF_3)(PPh_3)_2$]}$_2$·*trans-P,P-cis*-[Os(NO)$I_2(CF_3)(PPh_3)_2$]	X-Ray structure (*166*)
trans,trans-NO,I-[OsCl(I)$(\eta^1$-*C*-CS_2-Me)(NO)$(PPh_3)_2$]	Preparation, IR, ^1H NMR, and m.p. (*153*)
trans,trans-NO,CS$_2$Me-[Os(NO)I$(\eta^1$-*C*-CS_2Me)(CNBu^t)$(PPh_3)_2]^+$	Preparation, IR, ^1H NMR, and m.p. (*153*)
trans,trans-NO,C-[Os(NO)I$(\eta^2$-*C,S*-S=C(SMe))$(PPh_3)_2]^+$	Preparation, IR, ^1H NMR, and m.p. (*153*)
trans,trans-NO,C-[Os(NO)Cl$(\eta^2$-*C,S*-C=S(SMe))$(PPh_3)_2]^+$	Preparation, IR, ^1H NMR, and m.p. (*153*)
trans,trans-NO,C-[Os(NO)I$(\eta^1$-*C*-CS_2-Me)$(\eta^1$-$S_2CNMe_2)(PPh_3)_2$]	Preparation, IR, ^1H NMR, and m.p. (*153*)
trans,cis-[Os(NO)$(H)_2(\eta^1$-*C*-CS_2Me)$(PPh_3)_2$]	Preparation, IR, ^1H and ^{31}P NMR, and m.p. (*153*)
trans-P,P-cis-[Os(NO)(CS)$I_2(PPh_3)_2]^+$	Preparation, IR, and m.p. (*153*)
[Os(trpy)(bpy)(NO)]$^{2+}$	CV (*43*)
cis-[Os(N-N)$_2$(NO)(X)]$^{2+}$, N-N = bpy or phen; X = Cl^-, Br^-, OH^-, or NO_2^-	Synthesis, IR, CV (*247*)
cis-[Os(N-N)$_2$(NO)$(OH_2)]^{3+}$, N-N = bpy or phen	Synthesis, IR, CV (*247*)
[OsCl(NO)(ONPh)$(PPh_3)_2$]	Section II,C,4,g (*248*)

(*continued*)

TABLE III (*Continued*)

Complex	Studies and references
[Os(NO)]^7	
cis-[Os(N-N)$_2$(NO)(X)]$^{2+}$, N-N = bpy or phen; X = Cl^-, Br^-, OH^-, or NO_2^-	CV (*247*)
cis-[Os(N-N)$_2$(NO)(OH$_2$)]$^{3+}$, N-N = bpy or phen	CV (*247*)
[Os(NO)]^8	
trans-[OsCl(NO)(PPh$_3$)$_2$]	Reactive intermediate in equilibrium with the six-coordinate alkene complexes (*163*)
[Os(NO)Cl(PPh$_3$)$_3$]	Reaction with Cd(CF$_3$)$_2$ (*166*)
trans-[Os(NO)Cl(AsPh$_3$)$_3$]	Preparation and characterization by IR and m.p. (*246*)
trans-[Os(NO)(CS)(PPh$_3$)$_3$]$^+$	Preparation, IR, and m.p. (*153*)
trans-[Os(NO)Cl(CF$_2$)(PPh$_3$)$_2$]	Preparation and reaction with X_2/F^- (X = Cl or Br) (*166*)
trans-[Os(NO)I(CS)(PPh$_3$)$_2$]	Preparation, IR, and m.p. (*153*)
trans-[Os(NO)Cl(CS)(PPh$_3$)$_2$]	Preparation, IR, and m.p. (*153*)
trans-[Os(NO)(CO)(CS)(PPh$_3$)$_2$]$^+$	Preparation, IR, and m.p. (*153*)
trans-[Os(NO)(SeH)(CS)(PPh$_3$)$_2$]	Preparation, IR, ^{1}H NMR, and m.p. (*153*)
trans-[OsCl(NO)(C$_2$H$_4$)(PPh$_3$)$_2$]	Reaction with O=S=NSO$_2$C$_6$H$_4$Me-4 (*163*)
trans-[OsCl(NO){η^2-(*C,S*)-CS$_2$}(PPh$_3$)$_2$]	Synthesis and methylation (*153*)
trans,trans-*N,N*-[OsCl(NO)(NO)(L-L)(PPh$_3$)$_2$]	(L-L = η^2-*N,S*-S(O)N(SO$_2$C$_6$H$_4$Me-4). Preparation and characterization by IR and ^{1}H and ^{31}P NMR (*163*)
[OsCl(NO)$_2$(PPh$_3$)$_2$]	X-Ray, ^{15}N NMR (*248a*)

Hydrazine ligands such as *N'*-(2-hydroxybenzoly)-*N*-(4-toluenesulfonyl)hydrazine, *N*-(4-hydroxy-3-methoxylbenzylidene)hydrazine carbothioamide, and *N'*-benzoyl-*N*-(4-toluenesulfonyl)hydrazine react with $K_2[Os(O)_2(OH)_4]$ to form $[Os^{VI}(O)_2L_2]$. These are used as the basis of spectrophotometric determinations of Os (*250–253*). The value of the formation constant of the complex between the second ligand and $[Os(O)_2(OH)_4]^{2-}$ in acetic acid solutions is reported to be 6.8 at 28°C (*251*). It is uncertain whether any chemical transformations of the ligands have occurred during binding, because the products are not well characterized.

i. Thionitrosyl Complexes. The atomic charges and core binding energies of $[Os(NS)Cl_5]^{2-}$, $[Os(NS)Cl_3(PPh_3)_2]$, and $[Os(NS)Cl_4(OH_2)]^-$ have been calculated and compared with nitrosyl and Ru analogs. The conclusion is drawn that the NS ligand is a better electron acceptor than the NO ligand and that, consistent with experimental results, it should be better at labilizing a *trans* ligand (*240, 241*).

j. Dinitrogen Complexes. The preparation of $[Os(NH_3)_5(N_2)]Cl_2$ from $(NH_4)_2[OsCl_6]$ and $NH_2NH_2 \cdot H_2O$ is discussed in Section II, B,4,a (*47, 59*)

The reactions of *mer*-$[Os(X)_2(N_2)(PMe_2Ph)_3]$ ($X = Cl^-$ or Br^-) with RS^- in acetone result in the displacement of X^- to give *mer*-$[Os(X)(SR)(N_2)(PMe_2Ph)_3]$ (R = Ph, C_6F_5, Me, or CF_3). The structure of one complex ($X = Cl^-$, $R = C_6F_5$) was determined by X-ray crystallography. If the starting material is reacted with a dithiocarbamate ligand or RS^- at elevated temperatures, the dinitrogen ligand is lost (Section II,C,7,q) (*254*).

Reduction of *mer*-$[Os(Cl)_3(PMe_2Ph)_3]$ to *mer*-$[Os(Cl)_3(PMe_2Ph)_3]^-$ in the presence of N_2 yields *trans,mer*-$[OsCl_2(PMe_2Ph)_3(N_2)]$ (^{31}P NMR spectroscopy and CV), which reverts to the thermodynamically stable cis isomer. Both cis and trans isomers exhibit reversible Os(III/II) couples in thf, demonstrating that the corresponding Os(III) complexes are stable on the CV time scale. It appears that a range of other *trans,mer*-$[OsCl_2L_3(N_2)]$ complexes have been prepared inadvertantly following the reduction of *mer*-$[OsCl_3L_3]$ in CH_2Cl_2 (L = $PMePh_2$, $PEtPh_2$, PEt_2Ph, PEt_3, PPr^n_3, or PBu^n_3) under an N_2 atmosphere (*145*). The original authors did not recognize the reason for the irreversibility of the reduction process (*255*).

k. Imine Complexes. The preparations of $[Os(en)_2(enim)]^{2+}$, $[Os(en)_2(diim)]^{2+}$, and $[Os(en)(diim)_2]^{2+}$ are discussed in Sections II,C,4,b and V,E,2,b. The diim ligand imparts similar properties on both the Os(III/II) redox potentials, and the Os(II) charge-transfer spectra, as the N-heterocyclic ligands, bpy, phen, etc. Cyclic voltammetry shows that the Os(III) complexes are stable on the CV time scale even at low scan rates (*204, 205*). $[Os(bpy)_2(impy)]^{2+}$ is also prepared by an oxidative dehydrogenation reaction (*256*).

$[Os^{II}(NH_3)_5\{NH{=}C(Ch_3)R\}]^{2+}$ (R = H or CH_3) are prepared from the condensations of acetone or acetaldehyde with traces of $[Os(NH_3)_6]^{3+}$ in the presence of a large excess of $[Os(NH_3)_6]^{2+}$. The latter reduces the Os(III) condensation products with concomitant regeneration of the $[Os(NH_3)_6]^{3+}$ catalyst and in so doing results in the quanti-

tative conversion of $[Os(NH_3)_6]^{2+}$ to the corresponding Os(II) imine complex. The imine complexes are reversibly oxidized to their corresponding Os(III) complexes on the CV time scale (*194*).

l. η^1-(N)- and η^1-(N,O)-Oxime Complexes. $[Os(H)(Cl)(CO)(PR_3)_2]$ add aldoximes and ketoximes to give $[Os(H)(Cl)(CO)\{(N)N(OH)=CR'R''\}(PR_3)_2]$ ($R_3 = Pr^i_3$, $R' = R'' = Me$ or $R' + R'' =$ cyclohexyl; $R_3 = MeBu^t_2$, $R' = H$, $R'' = Me$, $R' = R'' = Me$ or $R' + R'' =$ cyclohexyl). Similarly, $[Os(H)(Cl)(CO)(PMeBu^t_2)_2]$ reacts with Na[ON=CR'R''], or $[Os(H)(CO)\{\eta^1\text{-}(N)\text{-}N(OH)=CR'R''\}(PMeBu^t_2)_2]$ reacts with NaH, to yield complexes containing deprotonated aldoxime or ketoxime ligands, $[Os(H)(CO)\{\eta^2\text{-}(N,O)\text{-}ON=CR'R''\}(PMeBu^t_2)_2]$. The latter ($R' = R'' = Me$) reacts with CO to give the O-bound ketoxime complex, *trans-P,P-cis-C,C*-$[Os(H)(CO)_2\{ON=C(CH_3)_2\}(PMeBu^t_2)_2]$. $[Os\{(E)\text{-}CH=CHPh\}(CO)\{\eta^2\text{-}(N,O)\text{-}N(O)=C(Me)_2\}(PMeBu^t_2)]$ is also prepared from the reaction of $[Os\{(E)\text{-}CH=CHPh\}(Cl)(CO)(PMeBu^t_2)_2]$ with $Na[N(O)=C(CH_3)_2]$ (*124*).

$[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ reacts with HONRR' to give Os(III) oxime complexes, which are reduced to Os(II) to yield nitrile complexes (Section V,E,4,g) (*195*).

m. Diazene Complexes. Reactions of $[Os(H)_2L_4]$ [L = $P(OEt)_3$ or $PPh(OEt)_2$] with arenediazonium cations result in the preparations of $[Os(RN=NH)_2L_4](BPh_4)_2$ and $[Os(H)(RN=NH)L_4](BPh_4)$ (R = Ph, 4-MeC_6H_4, or 4-$MeOC_6H_4$). They were characterized by NMR (^1H and ^{31}P) spectroscopy and ^{15}N isotopic substitution. $[Os(4\text{-}MeC_6H_4\text{-}N=NH)(4\text{-}MeC_6H_4NC)L_4](BPh_4)_2$ was prepared in a similar manner. Deprotonation of the bis(aryldiazene) complexes with Et_3N results in the formation of the five-coordinate Os(II) complexes, $[Os(RN_2)L_4](BPh_4)$ (R = Ph or 4-MeC_6H_4). Protonation of these complexes with CF_3CO_2H or HBF_4 gives the six-coordinate $[Os(CF_3CO_2)(RN=NH)L_4]^+$ and the five-coordinate $[Os(RN=NH)L_4]BPh_4$ (R = 4-MeC_6H_4), respectively (*188*).

n. Nitrile Complexes. Pentaammine complexes with acetonitrile (*59, 67, 176*), propionitrile (*176*), *tert*-butylnitrile (*176*), acrylonitrile (*176*), benzonitrile (*67, 176*), pentafluorobenzonitrile (*176*), 9-cyanoanthracene (*176*), 1,2-, 1,3-, and 1,4-dicyanobenzene (*196*), and glutaronitrile (*196*) are prepared from $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ and exhibit reversible Os(III/II) couples. There is a progressive decrease in the C≡N stretching frequency for both the Os(II) and Os(III) complexes along the series R = Me, CH_2=CH, Ph, or C_5F_5 (*176*). The intensities of the coordinated and free C≡N stretching

modes in the IR spectra have also been the subject of detailed analysis for the complexes with dinitrile ligands, $[Os(NH_3)_5L]^{3+/2+}$ (L = 1,2-dcb, 1,3-dcb, 1,4-dcb, and gn). These intensities were compared with analogous Co(III), Rh(III), Ir(III), Ru(III), and Ru(II) complexes and interpreted in terms of π backbonding and other factors (*196*). $[Os(NH_3)_5(NCCH_3)]^{3+}$ is less susceptible to nucleophilic attack at the nitrile than is its Ru analog (*67*). The IR spectra and reactivity patterns of nitrile complexes provide strong evidence for the importance of π-backbonding stabilization of the Os(III) complexes, in addition to the Os(II) complexes, albeit to a lesser extent for the former. The UV/Vis spectra of the Os(III) and Os(II) complexes have also been studied in detail (*176*).

trans-$[Os^{II}(NH_3)_4$(4-lutdn-H)(NCR)$]^{2+}$ (R = Me or Ph) are prepared by dissolving $[Os(NH_3)_5$(4-lutdn-H)$]^{2+}$ in the nitrile (*85*). *trans*-$[Os^{II}(CN)_4(NCMe)_2]^{2-}$, $[Os(CN)_2\{CNCH(Ph)CH_2OH\}_4]$ (Section II,C, 2,a), and *trans*-$[Os^{II}$(14-tmc)$(NCCH_3)_2]^{2+}$ have also been reported (Section II,C,4,c) (*39, 107, 108*). The Os(IV) nitrile complex *cis*-$[OsCl_4(NCCH_3)_2]\cdot\frac{1}{2}CH_3CN$ is prepared from the reaction of $[OsCl_5]$ with CH_3CN and has been characterized by X-ray crystallography and IR and Raman spectroscopies (*257*).

Luminescent spectra of *cis*-$[OsL_2(CO)\{NC(CH_2)_nMe\}]^{2+}$ (L = bpy or phen, n = 0–19) and *cis*-$[Os(bpy)_2(CO)(NCPh)]^{2+}$ (*258, 259*) have shown long-lived excited states at room temperature. The nitrile ligands undergo addition reactions with nucleophiles such as alcohols and are also photolabile. By contrast, the MLCT (metal–ligand charge transfer) excited states of the aminobenzonitrile complexes are short-lived and decay rapidly to the LLCT (ligand–ligand charge transfer) states, *cis*-$[Os(bpy)(bpy^-)(CO)(abn^+)]^{2+}$ (*259*). Heating *cis*-[Os(bpy)(dppe)Cl_2] in CH_3CN results in the displacement of one chloride to produce the *cis*-$[Os(bpy)(dppe)(NCCH_3)Cl]^+$ isomer in which the nitrile is trans to an Os—P bond. This isomer is thermally unstable and isomerizes to the cis isomer in which the nitrile is trans to an Os—N bond. The rate constants for the substitution and isomerization reactions were studied (*98*). CVs of these complexes reveal reversible Os(III/II) couples (*98, 260*). *mer*-$[OsCl_3(4\text{-pic})_2(NCCH_3)]$ is one of the products of the coupling of nitrido complexes to give dinitrogen. It has been characterized by UV/Vis, IR, and ^1H NMR spectroscopies and by an X-ray structure (*226*).

$[Os(H)(Cl)(PHRR')(CO)(Cl)(PPh_3)_2]$ (R = R′ = H; R = H, R′ = Ph; R = R′ = Ph) and $HClO_4/CH_3CN$ give an isomeric mixture of $[Os(Cl)(PHRR')(NCCH_3)(CO)(PPh_3)_2]^+$ in which the nitrile is a labile ligand (*131, 261*). The reactions of *trans*-$[OsCl_2(PMe_2Ph)_3]$ with RCN

give $[OsCl_2(PMe_2Ph)_3(NCR)]$ (R = CH_3 or Ph) (*145*) and $[OsCl(NCCH_3)(CO)(CTe)(PPh_3)_2]ClO_4$ have been reported (Section II, C,2,c) (*151*). The first η^1-N-bound complexes of tetracyanoethylene, *cis*-$[Os(S_2PR_2)_2(PPh_3)(tcne)]$, have also been reported (see Section II,C,7,r).

$[OsNX_5]^{2-}$ (X = Cl^- or Br^-) react with acetonitrile to give *trans*-$[OsNX_4(NCCH_3)]^-$, which were characterized by ^{35}Cl and ^{81}Br NQR spectroscopy and other techniques (*262, 263*). $[Os^{IV}(cp)_2(NCCH_3)]^{2+}$ is obtained from the disproportionation of $[(cp)_2OsOs(cp)_2]^{2+}$ in acetonitrile and its reactions with nucleophiles have been studied (*264*).

o. Chlorothionitrene Complex. Molten $(NSCl)_3$ reacts with $[OsCl_3(NO)]$ to yield a mixture of products, including $(PPh_4)\{cis$-$[OsCl_4(NO)(NSCl)]\}$, which has been characterized by IR spectroscopy and X-ray crystallography. The NO and NSCl ligands are disordered in the structure (*237*).

p. Imido Complexes. $[Os^{VIII}(NBu^t)_4]$ was prepared recently from the reaction of $[OsO_4]$ with excess $Bu^tNH(SiMe_3)$ and was characterized by mass, IR, and ^1H and ^{13}C NMR spectroscopies, and electrochemistry (*265*). The complex undergoes a reversible reduction to its Os(VII) analogue in CH_2Cl_2. A remarkable trigonal-planar Os(VI) complex $[Os(NAr)_3]$ (Ar = 2,6-$Pr^i_2C_6H_3$), has been prepared from the reaction of $[OsO_4]$ with ArNCO. The air-stable complex has been characterized by X-ray crystallography and IR and NMR (^1H and ^{13}C) spectroscopies. It is believed to be stabilized by a combination of steric hindrance and the strong σ- and π-donor properties of the ligand. It reacts with Me_3NO to give $[Os^{VIII}(O)(NAr)_3]$ and with PR_3 [R_3 = Me_2Ph, Me_3, $(OMe)_3$, or $(OPh)_3$] to give the square-planar $[Os^{IV}(NAr)_2(PR_3)_2]$. All complexes have been characterized by IR and NMR (^1H and ^{13}C) spectroscopies, and for the complex with PR_3 = PMe_2Ph, by X-ray crystallography (*22*). $[Os^{VI}(NR)_3]$ (R = 2,6-$Me_2C_6H_3$, 2,6-$Pr^i_2C_6H_3$) have also been prepared by heating $[OsO_4]$ in neat $NHR(SiMe_3)$ for several hours at 100–120°C. Both show two irreversible one-electron reductions (*265a*). Reactions of these Os(VIII) complexes with alkenes are discussed in Sections II,C,4,b and V,E,1,c.

The bis(imido) Os(VIII) complex $[Os(\eta^4$-hba-b$)(NPh)_2]$ is believed to be an intermediate in the formation of the amido complex, *cis*-β-$[Os\{\eta^2$-(*N,N'*)-$PhNC_6H_4NH\}(\eta^4$-hba-b$)]$ from *trans*-$[Os^{IV}(\eta^4$-hba-b$)(PPh_3)_2]$ and phenyl azide (*44*). Complexes of the type $[Os(NR')(R)_4]$ (R' = CH_3, CH_2Ph, or CH_2SiMe_3) and $[Os(O)(NBu^t)(mes)_2]$ are discussed in Section II,C,2,f, and *trans*-$[Os(NH)(CN)_4(OCOCF_3)]$ is discussed in Section II,C,6,o.

TABLE IV

MONONUCLEAR NITRIDO COMPLEXES

Complex	Studies and references
Os(VIII)	
$[Os(O)_3(N)]^-$ and $[Os(O)_3(N)L]^-$	Sections II,B,2 and II,C,6,b
Os(VI)	
$[Os(N)(CN)_5]^-$	Preparation, IR, UV/Vis, X-ray (*266*)
$[OsNR_4]^-$	Section II,C,2,f
cis-$[OsNR_2X_2]^-$	Section II,C,2,f
$[OsNX_4]^-$	IR, Raman, emission, Xtal Vis (*267*); ^{35}Cl, ^{81}Br, and ^{127}I NQR (*262, 263*); XPS (*268*)
$[Os(N)(NH_3)_4]^{3+}$	Preparation, react., UV/Vis, photochem., CV (*269, 270*)
$[Os(N)(\eta^4\text{-hba-b})]^-$	Section II,C,4,x
$[Os(N)X_5]^{2-}$	^{35}Cl, ^{81}Br, and ^{127}I NQR (*263*); XPS (*268*)
trans-$[Os(N)X_4L]^-$	^{35}Cl, ^{81}Br, and ^{127}I NQR (L = $NCCH_3$, H_2O) (*262, 263*), XPS (L = $NCCH_3$, H_2O, py) (*268*), preparation, cond., IR, photochem., reactions (X = CN^-, L = OH^-) (*266*)
$[Os(N)(trpy)X_2]^+$	Section II,C,4,e
$[Os(N)(L)_2Cl_3]$, L = N heterocycle	Section II,C,4,e
Os(V)	
trans-$[Os(N)L_2(OH_2)]$, L = 1-amidino-2-thioureas	Mag., therm. anal., IR (*271*)
trans$[Os(N)(CN)_4(OH)]^{3-}$	Preparation and reactions (*266*)
$[Os(trpy)(bpy)(N)]^{2+}$	Reactions (*43*)

q. Nitrido Complexes. Apart from the μ-nitrido complexes that are discussed in Sections II,B,3,b and II,D, a large number of mononuclear complexes have been prepared. General synthetic routes have been discussed in Section II,B,3,a and in Griffith's review (*2*). A summary of publications since Griffith's review is given in Table IV (*43, 262, 263, 266–271*).

r. Azido Complexes. $[Os(N_3)(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SNNMe_2)]$ has been reported (*185*).

s. Cyanato Complexes. *trans*-$[Os(O)_2(NCO)_4]^{2-}$ is prepared by the reaction of *trans*-$[Os(O)_2(OR)_4]^{2-}$ (R = H or CH_3) with KCNO in methanol. The binding mode has been assigned on the basis of IR and Raman

spectroscopies and its UV/Vis spectrum has been reported (*272*). *trans-O,O-cis-C,C*-$[Os(O)_2(CN)_2(NCO)_2]^{2-}$ has been characterized by IR and Raman spectroscopies (Section II,C,2,a) (*113*). On the basis of IR spectroscopy, the reaction product of $[OsF_6]$ with $(CH_3)_3Si(NCO)$ is believed to be either $[OsF_4(NCO)]$ or $[OsF_5(NCO)]$, but the product was not well characterized (*273*).

t. Thiocyanato Complexes. $[OsX_6]^{2-}$ (X = Cl, Br, or I) or $[Os(O)_2(OH)_4]^{2-}$ react with aqueous or methanolic solutions of KSCN to give $[Os^{III}(NCS)_n(SCN)_{6-n}]^{3-}$. The isomeric mixture is separated by chromatography to yield all possible isomers, i.e., $[Os(NCS)_6]^{3-}$, $[Os(NCS)_5(SCN)]^{3-}$, *cis-* and *trans*-$[Os(NCS)_4(SCN)_2]^{3-}$, *fac-* and *mer*-$[Os(NCS)_3(SCN)_3]^{3-}$, *cis-* and *trans*-$[Os(NCS)_2(SCN)_4]^{3-}$, $[Os(NCS)(SCN)_5]^{3-}$, and $[Os(SCN)_6]^{3-}$. Most of these complexes have been isolated previously (*2*), but it is the first time that the complete series has been characterized. The complexes are reversibly oxidized to the Os(IV) complexes and generally irreversibly reduced to Os(II). Chemical oxidation with Ce(IV) occurs without linkage isomerization to give the Os(IV) series, except for $[Os(SCN)_6]^{3-}$, which is obtained pure only by repeated crystallization. A complete IR, Raman, and electronic spectroscopic analysis of all of the Os(III) and Os(IV) complexes, including a study of the near-infrared electronic transitions, has been completed (*274, 275*).

$[Os(NH_3)_5(NCS)]^{2+}$ was first prepared by the reaction of $[Os(NH_3)_5(OH_2)]^{3+}$ with KSCN in water (*197*), and, more recently, by the reaction of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ with NH_4SCN in acetone (*198*). It undergoes a reversible reduction to the Os(II) complex and an irreversible oxidation to Os(IV). A complete analysis of the Raman and IR spectra (including deuteration experiments) has been reported, and the electronic spectra, including near-infrared bands, are discussed. $[Os(NH_3)_4(NCS)_2]^+$ and $[Os(NH_3)_3(NCS)_3]$ are by-products of the reactions, but have not been characterized (*198*).

trans-$[Os(O)_2(OR)_4]^{2-}$ (R = H or CH_3) react with KSCN in methanol to give *trans*-$[Os(O)_2(NCS)_4]^{2-}$, which on the basis of its Raman and IR spectra has all the NCS^- ligands N bound. The UV/Vis spectrum is strongly vibronically coupled at 10 K (*272*). $[OsO_4]$ reacts with either $NO_2^-/H^+/NCS^-$ or $NO_2^-/H^+/NCS^-$/phen to produce $[Os(NO)(NCS)_5]^{2+}$ and $[Os(NO)(NCS)_3(phen)]$, previously synthesized using NH_2OH instead of NO_2^- (*276*). *trans,trans,trans*-$[Os(O)_2(CN)_2(NCS)_2]^{2-}$ has been prepared and characterized by IR and Raman spectroscopies (Section II,C,2,a) (*113*). *cis*-$[Os(N)(CH_2SiMe_3)_2(NCS)(X)]^-$ (X = SCN^- or NCS^-) are obtained by the addition of two equivalents of KSCN to *cis*-$[Os(N)(CH_2SiMe_3)_2Cl_2]^-$ (*156*).

u. Selenocyanato Complexes. $[Os(NCSe)_n(SeCN)_{6-n}]^{3-}$ [n = 0–3, including cis and trans (n = 2) and fac and mer (n = 3) isomers] and $[Os^{III}(NH_3)_5(NCSe)]^{2+}$ have been prepared, purified, and characterized by IR, Raman, and UV/Vis spectroscopies in the same manner as their NCS^- analogs (*198, 277*). $[Os(NH_3)_4(NCSe)_2]^+$ and $[Os(NH_3)_3(NCSe)_3]$ are by-products of the preparation of $[Os(NH_3)_5(NCSe)]^{2+}$, but have not as yet been characterized (*198*).

v. Nitro and Thionitro Complexes. Treatment of *cis*-$[Os(L\text{-}L)(NO)(OH_2)]^{3+}$ with NO_2^-/NH_3 results in the formation of *cis*-$[Os(L\text{-}L)_2(NO_2)_2]$, which reacts with acid to form *cis*-$[Os(L\text{-}L)_2(NO)(NO_2)]^{2+}$ (L-L = bpy or phen). The complexes were characterized by IR spectroscopy (*247*). $[Os(trpy)(bpy)(NO_2)]^{2+}$ is prepared by the reaction of $[Os(trpy)(bpy)(NO)]^{3+}$ with OH^-. It undergoes reversible oxidation to the Os(III) analog (*43*). The reaction of $[Os(bpy)_2(CO)(Cl)]BF_4$ with Me_3NO and NO_2^- results in the synthesis of *cis*-$[Os(bpy)(NO_2)Cl]$ (*278*).

$[M(NO)(NH_3)_4(OH)][M'(NO)(NO_2)_4(OH)]$ (M = Os, M′ = Os or Ru; M = Ru, M′ = Os) have been prepared and characterized by electrical conductivity, X-ray phase and thermal analysis, and IR spectroscopy (*279*).

$[Os(NSO)(X)_2(PPh_3)_2]$ (X = Cl^- or Br^-) are obtained from reactions of $[Os(NO)(Cl)_3(PPh_3)_2]$ with elemental sulfur in benzene. They were characterized by magnetic measurements and IR and electronic absorption spectroscopies. No indication of the binding mode of the NOS^- ligand has been given, but it is presumably N bound. It is the first example of the binding of such a ligand to Os (*246*).

w. Schiff Base Complexes. Complexes of the type *trans*-$[Os(O)_2(salen)]$ have been prepared and characterized by CV and by IR, UV/Vis, and ^1H NMR spectroscopies, and the X-ray structure of *trans*-$[Os(O)_2(3\text{-}Bu^t\text{-}saltmen)]$ has been reported. All complexes exhibit irreversible oxidations and reductions in acetonitrile (*280*). *trans*-$[Os^{VI}(salen)(O)_2]$ is converted to *trans*-$[Os(salen)(ER)_2]$ (ER = OMe^-, OEt^-, or SPh^-) by methods similar to those of their porphyrinato analogs (Section II,C,4,d). The complexes were characterized by IR, UV/Vis, and ^1H NMR spectroscopies, and in the case of the phenylthiolato complex, by X-ray diffraction (*281*). More recently, a series of Schiff base complexes of the type *trans*-$[Os^{VI}(O)_2L]$ (L = $(ba)_2en$, $(aa)_2en$, $(Bu^t)_2en$)) and *trans*-$[Os^{IV}(SR)_2\{(ba)_2en\}]$ (R = C_6H_5, $CH_2\text{-}C_6H_5$, $3\text{-}MeC_6H_4$, $4\text{-}FC_6H_4$, 2-naphthyl, Et, Bu, cyclohexyl) have been prepared by similar methods and characterized by ^1H NMR, UV/Vis, and IR spectroscopies and electrochemistry. The X-ray structures

of *trans*-[$Os^{VI}(O)_2${$(ba)_2en$}] and *trans*-[$Os^{IV}(SCH_2C_6H_5)_2${$(ba)_2en$}] · 0.5 H_2O were also reported (*281a*). [OsL_3] and [OsL_2Cl_2] [HL = 2-$HOC_6H_4CR{=}NR'$; R = Me, R′ = 4-XC_6H_4 (X = H, Me, OMe, CO_2Et, or Cl)] have been prepared and characterized by CV, EPR, and UV/Vis/NIR spectroscopies. The complexes in the Os(II), Os(III), and Os(IV) oxidation states have been characterized from the electrochemistry (*282*). [$OsL(H)(CO)(PPh_3)_2$] and [$OsL(Cl)(CO)(PPh_3)_2$] [HL = 2-$HOC_6H_4CH{=}NR$; R = Ph, $C_6H_5CH_2$, or 2- or 4-XC_6H_4 (X = CH_3, Cl, Br, or NO_2)] have also been prepared and characterized by NMR spectroscopy (*129*).

x. Chelating Amide Ligands. Although, this area of Os chemistry has only been developed recently, it has resulted in a considerable amount of new and interesting chemistry. The structures of the chelating amide ligands are given in Fig. 6, along with the structures of the cis-α and cis-β isomers referred to in this section.

The reaction of $bpbH_2$ with $K_2[Os(O)_2(OH)_4]$ yields *trans*-[Os^{III}-$(bpbH_2)(O)_2]Cl_2$. This is deprotonated by Et_3N to give *trans*-[Os-$(bpb)(O)_2$] or reacts with PPh_3 in MeOH to give *trans*-[Os-$(bpb)(PPh_3)(Cl)$]. The structure of the latter has been determined by X-ray crystallography, and its CV exhibits a reversible Os(IV/III) redox couple and a quasi-reversible Os(III/II) redox couple. [$Os(bpb)(PPh_3)Cl$] reacts with PhIO to form a complex that is believed to be an Os(V) oxo complex. This species is a useful catalytic intermediate in the epoxidation of cyclohexane by PhIO (*283*).

Recently, complexes with tetradentate amide/phenol ligands have been studied extensively because of the abilities of the ligands to stabilize high oxidation states (*44, 146, 283–290*). $[Os(O)_2(OH)_4]^{2-}$ reacts with H_4chba-Et to yield *trans*-[$Os(\eta^4$-chba-Et$)(O)_2]^{2-}$, which, in the presence of O_2/PPh_3, gives K_2[{*trans*-$Os(\eta^4$-chba-Et$)(OPPh_3)$}$_2O$] (*290*) or, in the presence of py or 4-Bu^{t}py, gives *trans*-[$Os^{III}(\eta^4$-chba-Et$)(Xpy)_2]^-$ (*289*). The X-ray structure of the oxo dimer has been determined (*290*). The bis(pyridine) complexes exhibit rich redox chemistry that is both metal and ligand centered; they are reversibly reduced to Os(II) and are oxidized to Os(IV). An X-ray structure of *trans*-[$Os^{IV}(\eta^4$-chba-Et$)(py)_2$] has been determined and the Os(IV) complexes are irreversibly oxidized at the ligands. This oxidation occurs in stages, giving *trans*-[$Os(\eta^4$-chba-ethylene$)L_2$], *trans*-[$Os(\eta^4$-chba-*t*-1,2-diRO-Et$)L_2$] (R = H, Me, or Et), *trans*-[$Os(\eta^4$-chba-*t*-1-OH-2-OMe-Et$)L_2$], and *cis*- and *trans*-[$Os(\eta^2$-fo-chba$)_2L_2$] (L = py or 4-Bu^{t}py) (*289*). Heating the latter in acid results in the decarbonylation of the complexes to form *cis*- and *trans*-[$Os(\eta^2$-chba$)_2L_2$]. These complexes are also prepared via

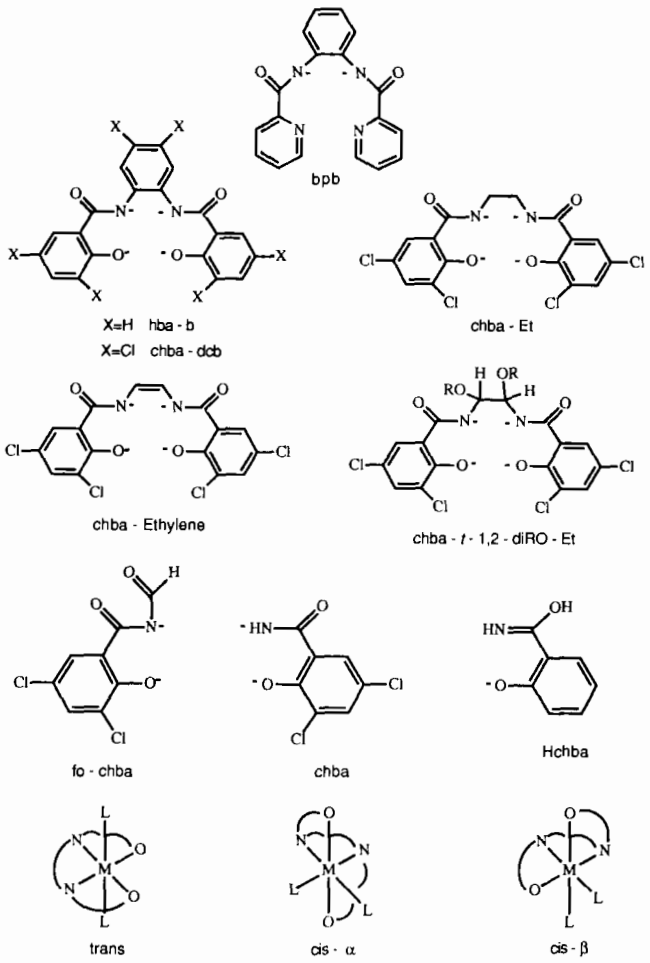
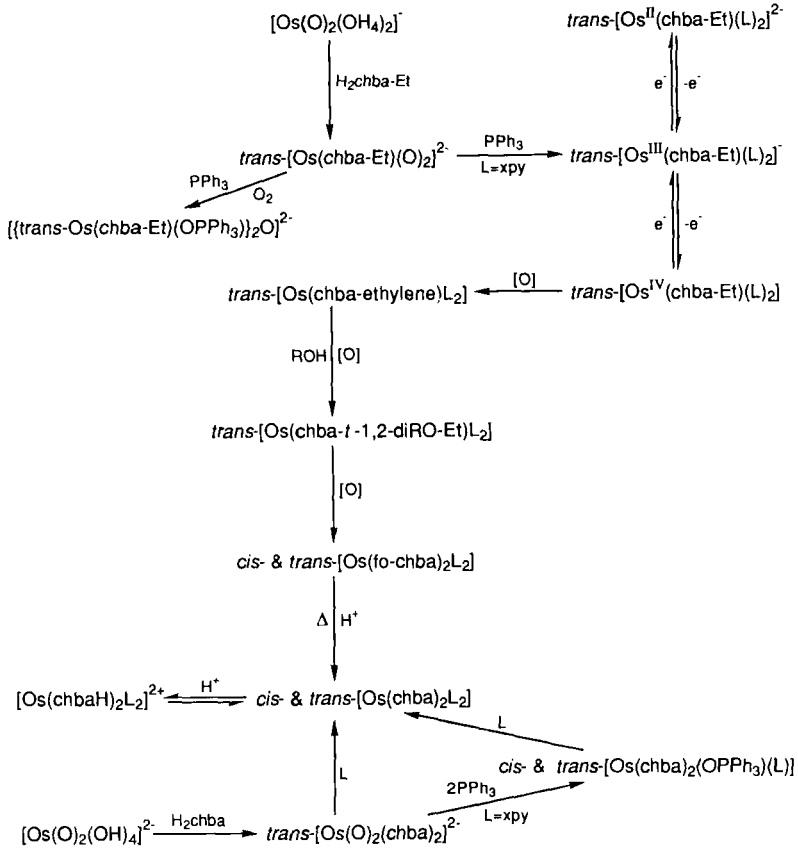


FIG. 6. Structures of the chelating amide ligands and the trans, cis-α, and cis-β geometric isomers of their complexes.

the $[Os(\eta^2\text{-chba})_2(O)_2]^{2-}$ intermediate (*287*). If $K_2[Os(\eta^2\text{-chba})_2(O)_2]$ is allowed to react with two equivalents of PPh_3, in the presence of 4-Bu^{t}py, *cis*- and *trans*-$[Os(\eta^2\text{-chba})_2(4\text{-Bu}^t\text{py})(OPPh_3)]$ are obtained. *cis*-α- or *trans*-$[Os(\eta^2\text{-chba})_2(4\text{-Bu}^t\text{py})_2]$ is protonated without isomerization to give *cis*-α- or *trans*-$[Os(\eta^2\text{-Hchba})(4\text{-Bu}^t\text{py})_2]^{2+}$, respectively (*287*). The structures of *trans*-$[Os(\eta^4\text{-chba-ethylene})(4\text{-Bu}^t\text{py})_2]$ (*287*), *trans*-$[Os(\eta^4\text{-chba-}t\text{-1-OH-2-OMe-Et})(py)_2]$ (*287*), *cis*- and *trans*-$[Os(\eta^2\text{-fo-chba})_2(4\text{-Bu}^t\text{py})_2]$ (*289*), and *trans*-$[Os(\eta^2\text{-chba})_2(4\text{-Bu}^t\text{py})_2]$ (*287*)

have been determined by X-ray crystallography and the complexes have been extensively characterized by NMR spectroscopy and other techniques. *trans*-[Os(η^4-chba-ethylene)L_2] exhibit two reversible one-electron reductions and reversible one-electron oxidations to the nominal Os(V) complexes in the absence of ROH (*289*). The electrochemistry of *trans*-[Os(η^4-chba-Et)(py)$_2$], *trans*-[Os(η^4-chba-ethylene)(py)$_2$], *trans*-[Os(η^4-chba-*t*-1,2-diEtO-Et)(py)$_2$], and *cis*-[Os(η^2-fo-chba)$_2$-(py)$_2$] have also been studied in liquid SO_2 at 40°C. All complexes show a series of reversible oxidations in addition to a reversible Os(IV/III) couple (*284*). The chemistry of this system is summarized in Scheme 12.

The complexes in which the ethylene bridge has been replaced by a phenylene bridge are considerably more stable to oxidation, and a



SCHEME 12. Chemistry of the Os/η^4-chba-Et system.

different type of chemistry ensues. $K_2[Os(O)_2(L)]$ (L = chba-dcb or hba-b) are prepared as indicated above (*288, 289*). Treatment with PPh_3 and CF_3CO_2H results in the synthesis of *trans*-$[Os^{IV}L(PPh_3)_2]$, or treatment with PPh_3 and 4-Xpy results in *trans*-$[Os^{IV}L(4\text{-Xpy})_2]$ (L = chba-dcb, X = H, MeO, Et, Me, Cl, Br, Ac, or Bu^t) (*288, 289*). *trans*-$[Os(\eta^4\text{-hba-b})(PPh_3)_2]$ reacts with one equivalent of CO to form *cis*-α-$[Os(\eta^4\text{-hba-b})(PPh_3)(CO)]$ (*146*); it reacts with phen to give *mer*-$[Os^{III}(\eta^3\text{-Hhba-b})(PPh_3)(phen)]$ (*286*) and with Bu^tNC or dppe to give *cis*-α-$[Os(\eta^4\text{-hba-b})(PPh_3)(CNBu^t)]$ and *cis*-β-$[Os(\eta^4\text{-hba-b})(dppe)]$, respectively (*288*). The structures of the first two complexes have been determined by X-ray crystallography (*146, 286*). *mer*-$[Os^{III}(\eta^3\text{-Hhba-b})(PPh_3)(phen)]$ is reversibly reduced to the corresponding Os(II) complex and oxidized to the Os(IV) complex. The ligand is also acetylated using Ac_2O to form *mer*-$[Os\{\eta^3\text{-}(CH_3CO)\text{hba-b}\}(PPh_3)(phen)]$ (*286*). $[Os(\eta^4\text{-hba-b})(PPh_3)_2]$ also reacts with azides to give $[Ph_3N\text{-}NH_2][Os^{VI}(\eta^4\text{-hba-b})(N)]$, in the case of Me_3SiN_3 and *cis*-β-$[Os^{VI}(\eta^4\text{-hba-b})(\eta^2\text{-PhNC}_6H_4NH)]$, in the case of PhN_3. Both products have been characterized by X-ray crystallography (*44*).

trans-$[Os^{IV}(\eta^4\text{-chba-dcb})(PPh_3)_2]$ reacts with one equivalent, or excess 4-Bu^tpy, to give *trans*-$[Os(\eta^4\text{-chba-dcb})(PPh_3)(4\text{-}Bu^t\text{py})]$ and *trans*-$[Os(\eta^4\text{-chba-dcb})(4\text{-}Bu^t\text{py})_2]$, respectively; it reacts with bpy, Bu^tNC, or dppe to give *cis*-α- and *cis*-β-$[Os(\eta^4\text{-chba-dcb})(bpy)]$, *cis*-$\alpha$-$[Os(\eta^4\text{-chba-dcb})(PPh_3)(CNBu^t)]$, or *cis*-$\beta$-$[Os(\eta^4\text{-chba-dcb})(dppe)]$, respectively. It is also oxidized by iodosylbenzoic acid to give *trans*-$[Os(\eta^4\text{-chba-dcb})(OPPh_3)_2]$ (*146, 288, 289*). The structures of *cis*-$[Os(\eta^4\text{-chba-dcb})(bpy)]$ and *cis*-α-$[Os(\eta^4\text{-chba-dcb})(PPh_3)(CNBu^t)]$ have been determined by X-ray crystallography. Treatment of *trans*-$[Os(\eta^4\text{-chba-dcb})(O)_2]$ with PPh_3 and $CNBu^t$ followed by oxidation was initially reported to yield *trans*-$[Os(\eta^4\text{-chba-dcb})(CNBu^t)_2]$ (*289*), but the isomer was shown subsequently to be *cis*-α-$[Os(\eta^4\text{-chba-dcb})(CNBu^t)_2]$ (*288*). These complexes undergo reversible oxidations to their corresponding Os(V) complexes and two reversible one-electron reductions to their Os(III) and Os(II) analogs. On either oxidation or reduction, the complexes undergo geometric isomerization reactions. In the case of *cis*-α-$[Os(\eta^4\text{-chba-dcb})(CNBu^t)_2]$, a two-electron reduction followed by a two-electron oxidation results in the preparation of *cis*-β-$[Os(\eta^4\text{-chba-dcb})(CNBu^t)_2]$. Oxidation of *trans*-$[Os(\eta^4\text{-chba-dcb})(L)_2]$ (L = 4-*t*-Bupy or $OPPh_3$) followed by reduction at low temperatures with Fc results in the isolation of the *cis*-α-$[Os(\eta^4\text{-chba-dcb})(L)_2]$ isomers together with their trans analogs. Generally, the equilibrium constants for the geometric isomerizations are oxidation-state dependent, with *cis*-α-$[Os(\eta^4\text{-chba-dcb})(4\text{-Xpy})_2]$ isomers becoming more stable relative to the trans

isomers as the higher oxidation states are obtained. The cis complexes are rare examples of complexes with nonplanar amides. Their formation can be rationalized by consideration of the electronic demands of the higher oxidation states, because nonplanar amides maximize π donation. The equilibrium constants for the cis-α to trans isomerizations for X = Ac, Cl, Br, H, Me, Et, Bu^t, and MeO have been determined in the formal oxidation states Os(V), Os(IV), Os(III), and Os(II). They fall in the range of 0.1–1, 10–10^2, 10^{11}–10^{12}, and 10^{13}–10^{15}, respectively, for the four oxidation states at ambient temperatures, consistent with the electronic arguments discussed above. The equilibrium constants correlate with the Hammett substitutent constant of *X* (*288, 289*), and the kinetics of the isomerization reactions of *cis*-α- and *trans*-[Os(η^4-chba-dcb)($OPPh_3$)$_2$]$^{0/+}$ have been followed using UV/Vis and ^{1}H NMR spectroscopies. There is no ligand exchange during the isomerization reaction, and together with other evidence, this suggests a twist mechanism (*285*). The electrochemistry of *trans*-[Os(η^4-chba-dcb)(L)$_2$] (L = py or PPh_3) has also been followed in liquid SO_2 at − 60°C. In addition to the reversible Os(IV/III) couple, three other reversible oxidations are observed, together with a less reversible fourth oxidation. It appears that these processes are ligand centered. The electrochemistry of *cis*-α-[Os(η^4-chba-dcb)($CNBu^t$)$_2$] has also been studied in liquid SO_2, but the oxidations are less reversible in this case (*284*).

The related complex containing a chelating amido/aldehyde ligand, H_2phenba, reacts with [Os(O)$_2$(OH)$_4$]$^{2-}$ to give *trans*-[Os(O)$_2$(phenba)], which reacts with PPh_3 to give *trans*-[Os^{II}(phenba)(PPh_3)$_2$]. All complexes have been characterized by UV/Vis, IR, and ^{1}H NMR spectroscopies and cyclic voltammetry (*291*).

y. Quinolol Complexes. $(NH_4)_2[OsX_6]$ react with Hquin to give [Os^{IV}(quin)$_2$X$_2$], which, on further reaction with Hquin, yield [Os^{III}-(quin)$_3$], (X = Cl^- or Br^-). [Os(quin)$_2$X$_2$] is reduced by $NH_2NH_2 \cdot H_2O$ to yield [Et_4N][Os^{III}(quin)$_2$X$_2$], and [Os(quin)$_3$] is oxidized by Ce(IV) to give [Os^{IV}(quin)$_3$]ClO_4. The tris bidentates are assigned as having a mer structure and the bis complexes are assigned a trans,trans,trans structure on the basis of IR spectra and other considerations. All complexes exhibit reversible Os(III/II) and Os(IV/III) redox couples and a further oxidation is observed. The near-infrared and EPR spectra have also been recorded and interpreted (*282*).

z. Benzotriazole, 1,3-Diaryltriazene, 2-(Phenylazo)pyridine, and (Phenylazo)acetaldoxime Complexes. [Os(H)$_2$(CO)(PPh_3)$_3$] reacts with benzotriazole to give *trans*-[Os(bta···H···bta)(H)(CO)(PPh_3)$_2$], which

X-ray crystallography has shown to have two hydrogen-bonded bta ligands to form a chelate. Similar reactions with $[OsCl_2(PPh_3)_3]$ result in the linkage isomers, $[Os(bta\cdots H\cdots bta)_2\{\eta^1\text{-}(N^2)\text{-}btaH\}(PPh_3)]$ and $[Os(bta\cdots H\cdots bta)_2\{\eta^1\text{-}(N^3)\text{-}btaH\}(PPh_3)]$. All complexes have been characterized by IR and NMR (^1H, ^{13}C, and ^{31}P) spectroscopies (*292*).

$[OsCl_2(PPh_3)_3]$ reacts with ArNNNAr (Ar = C_6H_5, 4-MeC_6H_4, or 4-ClC_6H_4) in aerobic benzene solutions to give $[OsCl_2\{\eta^2\text{-}(N,N'')\text{-}ArNNNAr\}(PPh_3)_2]$, which were characterized by IR spectroscopy and magnetic measurements (*293*). The complexes are identical to those prepared by the reactions of Li[PhNNNPh] with $[OsX_4(PPh_3)_2]$ or $[OsX_2(O)_2(PPh_3)_2]$ (*255*). $[Os(ArNNNAr)_3]$ are prepared from $[OsCl_6]^{2-}$ and the ligand and have been characterized by magnetic measurements and IR, Raman, and ^1H NMR spectroscopies, and $[OsCl_2(ArNNNAr)_2]$ have also been reported (*293*).

Geometric isomers of $[OsX_2(L\text{-}L)_2]$ [L-L = 2-(R-phenylazo)pyridine (R = H, 3-Me, or 4-Me_2N); X = Cl^- or Br^-], in which the ligand is bound via both the azo and pyridine nitrogens, have been characterized by ^1H NMR spectroscopy (*294*). The X-ray structure of the cis,cis,cis complex with R = 3-Me and X = Cl^- was determined (*295*). (Phenylazo)acetaldoxime (HL) reacts with $[OsBr_6]^{2-}$ to give *fac*-$[Os^{II}L_3]^-$. The uncoordinated oxygens of the oxime groups act as tridentate ligands for other metal ions to form trimers of the type $[OsL_3ML_3Os]$ (M = Mg, Mn, Co, or Ni) and $[OsL_3FeL_3Os]^+$. These complexes have been characterized by electrochemistry, ^1H NMR, and EPR spectroscopies (*296*).

5. *Phosphorus, Arsenic, and Antimony*

a. Phosphine Complexes. Complexes containing only phosphine ligands will be discussed. Table V lists relevant sections for phosphine complexes with other ligands, except for halide and hydride complexes, which are listed in Tables VI (*15, 97, 145, 234, 293, 297–305*) and VII (*128, 138, 297, 299, 301, 306–309*), respectively.

$[Os^0(PMe_3)_5]$ has been prepared from the Na reduction of *trans*-$[OsCl_2(PMe_3)_4]$ in thf containing an excess of PMe_3 and a catalytic amount of naphthalene. At room temperature, a singlet is observed in the $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectra, characteristic of fluxional behavior, whereas the spectra at $-100°C$ in thf are consistent with a trigonal-bipyramidal structure. The complex reacts with traces of moisture or triflic acid to produce the hydride complex, $[Os(PMe_3)_5H]^+$. In the absence of excess ligand, $[Os(PMe_3)_5]$ is in equilibrium with $[Os(PMe_3)_4]$, which undergoes an intramolecular oxidative addition reaction

TABLE V

PHOSPHINE COMPLEXES APART FROM HYDRIDES AND HALIDES

Complex or coligand	Section	Complex or coligand	Section
Osmaboranes	II,C,1	Osmacarboranes	II,C,1
CO	II,C,2,b	CS, CSe, CTe	II,C,2,c
CO_2	II,C,2,d	CS_2, CSSe, $SCSMe^-$	II,C,2,e
Alkyl and aryl	II,C,2,f	Carbene	II,C,2,g
Alkene	II,C,2,h	Allyl	II,C,2,l
Isonitrile	II,C,2,n	Formyl and C esters	II,C,2,o
SiR_3	II,C,3	Porphyrins	II,C,4,d
N heterocycles	II,C,4,e	NO, NO^+	II,C,4,f
Nitrosoarene	II,C,4,g	Hydroxylamine	II,C,4,h
NS, NS^+	II,C,4,i	N_2	II,C,4,j
Oximes	II,C,4,l	NCR	II,C,4,n
Imido	II,C,4,p	N_3^-	II,C,4,r
NOS^-	II,C,4,v	Schiff bases	II,C,4,w
Chelating amides	II,C,4,x	Diaryltriazenes	II,C,4,z
Benzotriazole	II,C,4,z	η^2-CH_2PR_2	II,C,5,c
Stibines	II,C,4,f	H_2O and OH^-	II,c,6,a
ROH, RO^-	II,C,4,c	Maltolate and tropolonate	II,C,6,d
Amide	II,C,6,g	Diketonates	II,C,6,k
O_2	II,C,6,m	CO_3^{2-}	II,C,6,n
RCO_2^-	II,C,6,o	RSO_3^-	II,C,6,q
O-sulfinate	II,C,6,r	RS^-	II,C,7,c
S_2	II,C,7,d	HSe^-	II,C,7,e
btd and bsd	II,C,7,h	*S*-dmso	II,C,7,i
$SNNMe_2$	II,C,7,j	Iminooxosulfane	II,C,7,k
SO_2, S_2O	II,C,7,l	*S*-sulfinato	II,C,7,m
$R_2NCS_2^-$ and xanthate	II,C,7,q	$R_2PS_2^-$	II,C,7,r
PyS, pymS	II,C,7,v	BH_4^-	II,C,9,b
H_2	II,C,9,c		

to form $[Os^{II}(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(H)]$. The latter is also prepared from the Na reduction of *trans*-$[OsCl_2(PMe_3)_4]$ in the absence of excess PMe_3. $[Os(PMe_3)_5]$ undergoes slow ligand exchange reactions with $P(CD_3)_3$, and the activation energy for the process, which is believed to occur via the $[Os(PMe_3)_4]$ intermediate, is ~116 kJ mol^{-1} (*15*). $[Os(PMe_3)_4]$ and $[Os(PMe_3)_3]$ are also believed to be intermediates in the thermolysis of *cis*-$[Os(PMe_3)_4(R)(H)]$ (*15, 165, 306, 310, 310a*).

b. Phosphite Complexes. Although less numerous, these complexes exhibit chemistry similar to that of their phosphine analogs, e.g., $[Os(4\text{-}MeC_6H_4N{=}NH)(4\text{-}MeC_6H_4NC)L_4]^+$ [L = $P(OEt)_3$ or $PPh(OEt)_2$; see

TABLE VI

MONONUCLEAR PHOSPHINE/HALIDE COMPLEXES

Complex	Studies and references
Os(II)	
mer-$[OsCl_3(PMe_2Ph)_3]^-$	CV, chloride loss (*145*)
$[OsCl_2(PMe_2Ph)_3]$	CV, addition of π-acid ligands (*145*)
$[OsCl_2(PPh_3)_3]$	Reactions with diarylazides (*293*)
cis-$[Os(PMe_3)_4(H)Cl]$	Prep. (*297*)
cis-$[OsX_2(PMe_3)_4]$, X = Cl^-, Br^-, or I^-	Preparation (*298*)
cis-$[OsCl_2(PR_2CH_2CH_2PR_2)_2]$	Preparation and reaction with H_2 (*299*)
cis-$[OsX_2(L\text{-}L)_2]$, L-L = dcpe, X = Cl^- or Br^-	Preparation, IR, UV/Vis, cond., ^{31}P NMR (*300*)
cis-β-[$OsCl_2$(*meso*-tetraphos)]	Reaction with H_2 (*301*)
trans-$[OsCl_2(PMe_3)_4]$	Na reduction (*15*)
trans-$[OsX_2(PR_3)_4]$, X = Cl^- or Br^-	Prep. (*302*)
trans-$[OsX_2(L\text{-}L)_2]$, L-L = dcpe, X = Cl^- or Br^-	Preparation, IR, UV/Vis, cond., ^{31}P NMR (*300*)
trans-$[OsX_2(L\text{-}L_2]$, L-L = dmpe, dppe, or dppm; X = Cl^- or Br^-	Prep. (*302*)
trans-$[OsX_2(L\text{-}L)_2]$, L-L = $(Ph_2P)]_2C{=}CH_2$	Preparations, X-ray (*303*)
trans-[Os(H)Cl(*meso*-tetraphos)]	Reaction with H_2 (*301*)
trans-P,P-$[OsBr_2(CO)_2(PPh_3)_2]$	X-Ray (*304*)
$[OsCl(L\text{-}L)_2]^+$, L-L = $Ph_2P(CH_2)_3PPh_2$ or $Ph_2P(CH_2)_2$(2-py)	Epoxidation catalysts (*305*)
$[OsX(L\text{-}L)_2]^+$, L-L = dcpe, X = Cl^- or Br^-	Preparation, IR, UV/Vis, cond., ^{31}P NMR, addition reactions with PhCN, MeCN, and CO (*300*)
Os(III)	
trans-$[OsX_4(PR_3)_2]^-$, L = PEt_3, PPh_3, PEt_2Ph, or $PEtPh_2$; X = Cl^- or Br^-	Preparation, IR, UV/Vis, mag., NMR, CV (L = PEt_3, X = Cl^-) X-ray (*302a*)
mer-$[OsL_3X_3]$, X = Cl^- or Br^-; L = PMe_3, PEt_3, $PEtPh_2$, PEt_2Ph, or PMe_2Ph	Preparation, UV/Vis, IR, CV (*97, 145, 234, 302*)
fac-$[Os(PEt_2Ph)_3Cl_3]$	Preparation, UV/Vis, IR, CV, X-ray (*234*)
trans-$[OsX_2(PR_3)_4]^+$	Preparation (*302*)
Os(IV)	
trans-$[OsX_4(PR_3)_2]$, L = PEt_3, PPh_3, PEt_2Ph, or $PEtPh_2$; X = Cl^- or Br^-	Preparation, IR, UV/Vis, mag., NMR, CV (*302*)
mer-$[OsL_3X_3]^+$, X = Cl^- or Br^-; L = PMe_3, PEt_3, $PEtPh_2$, or PEt_2Ph	Preparation, UV/Vis, IR, CV (*234*)

TABLE VII

MONONUCLEAR PHOSPHINE/HYDRIDE COMPLEXES

Complex	Studies and references
Os(II)	
cis-$[Os(H)_2(PMe_3)_4]$	Preparation (*297*)
cis-$[Os(H)_2(PR_2CH_2CH_2PR_2)_2]$	Preparation (*299*)
cis-α-[Os(H)$_2$(*rac*-tetraphos)]	Reaction with HBF_4 (*301*)
cis,mer-$[Os(H)_2(PMe_2Ph)_3(CO)]$	Preparation (*138*)
$[Os(H)(PMe_3)_4]^+$	Intermediate (*297, 306*)
$[Os(H)(PMe_3)_5]^+$	Preparation (*297, 306*)
Os(IV)	
$[Os(H)_4(PR_3)_3]$	Protonation (Section II,C,9,c), photochemistry (*307*)
$[Os(H)_4(CO)(PPr^i_3)_2]$	Preparation (*128*)
$[Os(H)_3(PR_3)_4]^+$	Preparation, R = Me (*297*); preparation, X-ray, ^{31}P NMR, fluxionality, R = Ph (*308*)
Os(VI)	
"$[Os(H)_5(PR_3)_3]^{+}$"	Reassignment as $[Os^{IV}(\eta^2\text{-}H_2)(H)_3(PR_3)_3]^+$ (Section II,C,9,c)
$[Os(H)_6(PPhPr^i_2)_2]$	Neutron diffraction (*309*)

Section II,C,4,m] and $[Os(H)(CNR)(L)_4]^+$ [L = $PPh(OEt)_2$, $P(OMe)_3$, or $P(OEt)_3$; R = 4-$MeOC_6H_4$ or 4-MeC_6H_4], which were characterized by NMR (^1H and ^{31}P) and IR spectroscopies (*187*), and *trans*-$[OsCl_2\{P(OPh)_3\}_4]$ (*18*) and $[Os(CO)_3\{P(OCH_2)_3CEt\}(SiMeCl_2)_2]$ (Section II,C,3). The hydride complexes $[Os(H)_2L_4]$ (L = $P(OEt)_3$ or $PPh(OEt)_2$) have also been prepared and characterized (*188*), and complexes with H_2 ligands have been reported (Section II,C,9,c).

c. η^2-CH_2PR_2 Complexes. The intramolecular oxidative addition of $[Os(PMe_3)_4]$—produced from the thermolysis of *cis*-$[Os(PMe_3)_4(H)(R)]$ or reduction of *trans*-$[OsCl_2(PMe_3)_4]$—gives $[Os(H)(\eta^2\text{-}CH_2PMe_2)(PMe_3)_3]$ (see Section II,C,5,a) (*15, 310*), and its hydrogenolysis has been studied (*297*).

d. Arsine Complexes. The new arsine complexes, *mer*-$[Os(AsEt_3)_3X_3]$ (X = Cl^- or Br^-) and *fac*-$[Os(AsMe_2Ph)_3Cl_3]$, are prepared (*234*) using standard methods (*2*). Oxidation of the mer isomers by aqueous nitric acid gives the Os(IV) complexes, *mer*-$[Os(AsEt_3)_3X_3]^+$, but

the fac isomers are too unstable to be isolated (*234*). *trans*-[$Os^{IV}Br_4(AsPh_3)_2$] is prepared from the reaction of $[(Bu^n)_4N]_2[OsBr_6]$ with $AsPh_3$ and NaOAc in acetic acid/acetic anhydride. Its structure has been determined by X-ray crystallography and it has an Os—As bond length of 2.569(1) Å (*311*). The syntheses, the IR, UV/Vis, and NMR spectroscopies, and the electrochemistry of *trans*-$[OsX_4(AsR_3)_2]^{0/-}$ (X = Cl^- or Br^-; R = Et or Ph) have been studied (*302a*).

Reaction of $[Os(H)(CO)Cl(AsPh_3)_3]$, $[Os(CO)Cl_2(AsPh_3)_3]$, or $[Os(H)_2(CO)(AsPh_3)_3]$ with NOCl in CH_2Cl_2 under reflux results in $[Os(NO)Cl_3(AsPh_3)_2]$ and in *trans-As,As-cis*-$[Os(CO)_2(Cl)_2(AsPh_3)_2]$ as a by-product. $[Os(H)(CO)Cl(AsPh_3)_3]$, $[Os(CO)Cl_2(AsPh_3)_3]$, and $[Os(H)_2(CO)(AsPh_3)_3]$ react with NOBr under the same conditions to produce $[Os(NO)Cl(Br)_2(AsPh_3)_2]$, $[Os(NO)Cl_2Br(AsPh_3)_2]$, and $[Os(NO)Br_3(AsPh_3)_3]$, respectively. In each instance, *trans-As,As-cis, cis*-$[Os(CO)_2Br_2(AsPh_3)_2]$ was the by-product. All the complexes were characterized by IR spectroscopy. $[Os(NO)X_3(AsPh_3)_2]$ react with $AsPh_3$ in benzene under reflux to produce $[Os(NO)X(AsPh_3)_3]$, which are believed to be distorted trigonal bipyramidal in which the arsines occupy equatorial positions. These complexes were characterized by IR and electronic absorption spectroscopy (*246*).

$[OsO_4]$ reacts with AsR_3 in concentrated HCl/EtOH at $-50°C$ to produce *trans,trans,trans*-$[Os(O)_2Cl_2(AsR_3)_2]$ (AsR_3 = $AsEt_3$, $AsMe_2Ph$, or $AsPh_3$), which have been characterized by IR and ^1H NMR spectroscopies. If the same reaction is performed at 0°C, a mixture of *trans*-$[OsCl_4(AsR_3)_2]$ and *trans,trans,trans*-$[Os(O)_2Cl_2(AsR_3)_2]$ is obtained (*209*).

cis-$[Os(bpy)_2(AsPh_3)Cl]^+$ is prepared by heating *cis*-$[Os(bpy)_2Cl_2]$ with $AsPh_3$ in 1:1 EtOH/water. It has been characterized from its UV/Vis spectrum and electrochemistry in CH_3CN, wherin it exhibits two reversible oxidations to the Os(III) and Os(IV) analogs and a reversible reduction. A second reduction is accompanied by loss of the Cl^- ligand (*97*).

e. Diarsine Ligands. Complexes of the type *trans*-$[Os(O)_2X_2(L\text{-}L)]$ [X = Cl^- or Br^-; L-L = 1,2-$C_6H_4(AsR_2)_2$ (R = Me, Ph), $Ph_2As(CH_2)_2AsPh_2$, $Me_2As(CH_2)_3AsMe_2$, or *cis*-$Ph_2AsCH{=}CHAsPh_2$] are prepared by the reactions of HX and the ligand with $[OsO_4]$ at low temperatures in EtOH. These complexes are readily converted to $[OsX_4(L\text{-}L)]$ by heating with HX in aqueous ethanol. Although no details of the preparation or properties of the tetrahalo complexes were given, they are reported to be prepared more conveniently from the reaction of [Os-

$X_6]^{2-}$ with L-L. The *trans*-dioxo complexes were characterized by IR, ^1H NMR, and electronic absorption spectroscopies (*209*).

The tris-bidentate complexes, $[Os(phen)_2(das)]^{2+}$, $[Os(bpy)_2(das)]^{2+}$, $[Os(phen)_2(dpae)]^{2+}$, $[Os(phen)(das)_2]^{2+}$, and $[Os(bpy)(das)_2]^{2+}$, are prepared by refluxing *cis*-$[Os(N\text{-}N)_2Cl_2]$ or $[Os(N\text{-}N)Cl_4]$ with the appropriate diarsine in ethylene glycol. These complexes exhibit reversible Os(III/II) oxidations and a reversible reduction that is centred at the phen or bpy ligand. In the case of $[Os(bpy)_2(das)]^{2+}$, a second ligand-centered reduction is observed in acetonitrile. The electronic absorption and emission spectra of these complexes have also been reported (*97*). $[Os(bpy)(das)_2]^{2+}$ has been used as an effective sensitizer in a photoelectrochemical half-cell (*312*).

f. Stibine Complexes. The Os(III) complexes (*2*) *mer*-$[Os(SbPh_3)_3X_3]$ ($X = Cl^-$ or Br^-) exhibit reversible reductions to *mer*-$[Os(SbPh_3)_3X_3]^-$ and oxidations to *mer*-$[Os(SbPh_3)_3X_3]^+$, but the Os(II) and Os(IV) complexes are too unstable to isolate (*234*). The structure of *mer*-$[Os(SbPh_3)_3Br_3]$ has been reported; it is the first structural determination of a complex with an Os—Sb bond. The mutually trans Os—Sb bond lengths [2.640(2) Å and 2.654(2) Å] and that trans to an Os—Br bond [2.644(2) Å] do not differ significantly (*313*). The complex containing the mixed P–Sb chelate $[Os(O)_2Cl_2\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}]$ has been prepared by the reaction of the ligand with $[OsO_4]$ and HCl in EtOH at 0°C (*209*). Similar reactions with distibine ligands result in chlorination of the ligands, rather than formation of Os complexes (*209*). The syntheses, the IR, UV/Vis, and NMR spectroscopies, and the electrochemistry of *trans*-$[OsX_4(SbPh_3)_2]^{0/-}$ have been studied (*302a*).

6. *Oxygen Donor Ligands*

a. Aqua and Hydroxo Complexes. $[Os(OH_2)_6]^{3+}$ has not been reported, but recent evidence suggests it may be obtained from reduction of $[OsO_4]$ or *trans*-$[Os(O)_2(OH)_4]^{2-}$ in aqueous acid. The complex has not been characterized fully as yet, so it is possible that it is a mixed hydride/aqua complex (*314*).

The species previously assigned as the hydroxo complex, $[Hpy]_2[Os(O)_2(OH)_2Cl_2]$ (*315*), and the aqua complex, $[Hpy]_2[OsO_3Cl_2(H_2O)]$ (*316*), have had their structures reassigned as $[Os(O)_2(py)_2Cl_2]$ and $[Os(O)_2(py)_2Cl_2]$, respectively (*235*).

A summary of the aqua and hydroxo complexes studied recently is given in Table VIII (*2, 17, 37, 46, 59, 70, 72, 94, 95, 113, 126, 133, 210, 211, 240, 241, 243–245, 247, 263, 266, 279, 298, 317–326*) and μ-hydroxo complexes are discussed in Section II,D,5,c.

TABLE VIII

AQUA AND HYDROXO COMPLEXES

Complex	Section	Ref.
Os(II)		
$[Os(NH_3)_5(OH_2)]^{2+}$	II,B,4,a	*70, 72*
trans-$[Os(NO)(NH_3)_4(OH_2)]Cl_3 \cdot H_2O$	II,C,4,f	*243, 244*
$[Os(NO)(NH_3)_3X(OH_2)]Y_2$, X = Cl^-, Y = Cl^-, Br^-, or I^-; X = Y = Br^- or I^-	II,C,4,f	*244*
cis,cis-$[Os(NO)(NH_3)_2X_2(OH)]$, X = Cl^- or Br^-	II,C,4,f	*317*
trans,trans-$[Os(NO)(NH_3)_2X_2(OH)]$, X = Cl^- or Br^-	II,C,4,f	*317*
trans-$[M(NO)(NH_3)_4(OH)]$*trans*-$[M'(NO)(NO_2)_4(OH)] \cdot nH_2O$ (M = Os, M′ = Os, Ru; M = Ru, M′ = Os)	II,C,4,f	*279*
trans-$[Os(NO)(NH_3)_4(OH)][Os(NO)Cl_5]$	II,C,4,f	*279*
trans-$[Os(NO)(NH_3)_4(OH)]Cl_2$	II,C,4,f	*243, 279*
trans-$[Os(NO)(NH_3)_4(OH)]^{2+}$	II,C,4,f	*245*
Na_2{*trans*-$[Os(NO)(NO_2)_4(OH)]$}	II,C,4,f	*279*
trans-$[Os(NX)Cl_4(OH_2)]^-$, X = O, S	II,C,4,f and II,C,4,i	*240, 241*
cis-$[Os(bpy)_2(NO)(OH_2)]^{3+}$	II,C,4,f	*247*
cis-$[Os(phen)_2(NO)(OH_2)]^{3+}$	II,C,4,f	*247*
cis-$[Os(PMe_3)_4(H)(OH)]$	—	*298*
$[Os(OSO_2R)_2(OH_2)(CO)(PPh_3)_2]$, R = Me, CF_3, or 4-MeC_6H_4	II,C,6,q	*126*
$[Os(H)(CO)(OH_2)(L)(PPh_3)_2]$, L = PPh_3 or CO	—	*133*
$[Os(H)(CS)(OH_2)(PPh_3)_3]^+$	II,C,2,c	*17*
cis-$[Os(bpy)_2(OH_2)_2]^{2+}$	—	*318*
$[Os(trpy)(bpy)(OH_2)]^{2+}$	—	*95*
Os_2^{5+}		
$[Os_2Cl_4(chp)_2(OH_2)]^-$	II,D,1,d	*319*
Os(III)		
$[Os(NH_3)_5(OH_2)]^{3+}$	II,B,4,a	*59, 70, 72*
$[Os(OH_2)Cl_5]^{2-}$	—	*320*
$[Os(bpy)_3(OH_2)]^{3+}$	—	*321*
$[Os(bpy)_3(OH)]^{2+}$	—	*321*
cis-$[Os(bpy)_2(OH_2)_2]^{3+}$	—	*94*
$[Os(trpy)(bpy)(OH_2)]^{3+}$	—	*95*
trans-$[Os(14\text{-}tmc)(OH)(OH_2)]^{2+}$	II,C,4,c	*210, 211*
trans-$[Os(14\text{-}tmc)(OH)_2]^+$	II,C,4,c	*210, 211*
$[Os_2Cl_4(chp)_2(OH_2)]$	II,D,1,d	*319, 322*

(*continued*)

TABLE VIII (*Continued*)

Complex	Section	Ref.
Os(IV)		
$[Os(OH_2)Cl_5]^-$	—	*320, 323*
$[Os(OH_2)_2Cl_4]$	—	*323*
$[Os_2(\mu\text{-}N)(NH_3)_8(OH_2)_2]^{5+}$	II,B,3,b and II,D,3,o	*46*
$[Os_2(\mu\text{-}N)(NH_3)_7(OH_2)_3]^{5+}$	II,B,3,b and II,D,3,o	*46*
$[Os(tpp)(OH)_2]$	II,B,4,d	*37*
Os(V)		
trans-$[Os(N)(CN)_4(OH)]^{3-}$	II,C,4,q	*266*
Os(VI)		
trans-$[Os(O)_2(OH)_4]^{2-}$	—	*2, 113, 324*
trans-$[Os(N)(CN)_4(OH)]^{2-}$	II,C,4,q	*266*
trans,trans,trans-$[Os(O)_2(CN)_2(OH)_2]^{2-}$	II,C,2,a	*113*
trans-$[Os(trpy)(O)_2(OH)]^+$	—	*325*
trans-$[Os(phen)(O)_2(OH)_2]$	—	*325*
$K[Os(N)X(OH_2)]$, X = Cl^- or Br^-	II,C,4,q	*263*
Os(VIII)		
$[Os(O)_4(OH)(H_2AsO_3)]^{2+}$	II,C,6,u	*326*

b. Oxo Complexes. Over the past 5 years literally hundreds of publications have appeared in which $[OsO_4]$ and related species have been used as oxidants in organic chemistry, for staining and fixing biological samples, as selective agents for DNA structure, and many other fundamental and applied studies. Even a cursory review of this work is far beyond the scope of this article. Therefore, only a few recent key references that have considerably advanced the understanding of the chemistry in each of these areas will be cited. An excellent account of the chemistry and applications of $[OsO_4]$ and related complexes, up to the mid-1980s, is given in the review by Griffith (*2*). Recently, a number of brief reviews and Ph.D. theses have been presented on the organic oxidation chemistry of Os(VIII) oxo complexes (*35, 36, 327–332*) and $[OsO_4]$ and its regeneration (*333*).

Recent developments in the understanding of the mechanisms of catalytic and asymmetric dihydroxylation reactions are discussed in Section V,E,1,b. An important aspect of this work is the kinetics and thermodynamics of the formation of adducts with N heterocycles, which have an important role in promoting many reactions. The crystal structure of the $[OsO_4]$ adduct with the cinchona alkaloid ligand (dimethyl-

carbamoyl)dihydroquinidine, which is a useful catalyst for asymmetric cis hydroxylation of olefins, shows the ligand bound via the apical aza group of the bicyclo[2.2.2]octane group. A similar structure has been assigned in solution on the basis of NMR experiments (*334*). The formation and thermodynamic stability of a range of $[OsO_4L]$ complexes in water and CCl_4 have been studied, wherein L is an amine ligand (Ctmen, hmt, and dabco) or an N-heterocyclic ligand (im, py, bpds, 4-pic, phen, and bpy) (*335, 336*).

Though $[OsO_4]$ and its adducts continue to find many applications as biological stains and fixatives for both optical and electron microscopy (e.g., *337–347*), $[OsO_4]$ is finding increased applications in selective staining of polymers with alkene functionalities (*348–350*), in the determination of DNA structure (e.g., *351, 352*), in the detection of point mutations in DNA due to mismatched T (and to a lesser extent C) groups (*353*), and in the chemiluminescent determination of proteins (*354*). There have also been many studies on the kinetics and mechanisms of the stoichiometric and the $[OsO_4]$-catalyzed oxidations of both organic and inorganic substrates. These are summarized in Table IX (*26, 28, 267, 324, 326, 334, 335, 355–397*).

$[OsO_4]^-$ has been prepared recently and studied by IR spectroscopy and cyclic voltammetry. It has also been used as a stoichiometric oxidant for benzylic and allylic alcohols to ketones and aldehydes (*398*). The ion pairs $\{[arene]^+[OsO_4]^-\}$ are prepared from irradiating the arene · $[OsO_4]$ charge-transfer bands, and such intermediates are involved in both the photochemical and thermal cis hydroxylation of arenes (*392*).

Numerous studies have been performed on dioxoOs(VI) and other oxo complexes; many of these are discussed in the relevant sections of this review. Those complexes that have been characterized in recent years by X-ray crystallography are summarized in Table X (*22, 24–26, 28, 30–33, 40, 215, 280, 281a, 290, 334, 392, 399–405*).

c. ROH, RO^-, and R_3SiO^- Complexes. For examples of those complexes prepared from the reaction of an alkene with Os(VIII), see Sections II,B,2 and II,C,6,b. There are many hundreds of examples of such complexes, but few have been characterized, as they are only synthetic intermediates in the cis dihydroxylation reactions. Alcohol complexes are also likely to be intermediates in the oxidation of ROH with $[OsO_4]$ (Table IX).

Porphyrinato complexes containing alcoholate and alcohol ligands are discussed in Section II,C,4,d; those containing cyano ligands are discussed in Section II,C,2,a, and those containing Schiff bases are

TABLE IX

KINETIC AND MECHANISTIC STUDIES ON OXIDATION REACTIONS OF $[OsO_4]$ AND $[OsO_4L]$ COMPLEXES

Reaction	Ref.
$[OsO_4]$ and/or *trans*-$[Os(O)_4(OH)_2]^{2-}$	
Reduction by Fc	*355*
Oxidation of arsenite	*326*
Catalysis of H_2O_2 decomposition	*356,357*
Catalysis of the $[Fe(CN)_6]^{3-}$ oxidation of selenium(IV)	*358*
Catalysis of the chlorate oxidation of the hydrazinium cation	*358a*
Catalysis of the diperiodatoargentate(III) oxidation of phosphite	*359*
Catalysis of the periodate oxidation of Na_2HAsO_3	*360*
Oxidation of alkenes; theoretical study	*361*
Oxidation of 1-octene	*362*
Oxidation of unsaturated organic molecules in H_2SO_4/AcOH	*363*
Oxidation of alcohols, diols, and 2-hydroxyacids in alkaline solution	*364*
Oxidation of 3-cresol	*365*
Oxidation of 2-methylpropan-1-ol and 2-butanol	*366*
Oxidation of butanol	*367*
Oxidation of methylglycol and diacetone alcohol	*368*
Oxidation of bis(2-hydroxyethyl) ether	*369*
Oxidation of ethyl digol	*370*
Oxidation of ethyl methyl ketone	*324*
Oxidation of triethylamine	*371*
Catalysis of the diperiodatoargentate(III) oxidations of cycloalkenones and acetophenone	*372,373*
Catalysis of the periodate oxidation of cyclic ketones	*374*
Catalysis of the oxidation of allyl and crotyl alcohols with chloramine-T, chloramine-B, bromamine-T, and bromamine-B	*375*
Catalysis of the chloramine-T oxidation of glycolic and lactic acids	*376*
Catalysis of the chloramine-T oxidation of cinnamaldehyde	*377*
Catalysis of the chloramine-T oxidation of hypophosphite	*377a*
Catalysis of the bromamine-B oxidation of MeSPh to MeS(O)Ph	*378*
Catalysis of the Fe(VI) oxidation of dmso	*379*
Catalysis of the diperiodatocuprate(III) oxidation of Me_2SO to Me_2SO_2	*380*
Catalysis of the ditelluratocuprate(III) oxidation of bis(2-aminoethyl) disulfide	*381*
Catalysis of the $[Fe(CN)_6]^{3-}$ oxidations of alkanals	*382*
Catalysis of the $[Fe(CN)_6]^{3-}$ oxidation of β-bromopropionic acid	*383*
Catalysis of the $[Fe(CN)_6]^{3-}$ oxidations of benzylphenylglycolic acids	*384*
Catalysis of the $[Fe(CN)_6]^{3-}$ oxidations of benzoin and its derivatives	*385*
Catalysis of the $[Fe(CN)_6]^{3-}$ oxidations of benzyl alcohol and benzylamine	*267*
Catalysis of the iodate oxidations of styrene and stilbene	*386*
Catalysis of the *N*-bromosuccinimide oxidation of 2-propanol	*387*
Catalysis of the Tl(III) acetate oxidation of benzilic acid	*388*
Metathesis polymerization of norbornene	*389*

TABLE IX (*Continued*)

Reaction	Ref.
Catalysis of the *N*-morpholine oxide cis hydroxylation of alkenes	*26*
Catalysis of the trimethylamine *N*-oxide cis hydoxylation of cyclohexene and α-pinene	*390*
Catalysis of the cis dihydroxylation of olefins	*391*
Light-catalyzed cis dihydroxylation of arenes	*392*
$[Os(O)_4L]$	
L = dihydroquinine and dihydroquinidine 4-chlorobenzoate; enantioselective cis hydroxylation of alkenes	*28*
L = dimethylcarbamoyl dihydroquinidine; preparation and solid-state and solution structures	*334*
L = (*S,S*)-*N,N'*-bis(2,4,6-trimethylbenzylidene)-1,2-diphenyl-1,2-diamine; catalytic asymmetric cis dihydoxylation of alkenes	*393*
L = dihydroquinidine or dihydroquinine 4-nitrobenzoate; catalytic asymmetric cis dihydoxylation of *trans*-stilbene	*394*
L = Xdhqd (X = Ac, dmc, MeO, or ClBz) or ClBzdhq; conformational changes of cinchona alkaloids on complexation to $[Os(O)_4]$	*395*
L = pyridine; cis dihydroxylation of arenes	*392*
L = RNH_2 (R = Et, Bu^n, or Pr^i), Et_2NH, Et_3N, or amino alcohols); catalysis of the chloroamine-T oxidation of amines and amino alcohols	*396,397*
L = imidazoles; oxidations of imidazoles	*335*

discussed in Section II,C,4,w. *trans*-$[Os^{IV}Br_3(OMe)(PPh_3)_2]$ is prepared by refluxing a mixture of $(Bu_4N)_2[OsBr_6]$, PPh_3, phthalic acid, and phthalic anhydride in CH_2Cl_2, and its structure has been determined by X-ray crystallography (*406*). $[Os^{III}Cl_3(PPh_3)_2(MeOH)]$ is prepared from $[OsCl_6]^{2-}$ in PPh_3/MeOH solutions and has been characterized using IR, UV/Vis, and EPR spectroscopies. It is a useful intermediate in the synthesis of *trans-P,P*-$[Os^{III}Cl_2(PPh_3)_2L]$ complexes, where L is an anionic bidentate oxygen ligand (*407*).

A number of *trans*-$[Os(O)_2(py)_2L]$ complexes (H_2L = glycolic, 2-hydroxyisobutyric, (*S*)-(+)-mandelic, or 2-salicylic acid) have been prepared from $[Os(O)_2(OMe)_4]^{2-}$ and py with the ligand. They have been characterized by IR, mass, and NMR (^1H and ^{13}C) spectroscopies (408) and X-ray structures for L = glycolate(2−) and salicylate (*401, 402*). The Os(V) complex, $(PPh_4)[Os(O)(ehba)_2]$ has been prepared from the reaction of the ligand with $(PPh_4)[OsO_4]$ and has been characterized by IR spectroscopy (*23a*).

TABLE X

STRUCTURAL STUDIES OF OXO COMPLEXES

Complex	Section	Ref.
Os(IV)		
$K_2[\{trans\text{-}Os(\eta^4\text{-chba-Et})(OPPh_3)_2\}_2O]$	II,C,4,x	*290*
Os(VI)		
$Ba[OsO_4]$	—	*399*
$[Os(O)(NBu^t)(mes)_2]$	II,C,2,f	*30*
$[Os(O)(NAr)(ArNCH_2CH_2NAr)]^a$	II,C,4,b	*22*
$[Os(O)_2(mes)_2]$	II,C,2,f	*32*
$[Os(O)_2(xylyl)_2]$	II,C,2,f	*31*
$[Os(O)_2(SSO_3)_2]^{2-}$	II,C,7,n	*33*
$[Os(O)(Ctmen\text{-}2H)(Ctmen\text{-}H)]^+$	II,C,4,b	*24*
$[Os(O)Cl_4]$	—	*400*
$[Os(O)(CH_2SiMe_3)_4]$	—	*25*
$[Os(O)(L)_2]^b$	—	*26*
cis-$[Os(O)_2L(L\text{-}L)]^c$	—	*28*
$[Os(O)_2(ONO_2)_2(mes)]^-$	II,C,2,f	*30*
$[Os(O)_2(4\text{-Metpp})] \cdot thf$	II,C,4,d	*40*
$[Os(O)_2(oep)]$	II,C,4,d	*215*
trans-$[Os(O)_2(3\text{-}Bu^t\text{-saltmen})]$	II,C,4,w	*280*
trans-$[Os(O)_2\{(ba)_2en\}] \cdot 0.5H_2O$	II,C,4,w	*281a*
trans-$[Os(O)_2(glycolate)_2(py)_2] \cdot MeOH$	II,C,6,c	*401*
trans-$[Os(O)_2(2\text{-oxobenzoato})(py)_2]$	II,C,6,c	*402*
$[CtmenH_2] \cdot$ *trans*-$[Os(O)_2Cl_4]$	—	*403*
cis-$[Os(O)_2(L\text{-}L)(L'\text{-}L')]^d$	—	*404*
$[Me_4N]_2[\{Os(O)_2(OCOMe)_2(\mu\text{-}OMe)\}_2]$	II,D,5,d	*405*
anti-$\{trans\text{-}O,O\text{-}[Os(O)_2L_2]_2(\mu\text{-}L')\}^e$	—	*392*
Os(VIII)		
$[Os(O)_4L]^f$	—	*334*

[a] Ar = 2,6-$Pr^i{}_2C_6H_3$.

[b] L = (3*aS*,5*S*,5*aS*,9*aR*,9*bR*)-octahydro-5,5*a*-dihydroxy-3*a*,6,6,-9*a*-tetramethyl-1*H*-benz[*e*]indene-3,7(2*H*,3*aH*)-dionato(2−)-O^5,O^{5a}.

[c] L = dihydroquinidine 4-chlorobenzoate, L-L = (3*S*,4*S*)-2,2,5,-5-tetramethyl-3,4-hexanediolato(2−); L = dihydroquinine 4-chlorobenzoate, L-L = (3*R*,4*R*)-2,5-dimethyl-3,4-hexanediolato-(2−).

[d] L-L = {*N*,*N*′-bis(neohexyl)-2,2′-bipyrrolidine}, L′-L′ = {(*S*,*S*)-1,2-diphenyl-1,2-ethanediolato(2−)}.

[e] L = py; L′ = η^2-O^3,O^4-η^2-O^5,O^6,-thch; η^2-O^1,O^2-η^2-O^3,O^4-ththa.

[f] L = (dimethylcarbamoyl)dihydroquinidine.

trans-$[Os(O)_2(OSiMe_3)_4]^{2-}$ is prepared from the reaction of *trans*-$[Os(O)_2Cl_4]^{2-}$ with $NaOSiMe_3$, and its reactions with $Mg(CH_2SiMe_3)_2$ or $ClMg(CH_2SiMe_3)$ have been studied (*26*). *trans*-$[Os(O)_2(OSiMe_3)_2\{NP(Ph)_2CH_2P(Ph)_2N\}]$ has also been reported (*33*).

d. Catechol and Quinone and Related Complexes. The preparation, characterization (X-ray structure, UV/Vis/NIR, and NMR), electrochemistry, and fluxional behavior of *mer*-$[Os(dpq)_3]$ have been studied. The complex exhibits a reversible oxidation and reduction, with a further one-electron quasi-reversible oxidation and reduction (*409*). $[Os(trop)_3]$ has been prepared from the reaction between $[OsCl_6]^{3-}$ and excess tropH, and has been characterized by mass, IR, and Raman spectroscopies (*410*).

$[Os(bpy)_2LL]^{2+/1+/0}$ (L-L are quinone, semiquinone, or catecholato ligands derived from catechol, 3,5-di-*tert*-butylcatechol, or tetrachlorocatechol) have been characterized by UV/Vis/NIR and EPR spectroscopies. These spectroscopic properties and the crystal structure of $[Os(bpy)_2(dbcat)]ClO_4$ confirm an Os(III)–catecholate ground state for the +1 ion. This contrasts with the ground state of the +1 ions of Ru analogs, which are best described as Ru(II)–semiquinone complexes (*411*).

Catecholate complexes of the type *trans*-$[Os(O)_2L_2]^{2-}$ (H_2L = dopa, dopamine, adrenaline, noradrenaline, or isoproterenol) are prepared from the reactions between *trans*-$[Os(O)_2(OH)_4]^{2-}$ and H_2L. The complexes have been characterized using Raman, IR, and NMR (^1H and ^{13}C) spectroscopies, which indicate that the ligands are bound via the catecholate oxygens. These types of complexes are believed to be models for the staining of catecholamine rich sites in biological tissues (*412*). Similar reactions occur with maltol (maltH) (*413*), tropolone (tropH) (*410*), and 2,3-naphthalenediol (ndH_2) (*414*), to give *trans*-$[Os(O)_2L_2]^{n-}$ (n = 0, L = malt or trop; n = 2, L = nd). The complexes have been characterized by mass, IR, Raman, and NMR (^1H and ^{13}C) spectroscopies.

$[Os^{III}Cl_3(PPh_3)_2(MeOH)]$ reacts with maltH and tropH to give $[Os^{III}Cl_2(PPh_3)_2L]$ (L = malt or trop). IR spectroscopy indicates that the phosphines are mutually trans. The complexes exhibit reversible oxidation and reductions to their Os(IV) and Os(II) analogs. The Os(III) complexes have been characterized by UV/Vis and EPR spectroscopies (*407*). Similarly, the methanol complex reacts with a variety of catechols (catechol, 4-methylcatechol, 3,5-di(*tert*-butyl)catechol, tetrachlorocatechol, tetrabromocatechol, and 2,3-dihydroxynaphthalene) to form the corresponding Os(III)-semiquinonate complexes $[OsCl_2(PPh_3)_2(SQ)]$. The complexes were characterized by electro-

chemistry, and UV/Vis and IR spectroscopies. They are good catalysts for promoting the *N*-morpholine oxide oxidation of alcohols (*414a*).

e. Triethylphosphate and Phosphine Oxide Complexes. Dissolution of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ in $(EtO)_3PO$ yields $[Os(NH_3)_5\{O\text{-}P(OEt)_3\}]^{3+}$, which has been characterized by IR spectroscopy. It is a useful intermediate for the synthesis of other pentaammine complexes (*67*).

$OPPh_3$ complexes with porphyrinato ligands and chelating amides are discussed in Sections II,C,4,d and II,C,4,x, respectively, and *cis*- and *trans*-$[Os(bpy)_2(OPR_3)_2]^{2+}$ complexes are discussed in Section V,E,1,b. The latter have been characterized by UV/Vis spectroscopy and CV. They are reversibly oxidized to their Os(III) analogs (*415*).

f. Pyridine Oxide Complexes. $[OsO_4(pyO)]$ is prepared by the reaction of $[OsO_4]$ with pyO in acetone/CCl_4. It has been characterized by IR and Raman spectroscopies and electrochemistry. A variety of *trans*-dioxo Os(VI) complexes containing diolato(2−) ligands are prepared by the reaction of this complex with an alkene in the presence of excess pyO. These include $[Os(O)_2(pyO)_2(O_2R)]$ (R = CH_2CH_2 or cyclohexane), which have been characterized by electrochemistry and UV/Vis, IR, and Raman spectroscopies (*235*).

g. Amide Complexes. $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ reacts with neat amides to form $[Os(NH_3)_5(O\text{-L})]^{3+}$ (L = dmf or dma) (*67, 120, 177*). These complexes exhibit reversible reductions, but the Os(II) dmf complex undergoes elimination reactions (Section V,E,4,h). The porphyrin complex $[Os^{II}(mix)(dmf)_2]$ (*144*), *cis*- and *trans*-$[OsCl_2(PMe_2Ph)_3(dmf)]$ (*145*), and *cis*-$[Os(bpy)(dppe)(dmf)_2]^{2+}$ (*98*) have been reported.

h. η^1-(O)-Oxime Complexes. See Section II,C,4,l.

i. O-Dimethyl Sulfoxide Complexes. $[Os(NH_3)_5(O\text{-dmso})]^{3+}$ is prepared from the reaction of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ with dmso (*67, 120, 200*). At sufficiently fast scan rates, it is reversibly reduced to $[Os(NH_3)_5(O\text{-dmso})]^{2+}$, which is unstable with respect to its S-bound linkage isomer (Section V,D,4). *trans*-$[Os(O\text{-dmso})(S\text{-dmso})_3Br_2]$ has also been reported (Section II,C,7,i).

j. η^1-(O)-Aldehyde and -Ketone Complexes. The reaction of aldehydes and ketones with $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$, or oxidation of $[Os^{II}(NH_3)_5(\eta^2\text{-}O{=}CR_2)]^{2+}$, results in the formation of $[Os^{III}$-

$(NH_3)_5(\eta^1\text{-}O=CR_2)]^{2+}$ (*67, 120, 168, 169, 177, 181*). The complexes prepared in these ways include acetaldehyde, acetone, 2-butanone, cyclopentanone, cyclobutanone, 2-cyclohexen-1-one, 2,2-dimethylpropiophenone, and benzophenone. These complexes have been characterized by CV and IR spectroscopy.

Acetone complexes are also prepared by the trans activation of the ammine ligands in $[Os^{II}(NH_3)_5(C\text{-Mepy})]^{2+}$ to form *trans*-$[Os(NH_3)_4(C\text{-Mepy})(O\text{-acetone})]^{2+}$ (*167*).

k. Diketonate Complexes. $[Os^{II}Cl_2(PPh_3)_3]$ or $[Os^{III}Cl_3(PPh_3)_2(MeOH)]$ reacts with 2,4-pentanedione ligands to give $[Os^{III}Cl_2\{RC(O)CHC(O)R'\}(PPh_3)_2]$ (R = R′ = CH_3; R = CH_3, R′ = CF_3; R = R′ = CF_3; R = Me, R′ = Ph; R = R′ = Ph), in which the phosphines are believed to be mutually trans from IR spectroscopy. The complexes exhibit reversible oxidation and reductions to their Os(IV) and Os(II) analogs and the Os(III) complexes have been characterized by UV/Vis and EPR spectroscopies (*407, 416*). *trans*-$[Os(H)(acac)(CO)(PPr^i_3)_2]$ is prepared from *trans*-$[Os(H)(Cl)(CO)(PPr^i_3)_2]$ (*18*) in a fashion similar to that described for the PPh_3 analogs (*417*), and has been characterized by IR, and ^1H and $^{31}P\{^1H\}$ NMR spectroscopies (*18*).

l. Ether Complexes. $[Os(NH_3)_5L]^{3+/2+}$ (L = thf, dme, furan, and anisole) are prepared by standard methods (*75, 120*). A dinuclear carboxylato containing thf has also been reported (*418*) (Section II,D,1,c).

m. Dioxygen Complexes. $[Os(H)(Cl)(CO)(PR_3)_2]$ (PR_3 = $PMeBu^t_2$ or PPr^i_3) (*419*) or $[Os(H)(Cl)(CO)(PPr^i_3)_2(\eta^2\text{-}H_2)]$ (*420*) bind O_2 to form $[Os(CO)(Cl)(H)(PR_3)_2(\eta^2\text{-}O_2)]$. These complexes have been characterized by IR and NMR spectroscopies.

n. Carbonato Complexes. $[Os(bpy)_2(CO_3)]$ and $[Os(bpy)(dppe)(CO_3)]$ are useful synthetic intermediates for the preparation of a large number of complexes. They are prepared from the reactions of the corresponding halo complexes with CO_3^{2-} and have been characterized by IR and electronic absorption spectroscopies (*97, 98*). Carbonate also displaces the Cl^- ligands in $[Os(N)(CH_2SiMe_3)_2Cl_2]^-$ to form $[Os(N)(CH_2SiMe_3)_2(CO_3)]^-$ (*157*). All of the complexes contain the η^2-O,O′ coordination mode.

o. Carboxylato Complexes. The complexes $[Os(NH_3)_5(OCOR)]^{2+}$ (R = H or CH_3) have been prepared and characterized by electrochemistry and IR spectroscopy. Reduction of the formato complex leads to

the carbonyl complex (Section V,E,4,g) (*119*). *cis*-$[Os(PPh_3)_2(CO)X\{\eta^2\text{-}(O,O')\text{-}O_2CCH_3\}]$ (X = Cl^- or Br^-) have been prepared and characterized by IR and NMR (^1H and ^{31}P) spectroscopies (*134*). The complexes are catalysts for the hydrogenation of aldehydes and ketones (*135*). The X-ray structure of the complex with X = Br^- has a cis,cis geometry in which Br^- is trans to an O atom of the acetato ligand (*134, 421*). *trans*-$[OsBr_2\{\eta^2\text{-}(O,O')\text{-}O_2CCH_3\}(PPh_3)_2]$ is prepared from refluxing $[OsBr_6]^{2-}$ in $MeCO_2H/(MeCO)_2O$ and its structure was determined by X-ray crystallography (*422*). The syntheses of $[Os(H)\{\eta^2\text{-}(O,O')\text{-}O_2CCH_3\}(CO)(PPr^i_3)_2]$ (*18*), $[Os(\eta^2\text{-}O,O\text{-}OAc)(PPh_3)_3(H_2)]^+$ (*423*), and *cis*-$[Os(O_2CCF_3)_2(PMe_3)_4]$ (*298*) were reported. $[Os(H)\{\eta^2\text{-}(O,O')\text{-}O_2CCF_3\}(CO)(PPh_3)_2]$ and $[Os(O_2CCF_3)_2(CO)(PPh_3)_2]$ are oligomerization catalysts for $C_6H_5C{\equiv}CH$ (*424*). The reactions of *trans*-$[Os(N)(CN)_4(OH)]^{2-}$ with CF_3CO_2H or $(CF_3CO_2)O$ yield *trans*-$[Os(NR)(CN)_4(OCOCF_3)]^-$ (R = H or $OCOCF_3$, respectively) (*266*).

Complexes with 2-hydroxycarboxylic acids, pyridine-2-carboxylate, and dicarboxylates are described in Sections II,C,6,c, II,C,4,f, and II,C,6,p, respectively.

p. Oxalate and Malonate Complexes. *trans*-$[Os(O)_2(CN)_2(C_2O_4)]^{2-}$ is prepared from the reaction of *trans*-$[Os(O)_2(OH)_4]^{2-}$ with stoichiometric amounts of CN^- and $H_2C_2O_4$. It has been characterized by IR, Raman, and UV/Vis spectroscopies (*113*). *trans*-$[^{191}Os(O)_2(malonate)_2]^{2-}$ is a useful parent complex for a $^{191}Os \rightarrow {}^{191m}Ir$ generator for medical applications (*425*).

q. Alkyl- and Arylsulfonato Complexes. The trifluoromethanesulfonato (triflato) ligand is a very good leaving group and the synthesis of complexes containing this ligand has opened up many new areas of Os ammine chemistry. The synthetic procedures for preparation of these complexes are outlined in Sections II,B,4 and II,B,6 and the kinetics of their substitution reactions are discussed in Section V,B. The complexes prepared include $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ (*59, 66, 67*), *cis*-$[Os(NH_3)_4(OSO_2CF_3)_2]^+$ and *trans*-$[Os(NH_3)_4(OSO_2CF_3)Cl]^+$ (*81*), *cis*-$[Os(bpy)_2(OSO_2CF_3)_2]^+$ (*94*), and $[Os(trpy)(bpy)(OSO_2CF_3)]^{2+/+}$ (*95, 96*). The ammine complexes have been used extensively in the synthesis of other pentaammine and tetraammine complexes (*26, 55, 59, 66–68, 70, 71, 74, 75, 80, 81, 85, 87–90, 118–120, 167–169, 171–181, 193–195, 198, 200, 201, 426–432*).

cis-$[Os^{II}(PMe_3)_4(H)(OSO_2CF_3)]$ is prepared from either the reaction of *fac*-$[Os(PMe_3)_3(\eta^2\text{-}C,P\text{-}CH_2PMe_2)(H)]$ with CF_3SO_3H (*306*), or *cis*-

$[Os(PMe_3)_4(H)(CH_3)]$ with CF_3SO_3H or $[Os(PMe_3)_4(H)_3]CF_3SO_3$ (*297*). The triflato complex has been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. In thf solution, the triflato complex is in dynamic equilibrium with a second species that is postulated to be $[Os(PMe_3)_4H]^+$ on the basis of NMR experiments (*306*), although the possibility of a six-coordinate *cis*-$[Os(PMe_3)_4(thf)(H)]^+$ intermediate cannot be discounted. The triflato complex is a useful intermediate for a number of substitution reactions (*297, 306*).

$[Os(OSO_2R)_2(OH_2)(CO)(PPh_3)_2]$ and $[Os(OSO_2R)_2(CO)_2(PPh_3)_2]$ (R = Me, CF_3, or 4-$CH_3C_6H_4$) and Ru analogs are obtained when RSO_3H reacts with $[M(H)_2(CO)(PPh_3)_3]$ or $[M(H)_2(CO)_2(PPh_3)_2]$, respectively (*126, 433*). In $[Os(OSO_2R)_2(OH_2)(CO)(PPh_3)_2]$, the sulfonato ligands are trans to PPh_3 and CO, with the OH_2 ligand being trans to the second PPh_3 ligand. $MeSO_3H$ also reacts with $[Os(H)(Cl)(CO)(PPh_3)_3]$ in $MeOCH_2CH_2OH$ to give $[OsCl(O_3SMe)(CO)(PPh_3)_3]$ (*433*).

r. O-Sulfinato Complex. $[OsCl(OS(O)C_6H_4Me\text{-}4)(CO)_2(PPh_3)_2]$ is prepared by a linkage isomerization reaction (Section V,D,5) (*434*).

s. Benzeneseleninato Complexes. $[Os(XC_6H_4SeO_2)_3]$, $[Os(XC_6H_4SeO_2)_2Y]$, $[Os(XC_6H_4SeO_2)Y_2]$, and $[Os_2(XC_6H_4SeO_2)_3Y_3]$ (X = H, 4-Cl, 3-Cl, 4-Br, 3-Br, or 4-Me; $Y = Cl^-$ or Br^-) have been prepared from the reactions of the appropriate quantity of the ligand with $OsCl_3$ in aqueous methanolic solutions. Based on IR and UV/Vis spectroscopic data, the benzeneseleninato ligands are believed to act as O,O′ chelates. The complexes were also characterized using magnetic susceptibility measurements (*435*).

u. Nitrato Complexes. $[Os(O)_2(ONO_2)_2(mes)]$ (Section II,C,2,f) (*30*) and $[Os(cp)_2(ONO_2)]^+$ (*264*) have been reported recently. Detailed IR and Raman spectroscopic studies have been performed on mixed NO/NH_3/NO_3^- complexes, including *trans*-$[Os(NO)(NH_3)_4(ONO_2)]^{2+}$ (*243, 436*).

v. Sulfato, Chromato, and Perrhenato Complexes. Sulfate displaces the Cl^- ligands in $[Os(N)(CH_2SiMe_3)_2Cl_2]^-$ to form $[Os(N)(CH_2SiMe_3)_2\{\eta^2\text{-}(O,O')\text{-}SO_4\}]^-$ (*157*). Similarly, Ag_2CrO_4 reacts with *cis*-$[Os(N)R_2Cl_2]^-$ (R = CH_2SiMe_3 or Me) in light to produce $[Os(N)R_2\{\eta^2\text{-}(O,O')\text{-}CrO_4\}]^-$. These are selective oxidants for the conversion of primary alcohols to aldehydes (*154*). By contrast, perrhenate reacts with $[Os(N)(CH_2SiMe_3)_2Cl_2]^-$ to form *cis*-$[Os(N)(CH_2SiMe_3)_2(OReO_3)_2]^-$, in which the perrhenato ligands are monodentate (*157*).

u. Arsenito and Hydrogenarsenito Complexes. The details of the kinetics of the oxidation of arsenite by Os(VIII) have been studied and the initial adduct is believed to be *trans*-$[Os^{VIII}(O)_4(OH)(H_2AsO_3)]^{2-}$, which decomposes to *trans*-$[Os(O)_2(OH)_4]^{2-}$ and NaH_2AsO_4. *trans*-$[Os(O)_4(H_2AsO_3)_2]^{2-}$ is also thought to be a reactive intermediate at high concentrations of $H_2AsO_3^-$ (*326*).

7. *Sulfur, Selenium, and Tellurium*

a. Complexes with Thioethers and Selenoethers. *mer*-$[Os^{III}LX_3]$ [X = Cl^- or Br^-; L = bis(3-methylthiopropyl) sulfide] has been reported in Griffith's review (*2, 437*), but more recently the triselenoether analogs have been prepared from the reaction of $[OsX_6]^{2-}$ with the appropriate ligand (*438*). The Os(IV) complex [L = $S(CH_2CH_2CH_2SMe)_2$, X = Br^-] has been isolated and characterized by UV/Vis and IR spectroscopies, electrochemistry, magnetic measurements, and solution conductivities. The other Os(IV) complexes of the series have been observed in cyclic voltammograms, because the oxidation of the Os(III) analogs is reversible, but the complexes have been too unstable to isolate. The Os(II) analogs *mer*-$[OsLX_3]^-$ (X = Cl^- or Br^-) have also been observed in the cyclic voltammograms, but have not been isolated (*234*).

$[Os^{IV}(L\text{-}L)X_4]$ [X = Cl^-, L-L = $RSe(CH_2)_2SeR$ (R = Me or Ph), $MeSe(CH_2)_3SeMe$, *cis*-MeSeCHCHSeMe, or $2Me_2Se$; X = Br^-, L-L = $MeSe(CH_2)_2SeMe$] are prepared by heating the ligand with $[OsX_6]^{2-}$ in 2-methoxyethanol and were characterized by IR and UV/Vis spectroscopies and by magnetic measurements (*439*). The syntheses, the IR, UV/Vis, and NMR spectroscopies, and the electrochemistry of *trans*-$[OsX_4(SeMe_2)_2]^{0/-}$ have also been studied (*302a*).

b. Complexes with Thioether Macrocycles. In a recent review by Blake and Schröder (*440*) on complexes with thioether macrocycles, a number of Os complexes were reported. Those that have been characterized crystallographically are $[Os([9]aneS_3)_2]^{2+}$ (*440*) and $[Os(4\text{-}MeC_6H_4Pr^i)([9]aneS_3)]^{2+}$ (*440, 441*). The only other complexes containing thioether macrocycles are $[OsCl_4([14]aneS_4)]$ (*437*) and $[Os_2Cl_2(arene)([18]aneS_6)]^{2+}$; both have the macrocycle bound in a bidentate fashion, the latter having the macrocycle as a bis(bidentate) bridging ligand (*441*).

c. Thiolato Complexes. $[Os^{IV}(oep)(SPh)_2]$ and $[Os^{IV}(tpp)(SPh)_2]$ (*214*) and *trans*-$[Os^{IV}(salen)(SPh)_2]$ and related Schiff base complexes

(*281*) have been discussed in Sections II,C,4,d and II,C,4,w, respectively. Dinuclear complexes with MeS^- ligands are discussed in Section II,D,6,a.

The reaction of *mer*-$[OsX_3(PR_3)_3]$ (PR_3 = PMe_2Ph, PEt_2Ph, $PMePh_2$, or $PEtPh_2$) with 1.5 mol equivalents of $Pb(SC_6F_5)_2$ yields *mer*-$[Os(SC_6F_5)_3(PR_3)_2]$. These paramagnetic Os(III) complexes have been characterized by IR and NMR (^1H, ^{31}P, and ^{19}F) spectroscopies. They tend to dimerize in solution, but in the solid state they are believed to be octahedral, with the sixth coordination site being occupied by an ortho F of a $C_6F_5S^-$ ligand. This assignment is based on the crystal structure of the analogous Ru complex, $[Ru\{\eta^2\text{-}(S,F)\text{-}SC_6F_5\}(\eta^1\text{-}(S)\text{-}SC_6F_5)_2(PMe_2Ph)_2]$ (*442*). In the presence of Zn/CO, they react to form $[Os(SC_6F_5)_2(CO)_2(PR_3)_2]$, with the preferred geometric isomer being dependent on the solvent and the reaction time. If the reaction is carried out in acetone, the trans,trans,trans isomer is obtained as the main product. However, the trans-P,P-cis,cis isomer is obtained if the reaction is performed in thf instead of acetone. *trans-C,C-cis,cis*-$[Os(SC_6F_5)_2(CO)_2(PR_3)_2]$ (PR_3 = PMe_2Ph or $PEtPh_2$) is obtained as the predominant isomer at longer reaction times and hence is the most thermodynamically stable. A fourth geometric isomer, trans-S,S-cis,cis, has been obtained from the reaction of *mer*-$[OsBr_2(N_2)(PEt_2Ph)_3]$ with $Pb(SC_6F_5)_2$ under a CO atmosphere. Therefore, only the cis,cis,cis isomer is yet to be isolated. All of the complexes have been characterized by ^1H, ^{19}F, and ^{31}P NMR and IR spectroscopies, and in the case of *trans,trans,trans*-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$, by an X-ray structural analysis (*443*). The Os — S bond length [2.447(1) Å] (*443*) is shorter than that in *mer*-$[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$ [2.507(1) Å] (*254, 444*), where the Os — S bond is trans to an Os — P bond.

mer-$[OsX_2(N_2)(PMe_2Ph)_3]$ react with either $Pb(SR)_2$ (R = Ph or C_6F_5), NaSMe, or $AgSCF_3$ to give *mer*-$[OsX(SR')(N_2)(PMe_2Ph)_3]$ ($X = Cl^-$, R' = Me, CF_3, Ph, or C_6F_5; $X = Br^-$, R' = C_6F_5). The complexes were characterized by NMR (^1H, ^{19}F, and ^{31}P) and IR spectroscopies. The $SC_6F_5^-$ ligand is trans to a phosphine ligand with the X^- and N_2 ligands being trans (*254, 444*).

Either *cis*- or *trans*-$[Os(N)(CH_2SiMe_3)_2Cl_2]^-$ react with 1,2-ethanedithiol in the presence of base to give $[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]^-$. This reacts with MeI to give the thioether complex, $[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2SCH_3)]$. All complexes have been characterized by NMR (^1H and ^{13}C) and IR spectroscopies (*156*). Spectrophotometric determinations of the complexation of Os(VI) with 2,3-dimercaptopropanesulfonate indicate the formation of $[Os(O)_2(dmps)_2]^{4-}$ in which the ligand is anticipated to act as a dithiolato chelate (*445*).

d. Sulfide and Polysulfide Complexes. $[Os(CO)Cl(NO)(PPh_3)_2]$ reacts with HS^- and $[OsCl(NO)(PPh_3)_3]$ reacts with S_8 to give $[OsCl(NO)(PPh_3)_2(S_2)]$ (*446*). $[OsO_4]$ reacts with S_2Cl_2, S_nCl_2, or S_2Br_2 to yield $[OsS_2O_2Cl_3]$, $[OsS_4Cl_2]$, and $[OsS_2Br_4]$, respectively. All of these complexes are poorly characterized and probably contain polysulfide groups (*447*).

e. Hydrogen Selenido Complexes. *trans*-$[Os(SeH)(NO)(CS)(PPh_3)_2]$ has been prepared and characterized by ^1H NMR and IR spectroscopies (*152*).

f. Thiophene Complexes. Until recently, relatively few transition metal thiophene complexes have been reported, but the ligand is now known to coordinate in at least six different modes (*448*). $[Os(NH_3)_5\{\eta^2\text{-}(C,C)\text{-thiophene}\}]^{2+}$ (Section II,C,2,j) apparently rearranges to form $[Os(NH_3)_5\{(S)\text{-thiophene}\}]^{3+}$ on oxidation (*90, 179*).

g. Thiourea and 1-Amidino-2-thiourea Complexes. The preparation of various salts of the well-known (*2*) $[Os(thio)_6]^{3+}$ ion has been reported by the reactions of Os(IV) chloro complexes with HCl and the ligand, or $[OsO_4]$ and H_2SO_4 with the ligand. These salts include $[Os(thio)_6]Cl_3 \cdot H_2O$, $[Os(thio)_6](HSO_4thio)_3 \cdot 3H_2O$, $[Os(thio)_6][Os^{IV}Cl_6]Cl$, and $[Os^{III}(thio)_6][Os^{III}Cl_6]$. In addition, the new Os(III) complexes, $[Os(thio)_5Cl]Cl_2$ and $[Os(thio)_5Cl][OsCl_6]$, have been reported. All complexes were studied by EPR, IR, and UV/Vis spectroscopies, X-ray powder diffraction, electrical conductivity, and thermal gravimetric analysis (*449*). They have also been studied by XPS spectroscopy, together with *trans*-$[Os(O)_2(thio)_4]SO_4$ (*450*), and detailed IR spectroscopic studies have revealed that all the thio ligands are S bound (*451*).

$[OsO_4]$ forms a 1:1 complex with allylthiourea, which is intensely absorbing and is the basis of a spectrophotometric method for the determination of Os(VIII) (*452, 453*). $[Os(cp)_2(thio)]^{2+}$ has also been reported (*264*).

$K[Os(O)_3N]$ reacts with the amidinothiourea ligands to give *trans*-$[Os^VNL_2(H_2O)]$ (HL = 1-amidino-2-thiourea, *N*-methyl-1-amidino-2-thiourea, or *N*-ethyl-1-amidino-2-thiourea) in which the ligands are believed to act as N,S donors with the sulfurs of the two ligands being mutually trans. The complexes were characterized by IR spectroscopy, thermogravimetric analysis, and magnetic measurements (*271*).

h. 2,1,3-Benzothiadiazole and 2,1,3-Benzoselenadiazole Complexes. The first Os complexes of these ligands, $[OsCl(C_6H_4Me\text{-}$

4)(CO)(PPh_3)$_2$L] (L = bsd or btd), have been prepared from the reactions of [OsCl(C_6H_4Me-4)(CO)(PPh_3)$_2$] with btd or bsd. The PPh_3 ligands are mutually trans, with the btd and bsd ligands being trans to the alkyl group. These S-donor or Se-donor ligands are readily displaced from the coordination sphere by CO or $SNNMe_2$. [OsCl_2(CS)(PPh_3)$_3$] also reacts with bsd to form *trans-P,P-cis*-[OsCl$_2$(CS)(PPh_3)$_2$(bsd)]. All of the complexes have been characterized by IR and NMR (^{1}H and ^{31}P) spectroscopies (*150*).

i. S-Dimethyl Sulfoxide Complexes. [Os(NH_3)$_5$(*S*-dmso)]$^{2+}$ is prepared by either the linkage isomerization of the *O*-dmso linkage isomer, or [Os^{II}(NH_3)$_5$(solvent)]$^{2+}$ with dmso (*67, 120, 200*). The Os(III) complex is observed in the CV at fast scan rates, but is unstable with respect to [Os(NH_3)$_5$(*O*-dmso)]$^{3+}$ (Section V,D,4). [Os^{II}(NH_3)$_5$(4-lutdm)]$^{2+}$ reacts with dmso to yield *trans*-[Os^{II}(NH_3)$_4$(4-lutdm)(dmso)]$^{2+}$. Although, the donor atom of the dmso ligand was not specified (*85*) it is expected to be S bound by analogy with [Os^{II}(NH_3)$_5$(*S*-dmso)]$^{2+}$ and other Os(II) dmso complexes. [Os(pc)(dmso)$_2$] has also been reported (Section II,C,4,d) (*186*), and, from the X-ray structure of its Fe(II) analog (*454*), it is expected to have both dmso ligands bound via S.

The thermal decompositions of *trans*-[Os(*S*-dmso)$_4$Cl$_2$] and *trans*-[Os(*O*-dmso)(*S*-dmso)$_3$Cl$_2$] [first prepared in 1980 (*445*)] to give μ-MeS$^-$ dinuclear complexes have been described recently (*456*) (Section II,D,6,a). *trans*-[Os(*S*-dmso)$_4$Br$_2$] is prepared from the prolonged heating of [Bu$^n_4$N]$_2$[OsBr$_6$] in dmso (*457*) and its crystal structure is isomorphous with its Ru analog. The Os — S bond lengths [2.351(2) Å] are similar to that found in [Os(η^6-4-cymene)(*S*-dmso)Cl$_2$] [2.324 Å (*458*)], which is prepared from the reaction of [{Os(η^6-4-cymene)Cl}$_2$(μ-Cl)$_2$] with dmso (*459*). The dmso product reacts with Al_2Me_6 in the molar ratios of 1:0.6 or 1:1.6 to give [Os(η^6-4-cymene)(*S*-dmso)(Me)Cl] and [Os(η^6-4-cymene)(*S*-dmso)(Me)$_2$], respectively. All of the dmso products have been characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopies (*459*). [Os(η^6-4-cymene)(*S*-dmso)(Me)Cl] undergoes an orthometalation reaction with $PhCO_2Ag$ to give [Os(η^6-4-cymene){η^2-(*O,C*^{2})-$O_2CC_6H_4$}(*S*-dmso)] (*460*).

Electrochemical reduction of *mer*-[Os(PMe_2Ph)$_3$Cl$_3$] in dmso results in the formation of *mer,trans*-[Os(PMe_2Ph)$_3$(dmso)Cl$_2$] in which the dmso ligand is believed to be S bound. This complex has been characterized by ^{31}P{^{1}H} NMR spectroscopy and exhibits a reversible oxidation to the Os(III) analog (*145*).

j. Thionitrosoamine Complexes. $SNNMe_2$ reacts with [Os(CO)(Cl)(H)(PPh_3)$_3$] to give [Os(CO)(Cl)(H)($SNNMe_2$)(PPh_3)$_2$], in which

the hydrido ligand is trans to $SNNMe_2$, whereas *cis,trans*-$[Os(CO)(H)(SNNMe_2)_2(PPh_3)_2]^+$ is obtained when the reactant is $[Os(H)(OH_2)(CO)(PPh_3)_3]^+$. $[Os(L)(Cl)(4\text{-}MeC_6H_4)(PPh_3)_3]$ (L = CO *or* CS) react with the ligand to give $[Os(L)(Cl)(4\text{-}MeC_6H_4)(SNNMe_2)(PPh_3)_2]$ (*153*). In the X-ray crystal structure of $[Os(Cl)(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SNNMe_2)]$, the thionitrosoamine ligand is essentially planar and is bound through its sulfur atom. The Os — S bond is short [2.411(2) Å] and the *trans*-Os — Cl bond is long [2.476(3) Å]. The long Os — Cl bond facilitates the substitution reactions of this complex to give $[Os(X)(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SNNMe_2)]$ (X = N_3^-, CO, 2-xylyl isocyanide, or Me_3CCN) (*185*). The complex with X = Cl^- was also prepared from the reaction of the ligand with $[OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(bsd)]$ (*26*).

k. Iminooxosulfane Ligands. The reaction of [(4-tolylsulfonyl)imino]oxo-λ^4-sulfane with the square-planar $[Os(NO)(Cl)(PPh_3)_2]$ yields the six-coordinate complex, *trans*-$[Os(NO)(Cl)(\eta^2\text{-}OSNSO_2C_6H_4Me\text{-}4)(PPh_3)_2]$, in which the ligand is bound via the N and S atoms of the sulfane group. However, if the same ligand is allowed to react with the octahedral $[Os(NO)(Cl)(\eta^2\text{-}CH_2{=}CH_2)(PPh_3)_2]$, then either electrophilic attack at the ethene occurs to give the metallocycle, *trans*-$[Os(NO)(Cl)\{\eta^2\text{-}CH_2CH_2S(O){=}NSO_2C_6H_4Me\text{-}4\}(PPh_3)_2]$ (Section II, C,2,f), or ethylene substitution occurs to give the iminooxosulfane products. Similar reactions occur with other alkene or alkyne complexes. The products were characterized by IR and NMR (^1H and $^{31}P\{^1H\}$) spectroscopies (*163, 164, 446*).

l. Disulfur Oxide and Sulfur Dioxide Complexes. $[Os(NH_3)_5(SO_2)]^{2+}$ has been prepared and characterized by electrochemistry and by UV/Vis and IR spectroscopies (*60*). $[OsCl(NO)(PPh_3)_2(S_2)]$ is oxidized to $[OsCl(NO)(PPh_3)_2(S_2O)]$ by 3-$ClPhCO_3H$ (*446*) and $[Os(NO)Cl(PPh_3)_2(SO_2)]$ is prepared from the hydrolysis of $[Os(NO)Cl(PPh_3)_2(\eta^2\text{-}OSNSO_2C_6H_4Me\text{-}4)]$ (*446*). $[OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2]$ reacts with SO_2 to form $[OsCl(C_6H_4Me\text{-}4)(CO)(PPh_3)_2(SO_2)]$, which is unstable toward rearrangement to the *S*-sulfinato complex, $[OsCl\{S(O)_2C_6H_4Me\text{-}4\}(CO)(PPh_3)_2]$ (*434*).

m. S-Sulfinato Complexes. $[OsCl\{S(O)_2C_6H_4Me\text{-}4\}(CO)(PPh_3)_2]$ is discussed above (*434*).

n. S-Thiosulfato Complexes. Thiosulfate reacts with $[OsO_4]$ to form the tetrahedral $[Os(O)_2(SSO_3)_2]^{2-}$ complex, which has had its structure

determined by X-ray crystallography. This complex is only the third example of a tetrahedral Os(VI) complex, and is the first example without aryl groups. The thiosulfate ligands are bound via S, with Os — S bond lengths of 2.218(1) Å. It is diamagnetic and Raman, IR, and ^{17}O NMR spectroscopies indicate that the tetrahedral structure is maintained in solution. The complex exhibits a reversible reduction to the Os(V) complex, $[Os(O)_2(SSO_3)_2]^{3-}$ (*33*).

o. Sulfito Complexes. $[Os(NH_3)_5(SO_3)]^+$ has been reported and studied by electrochemistry and UV/Vis spectroscopy (*60*). Sulfite reacts with *cis*-$[Os(NO)(bpy)_2Cl]^{2+}$ at pH 6.9–9.2 to give *cis*-$[Os(bpy)_2(NO)(SO_3)]$, which has been characterized by IR and electronic absorption spectroscopies. This complex undergoes a reversible one-electron reduction and an irreversible one-electron oxidation in dmf (*461*).

p. Isothiocyanato and Isoselenocyanato Complexes. For the synthesis and properties of $[Os(NCS)_n(SCN)_{6-n}]^{2-/3-}$ (*274, 275*) and $[Os(N)(CH_2SiMe_3)(NCS)(SCN)]^-$ (*156*), see Section II,C,4,t. $[Os(cp)_2(SCN)]SCN$ is prepared by the reaction of $[(cp)_2Os(SS)Os(cp)_2]$ with CN^-, and the X-ray structure has been determined (*462*).

$[Os(NCSe)_n(SeCN)_{6-n}]^{3-}$ (n = 0–3) have been discussed in Section II,C,4,u. *trans,trans,trans*-$[Os(O)_2(CN)_2(SeCN)_2]^{2-}$ (*113*) and *trans*-$[Os(O)_2(SeCN)_4]^{2-}$ (*272*) are prepared from the reactions of *trans,trans,trans*-$[Os(O)_2(CN)_2(OH)_2]$ and *trans*-$[Os(O)_2(OH)_4]^{2-}$, respectively, with the ligand. The structures were assigned in each case on the basis of IR and Raman spectroscopies (*113, 272*). The UV/Vis spectrum of *trans*-$[Os(O)_2(SeCN)_4]^{2-}$ is highly vibrationally coupled (*272*).

q. Dithiocarbamate and Xanthate Complexes. The chemistry and electrochemistry of Os dithiocarbamates were reviewed in 1984 and 1986 (*2, 463*). Recently, the reactions of $[Os(NO)Cl_3(PPh_3)_2]$ with $Na(S_2CNR_2)$ (R = Me or Et) have been studied (*246*). If the reactants are stirred together in benzene at room temperature, $[Os(NO)Cl_2(S_2CNR_2)(PPh_3)]$ results, but if the solution containing excess ligand is refluxed, the product is $[Os(S_2CNR_2)_3]$. The complexes were characterized by IR and electronic absorption spectroscopies and magnetic measurements. *trans*-$[OsI(NO)\{\eta^1\text{-}(C)\text{-}CS_2Me\}(S_2CNMe_2)(PPh_3)_2]$, in which the NO and CS_2Me ligands are mutually trans, has also been reported (Section II,C,2,e) (*152*). *mer*-$[OsCl_2(N_2)(PMe_2Ph)_3]$ reacts with $Na[S_2CNMe_2]$ to give *cis*-$[Os(S_2CNMe_2)_2(PMe_2Ph)_2]$ and with $Tl[S_2CNMe_2]$ to give $[OsCl(S_2CNMe_2)(PMe_2Ph)_3]$ as a 1:1.35 mixture of the mer:fac isomers. The complexes were characterized by ^1H

and ^{31}P NMR spectroscopies (*254*) and are identical to the products obtained if *mer*-$[OsCl_3(PMe_2Ph)_3]$ is used as a starting material (*464*).

The complexes $[Os^{III}L_3]$ (L = anilinodithiocarbamate, 2-, 3-, or 4-fluoroanilinodithiocarbamate, *N*-methylpiperizinodithiocarbamate, dicyclohexyldithiocarbamate, methylcyclohexyldithiocarbamate, benzylxanthate, and butylxanthate) have been prepared by the reaction of the K^+ salt of the ligands with $K_2[OsCl_6]$ or $Na_2[OsCl_6]$ (*465*). These complexes and their Ru analogs, were screened for antitumor activity in rats bearing Ehrlich ascites, P_{388}, and ADJ/PC6 tumors, and for antitrypanosomal activity in rats infected with *Trypanosoma bruceii bruceii, Trypanosoma congolense,* and *Trypanosoma cruzi.* The Os complexes were more active than their Ru analogs and dithiocarbamate complexes were more active than xanthate complexes in all assays. The most interesting complex was that in which L = anilinodithiocarbamate, which was of low nephrotoxicity and toxicity and is effective in all assays (*465*).

Recently, the synthesis and properties of *cis*- and *trans*-$[Os^{II}(Rxanthate)_2(PPh_3)_2]$ and *cis*- and *trans*-$[Os^{III}(Rxanthate)_2(PPh_3)_2]^+$ (R = Me, Et, Pr^i, CH_2Ph) have been reported (*465a*). These complexes have been studied by UV/Vis/NIR and EPR spectroscopies, magnetic measurements, and electrochemistry. The X-ray crystal structures of *cis*-$[Os(Mexanthate)_2(PPh_3)_2]$, *trans*-$[Os(Mexanthate)_2(PPh_3)_2]$ and *trans*-$[Os(Mexanthate)_2(PPh_3)_2]PF_6 \cdot 2H_2O$ were also reported. Using electrochemical and UV/Vis spectroscopic techniques, the kinetics and thermodynamics of the geometric isomerizations in both oxidation states have been studied. The *cis* isomers are favored thermodynamically for Os(II) and the *trans* isomers for Os(III) (*465a*). Similar results are found in related complexes with thioxanthate ligands and the crystal structures of *cis*-$[Os(EtSCS_2)_2(PPh_3)_2]$, *trans*-$[Os(EtSCS_2)_2(PPh_3)_2]$, and *trans*-$[Os(EtSCS_2)_2(PPh_3)_2]PF_6$ have been reported (*465b*).

r. Complexes and Dithiophosphinates. $[Os(2,4,5\text{-}Me_3C_6H_2PS_2)_3]$ is prepared from the reaction of the ligand with $(NH_4)_2[OsCl_6]$ and have been characterized by EPR and UV/Vis spectroscopies and magnetic measurements (*466*). *cis*-$[Os(S_2PR_2)_2(PPh_3)_2]$ (R = Me, Ph, or OEt) react with tetracyanoethylene to give *cis*-$[Os(S_2PR_2)_2(PPh_3)(tcne)]$. These complexes have been characterized by IR and UV/Vis spectroscopies and the X-ray structures of two complexes (R = Me or Ph) have been determined. They exhibit two reversible one-electron reductions that are centered on the tcne ligand and reversible oxidations to the Os(III) analogs (*467*).

s. Cysteine Complexes. Cysteine is reported to form a 1 : 1 complex with Os(VIII) in aqueous solution, but this complex is poorly characterized (*468*).

t. 2-(Tolylthio)picolinamide. $[OsL_2(OH)\cdot H_2O]$ and $[Os(HL)_2(OH)_2Cl]H_2O$ [HL = 2-(tolythio)picolinamide] are prepared by the reactions of HL with $[OsO_4]$ or $[OsCl_6]^{2-}$. In weakly acidic solutions, L^- is bidentate and coordinates via the pyridine N and the N or S atom of the thioamide group. In strongly acidic solutions, HL is monodentate and binds via the thioketone S atom (*469*).

u. 2-Aminobenzenethiol Complexes. 2-Aminobenzenethiol reacts with $[OsO_4]$ to give *fac*-$[Os^{VI}(abt)_3]$, which has been characterized by X-ray crystallography and mass, IR, and NMR spectroscopies. It is diamagnetic and contains three doubly deprotonated ligands. Electrochemical studies in acetonitrile show two one-electron reversible reductions to the Os(V) and Os(IV) analogs and two reversible one-electron oxidations to the formal oxidation states of Os(VII) and Os(VIII) (*24*). Os(VI) reacts with 4-sulfo-2-aminobenzenethiol (H_2L) to form 1 : 2 complexes that presumably contain the N,S chelates, *trans*-$[Os(O)_2(L)_2]$. The formation of this complex has been used as the basis of a spectrophotometric determination of Os(VI) (*470*).

v. 2-Pyridinethiolato, 2-Pyrimidinethiolato, and Thiopyrine Complexes. When $[Os(H)_2(CO)(PPh_3)_3]$ is refluxed with pySH in toluene, a mixture of *trans,trans-S,H-* and *trans,trans,-S,C*-$[OsH(pyS)(CO)(PPh_3)_2]$ in the ratio of ~4 : 1 was obtained. If the starting material was refluxed with pySSpy for longer periods of time, *cis,trans-S,S*-$[Os(pyS)_2(CO)(PPh_3)]$ results. Refluxing $[Os(H)_4(PPh_3)_3]$ with pySH in benzene leads to *trans,trans-S,C*-$[Os(H)(pyS)(CO)(PPh_3)_2]$, whereas the reaction between $[Os(H)(Cl)(CO)(PPh_3)_3]$ and pySH in cold benzene results in a mixture of *trans,trans-S,C*-$[Os(H)(pyS)(CO)(PPh_3)_2]$ and *trans,trans-S,H-* and *trans,trans-S,C*-$[Os(H)(Cl)(HpyS)(CO)(PPh_3)_2]$. The pyS ligand is bidentate, but the HpyS ligand is bound via S and protonated at N. If the same reaction is carried out in boiling toluene (18 hours), *trans,trans-S,H-* and *trans,trans-S,C*-$[Os(H)(pyS)(CO)(PPh_3)_2]$ and *trans*-$[OsCl(pyS)(CO)(PPh_3)_2]$ result, in the ratio 4 : 1 : 15. The geometric isomer of the latter is uncertain with respect to the ligand that is trans to the S atom. When pySSpy is reacted instead of the ligand, the product is solely $[OsCl(pyS)(CO)(PPh_3)_2]$. Similar reactions yield *trans,trans-S,H-* and *trans,trans-S,C*-$[Os(H)(Br)(HpyS)(CO)(P-$

$Ph_3)_2$] and [OsBr(pyS)(CO)($PPh_3)_2$]. All of the complexes were characterized by IR and NMR (^1H and ^{31}P) spectroscopies (*136*). Complexes in which pyS reacts as a bridging ligand are described in Section II,D,6,a.

Heating [$Os(H)_2(CO)(PPh_3)_3$] in boiling toluene or heating [Os(H)(Cl)(CO)($PPh_3)_3$] in boiling benzene with Me_2pymSH yields two geometic isomers of *trans*-[Os(H)(Me_2pymS)(CO)($PPh_3)_2$], in which the RS^- group of the chelate is trans to either the H^- or CO ligand. [$OsCl_2(PPh_3)_3$] reacts with an excess of the same ligand to form *trans*-[$Os(Me_2pymS)_2(PPh_3)_2$]. The complexes have been characterized by NMR (^1H, ^{13}C, and ^{31}P) and IR spectroscopies (*471*). 1-Pyridyl- and 1-(4′-phenylthiazolyl)-4,4,6-trimethyl-1*H*,4*H*-pyrimidine-2-thiol have been used as complexing agents for the spectrophotometric determination of Os, but the details of the complexes formed have not been given (*472*).

Os(VIII) reacts with thiopyrine to form [$Os(O)_2(C_{11}H_{12}N_2S)_2$]-($ClO_4)_2$, which is used as a method of extraction into $CHCl_3$ for the spectrophotometric determination of Os(VIII) (*473*).

w. Pyrimidinethione and Thiobarbituric Acid Complexes. Os(VIII) is reported to react with 3,4-dihydro-4,4,6-trimethyl-2-(1*H*)-pyrimidinethione (*474*) or 2-thiobarbituric acid (*475*) to form highly colored [$Os(L)_4$] complexes as a basis of spectrophotometric determinations of Os, but these complexes have not been well characterized.

8. *Halo Ligands*

Most halo complexes have been discussed in previous sections (Table XI). Table XII (*239, 268, 323, 400, 403, 476–499*) summarizes studies on complexes that contain only halo ligands or halo/oxo complexes.

a. Fluoro Complexes. Matrix isolation methods have been used to study the IR spectra of the molecular species [$Os(O)F_4$], [$Os(O)_2F_3$], and [$Os(O)_3F_2$] that have been obtained by the vaporization of the solids. The species have also been identified by mass spectrometry via the molecular ions $[Os(O)_3F]^+$, $[Os(O)_2F_2]^+$, $[Os(O)F_3]^+$, $[Os(O)_3F_2]^+$, and $[Os(O)_2F_3]^+$. Other products of the vaporization include [OsF_6] and another fluoride believed to be [OsF_5]. These products are consistent with the generation of the molecular ions, $[OsF_5]^+$ and $[OsF_4]^+$, in the mass spectra (*494, 500*).

b. Organofluorine Complexes. *mer*-[$Os(SC_6F_5)_3(PR_3)_2$] complexes (PR_3 = PMe_2Ph, PEt_2Ph, $PMePh_2$, or $PEtPh_2$) are believed to be octa-

TABLE XI

HALO COMPLEXES WITH OTHER LIGANDS

Complex or coligand	Section	Complex of coligand	Section
Osmaboranes	II,C,1	CN^-	II,C,2,a
CO	II,C,2,b	CS, CSe, CTe	II,C,2,c
CS_2, CSSe, $SCSMe^-$	II,C,2,e	Alkyl and aryl	II,C,2,f
Carbene	II,C,2,g	Alkene	II,C,2,h
Isonitrile	II,C,2,n	SiR_3	II,C,3
Ammine	II,C,4,a	Amines	II,C,4,b
Macrocycles	II,C,4,c	Porphyrins	II,C,4,d
N-heterocycles	II,C,4,e	NO, NO^+	II,C,4,f
Nitrosoarene	II,C,4,g	Hydroxylamine	II,C,4,h
NS, NS^+	II,C,4,i	N_2	II,C,4,j
Oxime	II,C,4,l	NCR	II,C,4,n
NSCl	II,C,4,o	N^{3-}	II,C,4,q
NCO^-	II,C,4,s	NO_2^-, NOS^-	II,C,4,v
Schiff bases	II,C,4,w	Quinololates	II,C,4,y
Diaryltriazenes	II,C,4,z	Penylazopyridines	II,C,4,z
Phosphines	II,C,5,a	Phosphites	II,C,5,b
η^2-CH_2PR_2	II,C,5,c	Arsines	II,C,5,d
Diarsines	II,C,5,e	Stibines	II,C,4,f
H_2O, OH^-	II,C,6,a	Oxo	II,C,6,b
ROH, RO^-	II,C,4,c	Maltolate and tropolonate	II,C,6,d
O-dmso	II,C,6,i	Diketonates	II,C,6,k
O_2	II,C,6,m	RCO_2^-	II,C,6,o
RSO_3^-	II,C,6,q	*O*-sulfinate	II,C,6,r
Benzeneseleninato	II,C,6,s	Thioether and selenoether	II,C,7,a
Thioether macrocycles	II,C,7,b	RS^-	II,C,7,c
S_2	II,C,7,d	Thiourea	II,C,7,g
btd and bsd	II,C,7,h	*S*-dmso	II,C,7,i
$SNNMe_2$	II,C,7,j	Iminooxosulfane	II,C,7,k
SO_2, S_2O	II,C,7,l	*S*-sulfinato	II,C,7,m
$R_2NCS_2^-$ and xanthate	II,C,7,q	2-(tolylthio)picolinamide	II,C,7,t
Pys, pymS	II,C,7,v	ECl_4 (E = S, Se, or Te)	II,C,8,d
BH_4^-	II,C,9,b	H_2	II,C,9,c

hedral, with one of the $SC_6F_5^-$ ligands acting as an η^2-S,F chelate via a fluoro substituent in the 2-position (Section II,C,7,c).

c. Chloro, Bromo, and Iodo Complexes. $[Os(NH_3)_5X]^{2+}$ (X = Cl^-, Br^-, or I^-) has been obtained from the triflato complex by heating in aqueous HX. The crystal structure of $[Os(NH_3)_5Cl]Cl_2$ has been determined. By comparison with isomorphous complexes, it is deduced that Os—Cl π bonding is comparable to that of Ru in these complexes (*501*).

TABLE XII

HALO AND OXO/HALO COMPLEXES

Complex	Studies and references
Os(II)	
$[OsCl_6]^{4-}$	CV (*476*)
Os(III)	
$[OsCl_6]^{3-}$	CV (*476,477*)
Os(IV)	
$[OsCl_4]$	Reaction with ECl_4 (E = Se or Te) (*478*)
$[OsBr_xCl_{4-x}]$, $0 < x < 2.3$	X-ray (*479*)
$[OsBr_4]$	X-ray (*479*)
$[OsF_6]^{2-}$	IR (*239*), Raman (*239*), normal coordinate analysis (*239*), XPS (*268*), CV (*476*)
$[OsF_nCl_{6-n}]^{2-}$	^{19}F NMR (*480*), oxidation (*481*)
$[OsCl_6]^{2-}$	IR (*239,482*) Raman (*239*), normal coordinate analysis (*239*), polarized absorption spectrum (*483*), X-ray (*482,484,485*), XPS (*268*), CV (*476,477*), electron density distribution (*485*), NQR (*486–488*), high-pressure NQR (*489*), DTA (*482*), aquation (*323*), ^{191m}Ir generator (*490*), doped into AgBr, photochem. (*491*)
$[OsCl_nBr_{6-n}]^{2-}$	IR, Raman, normal coordinate analysis (*492,493*)
$[OsCl_5I]^{2-}$	Far IR, normal coordinate analysis (*493*)
cis-$[OsCl_4I_2]^{2-}$	Far IR, normal coordinate analysis (*493*)
fac-$[OsCl_3I_3]^{2-}$	Far IR, normal coordinate analysis (*493*)
$[OsBr_6]^{2-}$	IR (*239*), Raman (*239*), normal coordinate analysis (*239*), X-ray (*484*), XPS (*268*)
$[OsI_6]^{2-}$	IR (*239*), Raman (*239*), normal coordinate analysis (*239*), XPS (*268*)
Os(V)	
$[OsF_6]^-$	CV (*476*)
$[OsF_nCl_{6-n}]^-$	Preparation, IR, Raman (*481*)
$[OsCl_6]^-$	CV (*476*)
Os(VI)	
trans-$[Os(O)_2Cl_4]^{2-}$	X-Ray (*403*)
$[OsOF_4]$	Matrix-isolation IR and UV/Vis (*494*), mass spectrum (*494*)
$[OsOCl_4]$	Electron diffraction (*400*)
$[OsF_6]$	Matrix-isolation IR and UV/Vis (*494*), mass spectrum (*494*), calc. of optical and magnetic properties (*495*), graphite interchelate, neutron scattering, EPR, Raman, mag. (*496–498*)
$[OsOF_3]^+$	Mass spectrum (*494*)

TABLE XII (*Continued*)

Complex	Studies and references
Os(VII)	
$[OsOF_5]$	Matrix-isolation IR and UV/Vis (*494*), mass spectrum (*494*)
$[OsOF_4]'$	Mass spectrum (*494*)
Os(VIII)	
$[Os(O)_3F_2]$	Matrix-isolation IR and UV/Vis (*494*), mass spectrum (*494*), force constants (499)

d. Sulfur, Selenium, and Tellurium Tetrahalide Complexes. The reaction of $[OsO_4]$ with SCl_2 yields *trans*-$[Os(SCl_4)_2Cl_4]$, which reacts with ECl_4 (E = Se or Te), to yield *trans*-$[Os(ECl_4)_2Cl_4]$. The structures of all three complexes have been determined by IR and ^{35}Cl NQR spectroscopies and X-ray crystallography. They contain long E—Cl bonds between the ECl_3^+ and $[OsCl_6]^{2-}$ groups (*447, 478, 502*). *trans*-$[Os(SeBr_4)_2Br_4]$ and $[Os(SF_4)F_5]$ have also been reported (*447, 503*).

e. Dichlorobis(triphenylphosphine)argentate(I) Complexes. $[OsCl_6]^{2-}$ reacts with Ag(I) and PPh_3 to form *trans*-$[Os\{\mu\text{-}\eta^2\text{-}(Cl,Cl)\text{-}AgCl_2(PPh_3)_2\}_2Cl_2]$, which has been characterized by X-ray crystallography (*504*).

9. Hydride and Dihydrogen Complexes

a. Hydride Complexes. The Os(II) hydride complexes, $Mg_2[OsH_6]$ and $Mg_2[OsD_6]$, are prepared from Os powder and MgH_2 and MgD_2, respectively. Powder X-ray and neutron diffraction of the hydride and deuteride, respectively, show that the complexes possess a $K_2[PtCl_6]$-type structure, with Os—D bond lengths of 1.68(1) Å (*505*). Other hydride complexes are discussed elsewhere in this review (Table XIII).

b. Borohydride Complexes. The reactions of $[Os(H)(Cl)(CO)(PR_3)_2]$ (R_3 = Pr^i_3 or $MeBu^t_2$) with $NaBH_4$ in MeOH yield the octahedral complexes, *trans*-$[Os(H)(CO)(\eta^2\text{-}BH_4)(PR_3)_2]$, which contain an η^2-H,H′ borohydride ligand. The structure is only rigid below −30°C; at higher temperatures, the bridging and terminal hydrides of the BH_4^- ligand undergo exchange on the NMR time scale. There is no exchange

TABLE XIII

HYDRIDE COMPLEXES WITH OTHER LIGANDS

Complex or coligand	Section	Complex or coligand	Section
Osmaboranes	II,C,1	H_2	II,C,9,c
CS, CSe, CTe	II,C,2,c	CO	II,C,2,b
CS_2, CSSe, $SCSMe^-$	II,C,2,e	CO_2	II,C,2,d
Alkene	II,C,2,h	Alkyl and aryl	II,C,2,f
Isonitrile	II,C,2,n	Allyl	II,C,2,l
Silyl	II,C,3	Ammine	II,C,4,a
Porphyrins	II,C,4,d	N heterocycles	II,C,4,e
NO, NO^+	II,C,4,f	Oxime	II,C,4,l
Diazenes	II,C,4,m	Schiff bases	II,C,4,w
Benzotriazole	II,C,4,z	Phosphines	II,C,5,a
Phosphites	II,C,5,b	η^2-CH_2PR_2	II,C,5,c
Arsines	II,C,5,d	Diketonates	II,C,6,k
O_2	II,C,6,m	RCO_2^-	II,C,6,o
RSO_3^-	II,C,6,q	$SNNMe_2$	II,C,7,j
PyS, pymS	II,C,7,v	BH_4^-	II,C,9,b

between the H^- ligand and the BH_4^- hydrides (*128*). This contrasts with the pentagonal-bipyramidal complex, $[Os(\eta^2\text{-}BH_4)(H)_3\{P(cyclo\text{-}C_5H_9)_3\}_2]$, in which the hydrides and the two sites occupied by the BH_4^- hydrides exchange rapidly on the NMR time scale at 90°C (*506*). The former BH_4^- complex, with $R_3 = MeBu^t_2$, is also prepared from the reaction of $[Os(H)(Cl)(CO)\{N\text{-}N(OH)=(CH_3)_2\}(PMeBu^t_2)_2]$ with $NaBH_4$ (*124*).

c. Dihydrogen Complexes. The reduction of $[Os(NH_3)_5(O\text{-}SO_2CF_3)]^{2+}$ in methanolic or aqueous solutions yields the η^2-dihydrogen complex, $[Os^{II}(NH_3)_5(H_2)]^{2+}$, which is reversibly oxidized to the Os(III) complex, $[Os^{III}(NH_3)_5(H_2)]^{3+}$. The Os(III) complex is only stable in strong acid and readily deprotonates to give the hydride complex, $[Os^{III}(NH_3)_5H]^{2+}$. The presence of the dihydrogen ligand has been established by NMR and IR spectroscopies in conjunction with deuterium labeling experiments (*201*). The complexes *cis*-$[Os(NH_3)_4(H_2)(\pi\ acid)]^{2+}$ and *cis*-$[Os^{III}(NH_3)_4(H_2)(X)]^{2+}$ (X = halide) are prepared from the reactions of a π acid or X^- with the Os(IV) complex, *cis*-$[Os(NH_3)_4(H)_2]^{2+}$ (*89*). The porphyrin dihydrogen complexes, $[Os(oep)(H_2)]^{2+}$ and $[Os(oep)(HD)]^{2+}$, have also been reported (Section II,C,4,d) (*507*).

Recently, *trans*-$[Os(\eta^2\text{-}H_2)(H)(depe)_2]^+$ and its Ru and Fe analogs

have been prepared and characterized by NMR spectroscopy. The barrier for exchange involving the dihydrogen and hydride ligands, at 300 K, is lower for Os (53 kJ mol^{-1}) than for Ru (>63 kJ mol^{-1}) and is approximately equal to that for the Fe (54 kJ mol^{-1}) analogs. The Os complex has a weak H—H bond and a strong Os—H_2 bond. When small changes to the bidentate phosphine ligand are made, i.e., replacing depe by dppe, the dihydrogen analogs only exist for the Fe and Ru complexes. The Os complex exists as the classical trihydride complex. The depe dihydrogen complex is made from the reaction of *trans*-[Os(H)(Cl)(depe)$_2$] with H_2 and the H—H bond length is estimated to be 1.12 ± 0.03 Å from NMR relaxation techniques. This is much longer than the typical H—H bond lengths of ~0.9 Å that are estimated for Ru and Fe analogs (*508, 509*). The crystal structure of the dihydrogen complex has been determined, but disorder has precluded an analysis of the H—H bond length (*510*). An even longer bond has been estimated from ^1H NMR experiments on *trans*-[Os(η^2-H_2)(H)($Et_2PCH_2CH_2PPh_2$)]$^+$ (*511*). Reactions of either *cis*-β-[Os(Cl)$_2$(*meso*-tetraphos)] or *trans*-[Os(H)(Cl)(*meso*-tetraphos)] with H_2 in thf yield *trans*-[Os(η^2-H_2)(H)(*meso*-tetraphos)]$^+$. *cis*-α-[Os(η^2-H_2)(H)(*rac*-tetraphos)]$^+$ is formed by protonation of *cis*-α-[Os(H)$_2$(*rac*-tetraphos)] with HBF_4. There is no exchange on the NMR time scale at 293 K between η^2-H_2 and H^- for the trans complex, but the cis complex undergoes extremely rapid exchange (*301*). Related *trans*-[Os(η^2-H_2)(H)(PR_3)$_4$] and *trans*-[Os(η^2-H_2)(Cl)(PR_3)$_4$] complexes are prepared from protonations of the hydride analogs (*299*). Similarly, protonation of [Os(H)$_2$(L)$_4$] (L = PhP(OEt)$_2$ or P(OEt)$_3$] with HBF_4 results in the complexes [Os(H)(η^2-H_2)L_4], which are assigned a trans structure on the basis of NMR experiments. The H_2 ligands in these complexes are readily displaced by other ligands, making them useful synthetic intermediates (*187, 512*). *trans*-(η^2-H_2),H^- complexes are formed via the reversible binding of H_2 to *trans*-[Os(H)(Cl)(CO)(PPr^i_3)$_2$] (*419, 420*) or *trans*-[Os(H)(Cl)(CO)($PMeBu^t_2$)] (*419*) to give *trans*-[Os(η^2-H_2)(H)(Cl)(CO)L_2]. [Os^{II}(η^2-*O,O'*-OAc)(PPh_3)$_3$(H_2)]$^+$ has also been reported recently (*423*). [Os($SiEt_3$)Cl(η^2-H_2)(CO)(PPr^i_3)$_2$] (Section II,C,3) and [Os^{II}{(η^2-*O,O'*)-OAc)(PPh_3)$_3$(η^2-H_2)]$^+$ have also been reported recently (*192a, 423*).

Although most of the stable hydrogen complexes have a formal oxidation state of Os(II), there is recent evidence for the formation of [Os^{IV}(H)$_3$(η^2-H_2)L_3]$^+$ complexes. These complexes were first assigned to be Os(VI) pentahydrides (*513*) and are obtained by protonations of the tetrahydrides, [Os^{IV}(H)$_4$$L_3$] [L = PMe_2Ph, PPh_3, or P(4-tolyl)$_3$], with HBF_4 at low temperatures (*423, 513–516*). The criteria for distin-

guishing between classical polyhydride and η^2-H_2 complexes have also been reviewed (*423, 514*).

D. Dinuclear and Polynuclear Complexes

This section excludes the quite extensive dinuclear and polynuclear Os/CO cluster chemistry, which will only be referred to where it overlaps with classical coordination chemistry. The general classes of Os dimers that are often encountered are Os_2^{n+} (n = 4–8) complexes with Os—Os bonds, with or without bridging ligands; Os(II) dimers, $[(L)_6Os_2(\mu\text{-}L')]^+$; $[A_{10}Os_2(\mu\text{-}L)]^{n+}$; $[(bpy)_4Os_2(\mu\text{-}L)]^{n+}$; Os(VI) dimers, $[L_8Os_2(\mu\text{-}O)_2]$; and Os(VIII) dimers $[\{Os(O)_n(NR)_{4-n}\}_2(\mu\text{-}L)]$. Because the nature of the bridging group has a dominant influence on chemical and physical properties of dimers, these dimers are arranged according to the nature of these bridging ligands.

1. Dimers with Os—Os Bonds

The variations in the Os—Os bond lengths and variations in other M—M bond lengths have been the subject of theoretical modeling, and these variations in bond lengths have been rationalized (*517*).

a. No Bridging Ligands. The electrochemistry of dinuclear Os prophyrinato(2−) complexes containing an Os=Os double bond has been studied. $[(oep)Os^{II}{=}Os^{II}(oep)]$ undergoes a series of one-electron reversible oxidation and reduction processes. The complexes $[(oep^+)Os^{III}{\equiv}Os^{III}(oep^+)]^{4+}$, $[(oep^+)Os^{III}{\equiv}Os^{III}(oep)]^{3+}$, $[(oep)Os^{III}{\equiv}Os^{III}(oep)]^{2+}$, $[(oep)Os^{III}{\doteq}Os^{II}(oep)]^+$, and $[(oep)Os^{II}{=}Os^{II}(oep^-)]^-$ have been identified in the CV. $[Os^{II}(oep)]_2$ is oxidized by one equivalent of Fc^+ or Ag^+ to form $[Os(oep)]_2^+$ and by two equivalents of Ag^+ to form $[Os^{III}(oep)_2]^{2+}$. The Os_2^{II} porphyrin complex has the unusual property of having an Os=Os double bond and triplet ground state, whereas the Os_2^{III} dimer has an Os≡Os triple bond and a singlet ground state. The properties have been rationalized in terms of an MO scheme of metal–metal bonding. Both the Os_2^{II} and the mixed-valence ions are EPR silent down to 77 K (*518*). Detailed IR and Raman spectroscopic studies of the 0, +1, and +2 ions have been performed (*519*).

The Os(III) dimers, $[Os_2X_8]^{2-}$ (X = Cl^-, Br^-, or I^-) each have an Os≡Os triple bond and terminal halogens. They have been characterized by X-ray diffraction, IR and UV/Vis spectroscopies, and electrochemistry (*232, 520–523*). The complexes have also been subjected to SCF-X_α-SW calculations of the energies of their electronic states (*521*).

The complexes exhibit reversible oxidations to the $[Os_2X_8]^-$ analogs and irreversible reductions (*522, 523*). Decomposition and substitution chemistry of the complexes has also been studied (*302, 523*). The tetrameric complex $[I_4OsOsI_2(\mu\text{-}I)_2I_2OsOsI_4]^{2-}$ contains two $[Os_2I_8]$ units fused together via two bridging iodides, as shown by X-ray diffraction (*524*). $[(cp)_2Os{\equiv}Os(cp)_2]^{2+}$ has been prepared and characterized by X-ray diffraction (*264*).

b. μ-Porphyrinato Complexes. The dimeric complex $[(py)_2Os(dpb)Os(py)_2]$ undergoes pyrolysis to form the Os dimer with an Os=Os double bond, [Os(dpb)Os]. [Ru(dpb)Os] is prepared in a similar manner from $[(py)_2Ru(dpb)Os(py)_2]$ (*141*).

c. μ-Carboxylato Complexes. $[Os_2(\mu\text{-}O_2CCH_3)_4Cl_2]$ is the standard starting material for the synthesis of a variety of diosmium complexes with metal–metal bonds (*303, 319, 322, 525–529*). Detailed IR and Raman spectroscopic studies, including excitation profiles, have been performed with $[Os_2(\mu\text{-}O_2CR)_4Cl_2]$ R = CH_3, CD_3, Et, or Pr^n). All resonance Raman spectra exhibit progressions of $\nu_1(Os{\equiv}Os)$ (*530, 531*). $[Os_2(\mu\text{-}O_2CR)_4Br_2]$ (R = Et or Pr^n) are prepared from their chloro analogs and have been characterized by electrochemistry and ^1H NMR and UV/Vis spectroscopies. They exhibit reversible oxidations to the mixed-valence Os(IV)–Os(III) complexes but the reductions are irreversible (*525*).

Treatment of $[Os_2(\mu\text{-}O_2CCH_3)_4Cl_2]$ with appropriate Grignard reagents leads to the formation of $[Os_2(\mu\text{-}O_2CCH_3)_2(R)_4]$ (R = CH_2CMe_3 or CH_2SiMe_3), but unlike the Ru analogs, further treatment with Grignard reagents does not remove the remaining acetate bridges. These complexes have been characterized by ^1H and ^{13}C NMR spectroscopies (*527*). $[Os_2(CO)_6(\mu\text{-}O_2CMe)_2]$ reacts with dppm or dppmS to form $[Os_2(CO)_4(\mu\text{-}O_2CMe)_2(\eta^1\text{-}L)_2]$, and the dppm complex is oxidized by H_2O_2 to give the analogous complex containing dppmO ligands. All complexes were characterized by IR and ^1H and ^{31}P NMR spectroscopies (*532*). The complexes in which L = PR_3, NCMe, or py are also known, but with thf only one CO ligand is lost to form $[Os_2(CO)_5(\mu\text{-}O_2CMe)_2(thf)]$. Reaction of the latter with PH_3 or PMe_2Ph gives $[Os_2(CO)_5(\mu\text{-}O_2CMe)_2(PR_3)]$, and reaction with Cl^- gives $[Os_2(CO)_5(\mu\text{-}O_2CMe)_2Cl]^-$, which was characterized by X-ray crystallography (*418*).

d. μ-2-Hydroxypyridine Complexes. The mixed-valence ions $[Os_2(\mu\text{-}L)_4Cl]$ (L = chp or fhp), have been prepared from $[Os_2(\mu\text{-}O_2CCH_3)_4Cl_2]$ and were characterized by X-ray diffraction, UV/Vis

spectroscopy, and electrochemistry. The Os(II) center is five coordinate, with four pyridine groups and the Os completing a square pyramid, whereas the Os(III) center is octahedral with the four alcoholates, Cl^-, and Os completing the coordination sphere (*319, 322, 528*). The fhp complex is reversibly oxidized but is irreversibly reduced, whereas both the reduction and oxidation of the chp complex are reversible (*322, 528*). The chp complex has also been characterized by magnetic measurements, IR spectroscopy, and low-temperature EPR spectroscopy (*322*). The other product of the reaction with chp is $[Os_2(\mu\text{-chp})_2Cl_4]$, which reacts with L′ to give $[Os_2(\mu\text{-chp})_2Cl_4(L')]$ (L′ = py or OH_2), both of which have been characterized by UV/Vis spectroscopy, electrochemistry, and X-ray diffraction. Both complexes exhibit reversible one-electron reductions (*319*).

$[Os_2(hp)_4Br_2]$ has been prepared from its chloro analog and has been studied by electrochemistry and UV/Vis and ^1H NMR spectroscopies (*525*).

e. μ-2-(Diphenylphosphine)pyridine Complexes. Two crystal structures of $[Os_2(\mu\text{-}O_2CMe)(\mu\text{-}Ph_2Ppy)_2Cl_4]$ have been reported in which each Os is octahedrally bound to P, N, O, Os, and two Cl donors. The complex undergoes reversible oxidation and reduction (*526, 529*).

f. μ-Orthometalated Triphenylphosphine Complexes. $[Os_2(\mu\text{-}O_2CMe)_2\{\mu\text{-}(C,P)\text{-}Ph_2PC_6H_4\}_2Cl_2]$ reacts with Me_3SiCl in refluxing thf to form $[Os_2\{\mu\text{-}(C,P)\text{-}Ph_2PC_6H_4\}_2Cl_4]$, in which the bridging ligands adopt a cis geometry, with each Os being bonded to two Cl and P, C, and Os donors. The complex has been characterized by IR spectroscopy, X-ray diffraction, and cyclic voltammetry. It reveals a reversible reduction to its Os^{III}–Os^{II} analog (*533*).

g. μ-η⁵,η¹-Cyclopentadienyl(2−) Complex $[(cp)_2Os{\equiv}Os(cp)_2]^{2+}$ is oxidized to the Os(IV) dimer $[(cp)Os(\mu\text{-}\eta^5,\eta^1\text{-}C_5H_4)_2Os(cp)]^{2+}$, which has been characterized by X-ray crystallography (*264*).

2. Carbon Ligands

a. μ-CO_2 Complexes. The dimeric complex $[(cod)Rh(H)_3Os(PMe_2Ph)_3]$ reacts with CO_2 to give *cis, mer*-$[Os(H)_2(CO)(PMe_2Ph)_3]$, $[(cod)_2Rh_2(CO_2)Os(PMe_2Ph)_3(H)_2]$, and H_2O. Both the CO in the first complex and the CO_2 in the second are derived from the gaseous CO_2, as shown by labeling experiments. The trimer was analyzed by X-ray crystallography, which shows the CO_2 bound to Os via the carbon and to each of the Rh atoms via an oxygen atom (*138*).

b. Isopropylcarbamoyl as a Bridging Ligand. The complex μ-bromo-μ-(isopropylcarbamoyl-*O,C*)bis(bromotricarbonylosmium) has been prepared and characterized by X-ray crystallography (*534*).

c. η^2-Arene-Bridged Complexes. Benzene, naphthalene, pyrene, and diphenylacetylene act as bridging ligands to form dinuclear $[(NH_3)_5Os(arene)M(NH_3)_5]^{4+}$ complexes [M = Os (*88, 171, 173, 174*), Ru (*172*)]. The former complexes are made from the self-condensation of $[Os(NH_3)_5(arene)]^{2+}$ with concomitant release of a mole of arene per mole of dimer (*173*), whereas the latter complexes are prepared from the reaction of $[Os(NH_3)_5(arene)]^{2+}$ with $[Ru(NH_3)_5(solvent)]^{2+}$ (*172*). These complexes are believed to have the ligand coordinated in a trans fashion to the 2,3 and 4,5 positions of one ring and this has been confirmed in the X-ray structure of $[(NH_3)_5Os(benzene)Os(NH_3)_5]^{4+}$ (*88*). In the case of the dinuclear pyrene complex, the osmium centers bind to the two exterior double bonds of the central rings in a trans geometry, as shown in the X-ray structure of $[(NH_3)_5Os(\mu\text{-pyrene})Os(NH_3)_5](CF_3SO_3)_4 \cdot 4(CH_3)_2CO$ (*174*). The mixed-valence +5 ions have been observed but lose an η^2-linkage to form the M(III) solvent complex and $[Os^{II}(NH_3)_5(arene)]^{2+}$. The timescales of these decomposition reactions are fast (seconds) for M = Ru (*172*) and the dinuclear Os pyrene complex (*174*); however, $[(NH_3)_5Os(\mu\text{-benzene})Os(NH_3)_5]^{5+}$ is stable for 0.5 hr or more at 20°C (*173*). Further oxidations to the +6 ions are irreversible on the conventional CV time scales and result in the loss of the arene ligands, and in the case of diphenylacetylene, formation of $[Os(NH_3)_5\{\eta^2\text{-}(alkyne)\text{-}PhC{\equiv}CPh\}]^{3+}$. Pyrolysis of $[(NH_3)_5Os(benzene)Os(NH_3)_5]^{4+}$ results in the formation of $[(NH_3)_5Os(\mu\text{-}\eta^2,\eta^6\text{-benzene})Os(NH_3)_3]^{4+}$ (*88*).

d. μ-1,3-Butadiene Complexes. $[(NH_3)_5M(1,3\text{-butadiene})M'(NH_3)_5]^{4+}$(M = M′ = Ru; M = Ru, M′ = Os; M = M′ = Os) have been prepared and characterized by ^1H NMR spectroscopy and electrochemistry (*70*).

e. μ-Cyano Complexes. $[(NH_3)_5Os^{III}NCM^{II}(CN)_5]^-$ (M = Fe, Ru, or Os) and $[(NC)_5OsCNCo(CN_5)]^{6-}$ have been prepared and their UV/Vis spectroscopy, electrochemistry, and photochemistry have been studied (*535*).

3. Nitrogen Donor Ligands

a. μ-Dinitrogen Complexes. Much of this chemistry has been covered in the review by Griffith (*2*). However, a full account of the

chemistry is presented here to place it in context with recent developments. $[(NH_3)_5Os(N_2)Os(NH_3)_5]^{5+/4+}$ complexes were the first of the decaammine dinuclear complexes of Os to be reported. They were prepared from the reduction of $[Os(NH_3)_5(OH_2)]^{3+}$ in the presence of $[Os(NH_3)_5(N_2)]^{2+}$, but the yields were poor (*536*). Improved yields have been obtained from the partial oxidation of $[Os(NH_3)_5(N_2)]^{2+}$ by I_2 in neat CF_3SO_3H, or the reduction of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ in dma/dme in the presence of $[Os(NH_3)_5(N_2)]^{2+}$ (*537*). The analogous +6 ion is unstable at room temperature, but it can be generated quantitatively in solution at 5°C by the oxidation of the +5 ion by Ce(IV). It is also obtained analytically pure from the solid-state oxidation of the chloride salt of the +5 ion by Cl_2. Provided that it is kept dry, it is stable for weeks at −4°C (*426, 537*).

Unlike the remarkably stable mixed-valence diosmium complex, the much less stable heterodinuclear $[(NH_3)_5Os(N_2)Ru(NH_3)_5]^{5+}$ decomposes to $[Os(NH_3)_5(N_2)]^{2+}$ and $[Ru(NH_3)_5(OH_2)]^{3+}$ in water over a period of hours (*537*). This is to be contrasted with the Ru_2 mixed-valence analog that decomposes over a matter of minutes at room temperature (*536*). The heterodinuclear +5 and +4 ions have been reported by a number of workers (*538–540*), though not completely characterized until recently (*537*). Similarly, the oxidation of the +5 ion to the +6 ion has been known for some time (*539*). However, its properties have only recently been studied in solution by Ce(IV) oxidation, or in the solid state, by the Cl_2 oxidation. It is much less stable than its diosmium analogs. There is also evidence for the formation of the unstable $[(NH_3)_5Os(N_2)Rh(NH_3)_5]^{5+}$ heterodinuclear species from the reaction of $[Os(NH_3)_5(N_2)]^{2+}$ with $[Rh(NH_3)_5(OSO_2CF_3)]^{2+}$ in neat CF_3SO_3H (*537*).

A large variety of nonaammine and octaammine complexes of the form *cis*-$[(NH_3)_5Os(N_2)Os(NH_3)_4X]^{5+/4+/3+}$ (X = Cl^-, Br^-, I^-, or $CF_3SO_3^-$), *cis*-$[(NH_3)_5Os(N_2)Os(NH_3)_4L]^{6+/5+/4+}$ (L = OH_2 or N_2), *cis,cis*-$[X(NH_3)_4Os(N_2)Os(NH_3)_4X]^{4+/3+/2+}$ (X = Cl^-, Br^-, I^-, or $CF_3SO_3^-$), *cis,cis*-$[L(NH_3)_4Os(N_2)Os(NH_3)_4X]^{5+/4+/3+}$ (L = N_2, X = Cl^- or $CF_3SO_3^-$; L = OH_2, X = Cl^-), and *cis*-$[L(NH_3)_5Os(N_2)Os(NH_3)_4L]^{6+/5+/4+}$ (L = N_2) were prepared and characterized by methods similar to those described above, using either the reaction of *cis*-$[Os(NH_3)_4(N_2)_2]^{2+}$ with $[Os(NH_3)_5(N_2)]^{2+}$, or self-condensation of *cis*-$[Os(NH_3)_4(N_2)_2]^{2+}$ (*78, 79, 537*). *cis,cis*-$[(CO)(NH_3)_4Os(N_2)Os(NH_3)_4(CO)]^{4+}$ has also been prepared by the oxidative coupling of amine ligands (*58*). Other coupling reactions have been used to prepare *trans,trans*-$[(CH_3CN)(NH_3)_4Os(N_2)Os(NH_3)_4(NCCH_3)]^{5+}$ from $[Os^{VI}(NH_3)_4(N)]$ under UV/Vis irradiation in acetonitrile (*269*).

$[(4\text{-pic})Cl_3Os(N_2)OsCl(4\text{-pic})_4]^+$ has been prepared from the coupling reactions of *trans*-$[Os(N)Cl_3(4\text{-pic})_2]$ in the presence of 4-pic (*42, 226*).

In addition to the homodinuclear nonaammine complexes, the heterodinuclear complexes *cis*-$[(NH_3)_5Os(N_2)Ru(NH_3)_4Cl]^{5+/4+/3+}$ (*79, 537, 539*) and *cis*-$[(NH_3)_5Ru(N_2)Os(NH_3)_4(isn)]^{6+/5+/4+}$ (*79, 537*) have also been reported.

b. μ-Pyrazine Complexes. The preparations of the μ-pyrazine/ammine complexes are outlined in Scheme 13 (*80*), using the general methods previously described. Details about their spectroscopic and electrochemical properties are given in Sections III,C,1 and IV, B,1, respectively. The heterodinuclear $[A_5RupzOsA_5]^{n+}$ complexes have also been isolated recently.

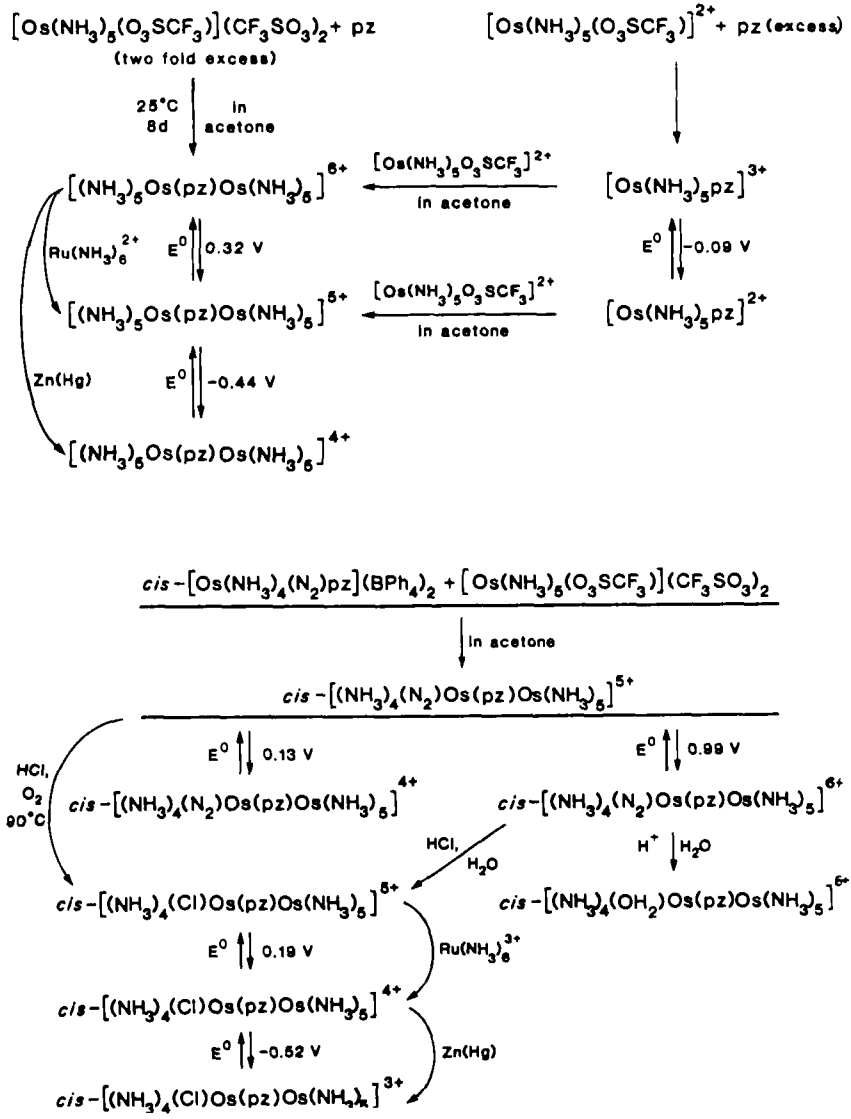
cis-$[(bpy)_2ClOspzRu(NH_3)_5]^{5+/4+/3+}$ complexes have been prepared and characterized by UV/Vis and near-infrared spectroscopies and electrochemistry. Different electronic isomers are obtained for the ground state of the mixed-valence ion, depending on the solvent (Section III,C,2) (*541*). The Os(VI) dimer, *trans,trans*-$[Cl_4(N)Os(pz)Os(N)Cl_4]^{2-}$, has been prepared and characterized by X-ray crystallography (*226*).

c. μ-Isonicotinamide and μ-Isonicotinamidepoly(proline) Complexes. Complexes of the type $[(NH_3)_5Os(\mu\text{-L})M(NH_3)_5]^{n+}$ (L = isn or $isn(pro)_m$; M = Co or Ru) have been prepared and characterized by a variety of techniques (*429, 430*). They have been used in studying intramolecular electron transfer along protein chains (Section V,C,2).

d. μ-Pyrimidine, μ-4,4′-Bipyridine, and Related Complexes. The decaammine complexes have been prepared by methods analogous to those described for the μ-pyrazine complexes. Although most have not been fully characterized as yet, the μ-4,4′-bipyridine complex has been studied by UV/Vis/NIR, MCD, and IR spectroscopies and electrochemistry (*182, 428, 542–544*).

$[(trpy)(bpy)Os^{II}(4,4'\text{-bpy})Ru^{II}(OH_2)(bpy)_2]^{4+}$ has been prepared and its redox chemistry and spectroelectrochemistry studied. All oxidation states up to $[Os^{III}Ru^{IV}(O)]^{5+}$ are observed, and in some oxidation states proton-induced intramolecular electron transfer is observed (Section V,C,2) (*228*). The preparation, electrochemistry, and photophysics of $[(bpy)_2(CO)Os^{II}(\mu\text{-L})Os^{II}(phen)(dppene)Cl]^{3+}$ (L = 4,4′-bpy or bpa) were reported (*545*).

e. μ-2,3-Bis(2′-pyridyl)pyrazine and μ-2,3-Bis(2′-pyridyl)quinoxaline Complexes. $[(bpy)_2Os(\mu\text{-dpp})M(bpy)_2]^{4+}$ complexes (M = Ru or



SCHEME 13. Preparation of μ-pyrazine complexes. Reprinted with permission from *Inorganic Chemistry*, Ref. *80*. Copyright 1988, American Chemical Society.

Os) have been prepared and characterized by electronic absorption and emission spectroscopies and electrochemistry (*546*). $[(OC)_3ClRe(L\text{-}L)Os(bpy)_2]^{2+}$ (L-L = dpp or dpq) were prepared by the reaction of $[Os(bpy)_2(L\text{-}L)]^{2+}$ with $[ReCl(CO)_5]$ and characterized by UV/Vis spectroscopy and electrochemistry (*232*). The tetranuclear complex [Os{(μ-

dpp)Ru(bpy)$_2$}$_3$]$^{8+}$ has been prepared and its electrochemistry and UV/Vis and luminescence spectra have been studied (*547*).

f. μ-3,5-Bis(2-pyridyl)-1,2,4-triazolato and μ-3,6-Bis(2-pyridyl)-1,2,4,5-tetraazine Complexes. [(bpy)$_2$M(bpt)M′(bpy)$_2$]$^{n+}$ complexes [M = M′ = Ru; M = M′ = Os; M = Ru, M′ = Os (two isomers)] have been prepared and characterized by UV/Vis/NIR and ^{1}H NMR spectroscopies, electrochemistry, and an X-ray structure of one of the heterodinuclear complexes (*548*). Similar complexes with bptz have also been prepared and characterized by electrochemistry, UV/Vis spectroscopy, and Hückel calculations (*549*).

g. μ-trans-1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethene and Related Complexes. The complexes [(4,4′-Me$_2$bpy)$_2$M(bbpe)M(4,4′-Me$_2$bpy)$_2$]$^{4+}$ [bbpe = *trans*-{4-(4′-Mebpy)}$_2$-CH=CH; M = Ru or Os] have been prepared and characterized by electrochemistry, UV/Vis/NIR, and emission spectroscopies. Although details of the Os$_2$ complex have not been given, the complexes exhibit interesting electrochemical and photophysical properties (*550*). Similar studies have also been reported on [(bpy)$_2$M(μ-L)M′(bpy)$_2$]$^{4+}$ [L = {4-(4′-Mebpy)}$_2$CH$_2$CHOHCH$_2$, M = M′ = Ru; M = Ru, M′ = Os; M = M′ = Os] (*551*).

h. μ-Bis(benzylimidazolato) Complexes. [(bpy)$_2$M(bibzim)M′(bpy)$_2$]$^{2+}$ (M = M′ = Ru; M = Ru, M′ = Os; M = M′ = Os) have been prepared and characterized by CV. They exhibit several reversible one-electron oxidations and reductions that are both metal and ligand centered. The UV/Vis/NIR spectra have also been recorded for the M(II)-M′(II), M(II)-M′(III) and M(III)-M′(III) oxidation states (*552*).

i. μ-Diacetylhydrazinato(2−) Complexes. [(bpy)$_2$M(adc-Me)M(bpy)$_2$]$^{n+}$ (M = Ru or Os) has been prepared and characterized by electrochemistry, UV/Vis spectroscopy, and Hückel calculations (*549*).

j. Porphyrin Dimers. Reactions of the dinuclear porphyrin, H$_4$dpb, with [Os$_3$(CO)$_{12}$] in the presence of py gives [(CO)(py)Os(dpb)-Os(CO)(py)]. On irradiation, it reacts further with py to give [(py)$_2$Os(dpb)Os(py)$_2$]. The heterodinuclear complexes [(CO)(CH$_3$-OH)Ru(dpb)Os(CO)(CH$_3$OH)] and [(CO)(OH$_2$)Os(dpb)Zn] are prepared by the reaction of [Os$_3$(CO)$_{12}$] with [Ru(CO)(CH$_3$OH)(H$_2$dpb)] and [Zn(H$_2$dpb)], respectively. The heterodinuclear Ru/Os complexes are prepared under a set of reactions similar to those of the Os/Os dimers, to produce [(py)$_2$Ru(dpb)Os(py)$_2$] (*141*).

k. μ-Cyanogen Complexes. $[(NH_3)_5OsNCCNOs(NH_3)_5]^{5+}$ is prepared from the oxidative dehydrogenations of the dinuclear 1,2-ethanediamine complex (Section V,E,2,b). It has been studied by UV/Vis/NIR and IR spectroscopies and electrochemistry, and the susceptibilities of the +4, +5, and +6 complexes toward ligand hydrolysis are discussed in Section V,E,3.

l. μ-Dicyanoamide Complexes. $[(NH_3)_5Os(NCNCN)Os(NH_3)_5]^{5+}$ has been prepared by standard methods and characterized by UV/Vis, NIR, and IR spectroscopies and electrochemistry (*542*).

m. μ-Dicyanobenzene and μ-Dicyanobicyclo[2.2.2]octane Complexes. Decaammine complexes have been prepared, but to date their characterization is incomplete (*542, 553*).

n. Bicyclo- and Tricyclo-N Heterocycles. Dinuclear adducts of dabco or tatd with $[OsO_4]$ and $[Os(O)_3(NR)]$ have been known for some time. Recent examples that have been prepared and characterized by ^1H NMR, Raman, IR, and ESCA spectroscopies include $[\{Os(O)_3(NC_8H_{17})\}_2(\mu\text{-L})]$ (*208*).

o. μ-Imido Complexes. One of the products of the reaction between $Bu^tNH(SiMe_3)$ and $[OsO_4]$ is the tetrameric complex *anti*-$[(Bu^tN)_2Os(\mu\text{-}Bu^tN)_2Os(NBu^t)(\mu\text{-}O)_2Os(NBu^t)(\mu\text{-}Bu^tN)_2Os(NBu^t)_2]$. The terminal Os atoms are four coordinate, whereas the central osmiums are five coordinate, as shown from an X-ray structure analysis (*265*).

Reduction of $[Os(NBu^t)_4]$ with PPh_3 or $PMePh_2$ yields a dimeric Os(VI) complex, $[(Bu^tN)_2Os(\mu\text{-}Bu^tN)_2Os(NBu^t)_2]$, whereas reduction with $Me_3O^+BF_4^-$ yields the analogous Os(VII) dimer, $[(Bu^tN)_2Os(\mu\text{-}Bu^tN)_2Os(NBu^t)_2](BF_4)_2$. Both have a tetrahedral arrangement of ligands about the Os centers, as shown by X-ray crystallography. The complexes were further characterized by ^1H NMR, mass, and IR spectroscopies, and electrochemistry. The Os(VII) dimer undergoes a reversible two-electron reduction to Os(VI) dimer and a further reversible two-electron reduction to presumably the Os(V) dimer (*265a*).

p. μ-Nitrido Complexes. The preparation of these complexes is given in Scheme 2 (Section II,B,3,b). $[Os_2(NH_3)_{10}N]^{5+}$ has been characterized by UV/Vis and IR spectroscopies and the electronic structure of this and related complexes has been discussed with the aid of a molecular orbital diagram (*47*). The properties of $[Os_2(N)(NH_3)_8Cl_2]Cl_3\cdot 2H_2O$ and $[Os_2(N)(NH_3)_7Cl_3]Cl_2\cdot H_2O$ have been reported, as well as their

aquations to $[Os_2(N)(NH_3)_8(OH_2)_2]^{5+}$ and $[Os_2(N)(NH_3)_7(OH_2)_3]^{5+}$, respectively. The later undergo successive deprotonations to give the mixed aqua/hydroxo and hydroxo complexes. The complexes have been characterized by IR and UV/Vis spectroscopies and electrochemistry (*46*). *trans,trans,trans*-$[\{(4\text{-pic})_2Cl_3Os(\mu\text{-}N)\}_2Os(4\text{-pic})_2Cl_2]$ is a minor product of the coupling of $[Os(N)(4\text{-pic})_2Cl_3]$ (Section II,D,3,a) (*42, 226*).

4. Phosphide-Bridged Complexes.

The diphosphide-bridged *cis,cis*-$[(H)_2(PMe_2Ph)_2Os(PMePh)_2Os(PMe_2Ph)_2(H)_2]$ complex is one of the products of the photolysis of $[Os(PMe_2Ph)_3(H)_4]$ in benzene (see Sections II,C,5,a and II,D,8,a for other products). This complex has been characterized by X-xay diffraction and ^1H and ^{31}P NMR spectroscopies (*307*). Deprotonation of $[OsCl(PH_3)(NCMe)(CO)(PPh_3)_2]^+$ results in the formation of $[\{Os_2(\mu\text{-}PH_2)Cl(CO)(PPh_3)_2\}_2]$. It has been characterized by X-ray crystallography (*261*).

5. Oxygen Donor Ligands

a. Mono(μ-oxo) Complexes. The crystal structure of the complex $[\{trans\text{-}[Os(\eta^4\text{-chba-Et})(OPPh_3)]\}_2O]^{2-}$ has been reported (Section II,C,4,x) (*290*). *cis,cis*-$[(bpy)_2(H_2O)Os^{III}(\mu\text{-}O)Os^{IV}(OH)(bpy)_2]^{4+}$ has been characterized by UV/Vis spectroscopy and electrochemistry (*318, 554*).

b. Bis(μ-oxo) Complexes. trans,trans-$[(py)_2(O)_2Os(\mu\text{-}O)_2Os(O)_2(py)_2]$ has been characterized by ^1H NMR, IR, and Raman spectroscopies (*235*). A variety of bis(μ-oxo) complexes of the general formulas $[\{Os(O)(OCR'R''CH_2NR)(\mu\text{-}O)\}_2]$, $[\{Os(O)OC_6H_{10}NR)(\mu\text{-}O)\}_2]$, and $[\{Os(O)(OCR'R''CH_2NR)L(\mu\text{-}O)\}_2]$ are obtained when either $[Os(O)_3(NR)]$, $[Os(O)_3(NR)L]$, or $[\{Os(O)_3(NR)\}_2(\mu\text{-}L)]$ (R = Bu^t, Ad, C_5H_{11}, or C_8H_{17}; L = qncd, tatd, or dabco) reacts with an alkene. The complexes have been characterized by IR, Raman, ESCA, and ^1H NMR spectroscopies (*208*).

c. μ-Hydroxo Complexes. Treatment of the cymene complex $[Os_2(\eta^6\text{-cym})Cl_2(\mu\text{-}Cl)_2]$ with NaOH results in the formation of $[(\eta^6\text{-cym})Os(\mu\text{-}OH)_3Os(\eta^6\text{-cym})]^+$. This reacts with RCO_2H (R = *trans*-PhCH=CH, Ph, Me, or H) or RCHO in acetone (R = *trans*-PhCH=CH, Ph, or Bu^t) to give $[(\eta^6\text{-cym})Os(\mu\text{-}OH)_2(\mu\text{-}O_2CR)Os(\eta^6\text{-cym})]^+$ and with RCHO in water to give $[(\eta^6\text{-cym})Os(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}O_2CR)Os(\eta^6\text{-cym})]^+$ (R = H, Me, or Et). The latter complex with R = H has been

characterized by X-ray crystallography and all complexes were characterized by ^{1}H NMR spectroscopy (*555*).

d. μ-RO⁻ Complexes. CO inserts into $[Os(O)_2(OMe)_4]^{2-}$ to form the transdioxo dimer $[(MeCO_2)_2(O)_2Os(\mu\text{-}OMe)_2Os(O)_2(OCOMe)_2]^{2-}$, which has been characterized by IR and NMR (^{1}H and ^{13}C) spectroscopies and an X-ray structure (*405*). $[(\eta^6\text{-cym})Os(\mu\text{-}OMe)_3Os(\eta^6\text{-cym})]^+$ has been prepared and characterized by IR, mass, and NMR [^{1}H(^{187}Os) reverse INEPT] spectroscopies (*556*).

e. μ-Dioxane Complexes. trans,trans-$[Cl_4(N)Os(dioxane)Os(N)Cl_4]^{2-}$ has been prepared and characterized (*226*).

6. Sulfur Donor Ligands

a. μ-Thiolato Complexes. Thermolysis of *trans*-$[Os(S\text{-dmso})_4Cl_2]$ or *trans*-$[Os(O\text{-dmso})(S\text{-dmso})Cl_2]$ at 150°C *in vacuo* results in the formation of the dimer species, $[Os_2(\mu\text{-}MeS)_2(Me_2S)_2Cl_4]$ and $[Os_2(\mu\text{-}MeS)_2(Me_2S)(O\text{-dmso})Cl_4]\cdot Me_2SO$. These diamagnetic Os(III) dimers have been characterized by IR, electronic absorption, and ^{1}H NMR spectroscopies, in addition to their conductivities and XPS spectra (*456*).

$[Os(N)(CH_2SiMe_3)_2Cl_2]$ reacts with excess pySH to give the dimeric *cis,cis*-$[Os(N)(CH_2SiMe_3)_2(\mu\text{-pyS})]_2$ in which each pyS ligand is both a chelate and provides a μ-RS^- bridge. In solution, NMR evidence shows the presence of two geometric isomers (syn and anti) and they crystallize in different forms, which are separated manually. The structure of one of the isomers has been determined by X-ray crystallography, and when pure crystals of either of the isomers are redissolved in solution, they equilibrate to a mixture of isomers over several hours (*156*).

fac-$[Co(SCH_2CH_2NH_2)_3]$ reacts with $OsCl_3$ to give the trimer in which the Os(III) center is bound via six thiolato bridging ligands, $[\{fac\text{-}Co(SCH_2CH_2NH_2)_3\}_2Os]^{3+}$. It has been characterized by IR, UV/Vis, and ^{1}H NMR spectroscopies (*557*).

b. μ-Disulfide and μ-Supersulfide Complexes. $[(cp)_2Os{\equiv}Os(cp)_2]^{2+}$ reacts with elemental sulfur to give the Os(IV) dimer, $[(cp)_2Os(SS)Os(cp)_2]^{2+}$, which has been characterized spectroscopically and by X-ray crystallography. It undergoes a reversible one-electron oxidation to its supersulfide analog (*462*).

7. *Halide-Bridged Complexes*

Oxidation of $[Os(NC_6H_3Me_2\text{-}2,6)_3]$ by $AgBF_4$ results in the Os(VI) dimer, $[(RN)_2Os(\mu\text{-}F)_2Os(NR)_2](BF_4)_2$, but no details of its characterization have been given (*265a*).

$[Os_2X_9]^{n-}$ (X = Cl^- or Br^-, n = 1–4) have been prepared and characterized recently by low-temperature electrochemistry and UV/Vis spectroscopy. The far-IR data of $(Bu_4N)_2[Os_2Br_{10}]$, $(Bu_4N)[Os_2Br_9]$, and $(Bu_4N)_3[Os_2Br_9]$ have also been reported. The redox series $[Os_2X_{10}]^{n-}$ (X = Cl^- or Br^-, n = 1–5) have also been characterized for the first time using low-temperature cyclic voltammetry (*558*). Detailed Raman, IR, and electronic absorption (UV/Vis/NIR) spectra have also been recorded at ambient and low temperature for the −2 species (*559*).

$[Os_2(\mu\text{-}X)_3(PR_3)_6]^+$ (X = Cl^- or Br^-) are prepared from the reactions of $[Os_2X_8]^{2-}$ with PR_3, and the structure of $[Os_2(\mu\text{-}Cl)_3(PEt_3)_6]^+$ has been determined by X-ray crystallography (*302*). $[Os_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]^+$ and $[Os_2(\mu\text{-}Cl)_2Cl_2(PEt_3)_6]$ are formed from $[OsCl_2(PMe_2Ph)_3]$ in noncoordinating solvents (*145*).

$[(\eta^6\text{-cym})ClOs(\mu\text{-}Cl)_2OsCl(\eta^6\text{-cym})]$ and related complexes are often used as synthetic intermediates in organometallic chemistry, but they are also useful intermediates for the synthesis of a variety of dinuclear Os complexes with inorganic bridges (*555*, *556*). On heating, they form $[(\eta^6\text{-cym})Os(\mu\text{-}Cl)_3Os(\eta^6\text{-cym})]^+$, which reacts with propanol to give $[(\eta^6\text{-cym})ClOs(\mu\text{-}Cl)(\mu\text{-}H)OsCl(\eta^6\text{-cym})]$. All complexes have been characterized by IR, mass, and NMR [$^1H(^{187}Os)$ reverse INEPT] spectroscopies (*556*).

8. *Hydride-Bridged Complexes*

a. Hydride-Bridged Complexes. The hydride-bridged complexes, *fac,fac*-$[(H)(PMe_2Ph)_3Os(H)_2Os(PMe_2Ph)_3(H)]$ and *cis,fac*-$[(H)(PMePh_2)_2Os(H)_3Os(PMePh_2)_3]$, are prepared from the photolysis of a saturated solution of the appropriate $[Os(H)_4(PR_3)_3]$ complex, in thf or benzene for the former dimer, and in ethanol for the latter. The dihydride dimer is photosensitive and undergoes a slow photolysis reaction in thf to produce $[(PMe_2Ph)_3Os(H)_3Os(PMe_2Ph)_3]$. All of these dimers have been characterized by X-ray diffraction and ^1H and ^{31}P NMR spectroscopies. All of the dimeric complexes contain Os—Os bonds in addition to the hydride bridges (*307*).

The heterodinuclear complexes $[(cp)_2(H)Zr(\mu\text{-}H)_3Os(PMe_2Ph)_3]$ and $[(1,5\text{-cod})Rh(\mu\text{-}H)_3Os(PMe_2Ph)_3]$ are obtained from treating [Os-

$(H)_3(PMe_2Ph)_3]$ with $[Zr(cp)_2(H)Cl]$ or $[\{Rh(1,5\text{-cod})Cl\}_2]$, respectively (*560*). Protonation of $[Os_2(O_2CMe)_2(CO)_4L_2]$ (L = PMe_2Ph, $PMePh_2$, PPh_3, or py) gives $[Os_2(\mu\text{-H})(\mu\text{-}O_2CMe)_2(CO)_4L_2]^+$, which have been characterized by NMR spectroscopy, and for L = PMe_2Ph, by X-ray crystallography (*561*).

$[(\eta^6\text{-cym})Os(\mu\text{-H})_3Os(\eta^6\text{-cym})]^+$ is prepared by treating $[(\eta^6\text{-cym})Os(\mu\text{-OH})_3Os(\eta^6\text{-cym})]^+$ with 2-propanol, whereas $[(\eta^6\text{-cym})_4Os_4(\mu\text{-H})_4]^{2+}$ is obtained under reflux conditions. Along with $[(\eta^6\text{-cym})ClOs(\mu\text{-Cl})(\mu\text{-H})OsCl(\eta^6\text{-cym})]$, $[(\eta^6\text{-cym})Os(\mu\text{-Cl})(\mu\text{-H})(\mu\text{-}O_2CMe)Os(\eta^6\text{-cym})]^+$, $[(\eta^6\text{-cym})Os(\mu\text{-H})_2(\mu\text{-}O_2CMe)Os(\eta^6\text{-cym})]^+$, and $[(\eta^6\text{-cym})Os(\mu\text{-H})(\mu\text{-}O_2CMe)_2Os(\eta^6\text{-cym})]^+$, all complexes have been characterized by IR, mass, and NMR [$^1H(^{187}Os)$ reverse INEPT] spectroscopies (*556*).

b. Aluminohydride Bridges. Reaction of $[OsCl_2(PPh_3)_3]$ with $LiAlH_4$ in diethyl ether or $[OsCl_2(PMe_3)_4]$ with $LiAlH_4$ in thf yields the aluminohydride-bridged complexes, *fac,fac*-$[(R_3P)_3(H)Os(\mu\text{-H})_2Al(H)(\mu\text{-H})_2Al(H)(\mu\text{-H})_2Os(H)(PR_3)_3]$. The complexes were characterized by IR and ^1H, ^{31}P, and ^{27}Al NMR spectroscopies (*562*).

E. Polymers

1. Porphyrin Polymers

The conducting polymers $[Os(oep)(L\text{-}L)]_n$ (L-L = pz, dabco, or 4,4′-bpy) have been prepared by the reaction of $[Os(oep)]_2$ with L-L in a 1:2 molar ratio. They are partially oxidized to form mixed-valence ions (Section IV,D,1) (*563–565*).

2. μ-Phosphine Oxide Polymers

trans-$[Os^{VI}(bpy)_2(O)_2]^{2+}$ reacts with dppm or dppene to give polymers of the type *trans*-$[\{Os(bpy)_2(\mu\text{-}OPPh_2RPPh_2O)^{2+}\}_n]$ (*415*).

3. 4-Vinylpyridine and 4-Vinyl-2,2′-bipyridine Polymers

A considerable amount of research has been performed on polyvinylpyridine and polyvinyl-2,2′-bipyridine polymers of $[Os(bpy)_3]^{2+}$-like complexes. These polymers are prepared by electropolymerization of complexes such as *cis*-$[Os(bpy)_2(vpy)_2]^{2+}$ (*566*), $[Os(vbpy)_nL_m]^{x+}$ (*567, 568*), and $[M(bpy)_2(4\text{-cinn})_2]^{2+}$ (*568*).

4. *Copolymers*

A polymer containing anthracene, $[Ru(bpy)_3]^{2+}$, and $[Os(bpy)_3]^{2+}$ [all covalently linked to a 1:1 copolymer of styrene and *m,p*-(chloromethyl)styrene] has been prepared, and its emission spectrum and intramolecular electron-transfer properties have been studied (*569*).

5. *[OsO_4]-Derivatized Polymers*

Recently, polymers in which $[OsO_4]$ is covalently bound to either a pyridine group, a dabco group in pvp, or a dabco-derivatized crosslinked styrene–divinylbenzene copolymer have been prepared and used as selective catalysts for the oxidation of alkenes (*570, 571*).

III. Electrochemistry of Coordination Complexes

A. General

1. *Books and Reviews*

There have been two books that contain compilations of the electrochemistry of Os (*572, 573*). There have also been reviews that cover the electrochemistry of certain classes of complexes with ligands such as porphyrins (*142*), dithiocarbamates (*463*), and macrocyclic complexes (*39, 93*). The purpose of this section is not to provide a comprehensive review of electrochemical studies over recent years, but rather to give some insight into the factors that affect the redox potentials and their use in obtaining information about π bonding and backbonding. Particular emphasis is placed on the similarities and differences between analogous Os and Ru complexes.

2. *Ionization Potentials*

Correlations have been made between gas-phase ionization potentials of free ions and the redox potentials of isostructural $[MX_6]^{n-}$ complexes of the elements of the same row of the periodic table (*476*). Despite the observation of such correlations, caution must be taken, because they ignore both σ and π ligand field effects. The latter are often more important in influencing the relative oxidizing or reducing strength of complexes.

3. *Ligand Field Effects*

The strength of ligand field interactions increases down a group of the periodic table. Therefore, Os(III/II) redox couples are expected, and have been observed, to be shifted to more negative potentials by CFSE contributions and stronger σ bonding, compared to analogous Ru(III/II) couples. For example, the $[Os(NH_3)_6]^{3+/2+}$ redox couple is 0.83 V more negative than the Ru analog (*69, 574*), although the interpretation is complicated by the different gas-phase ionization potentials of Ru^{2+} and Os^{2+}.

4. *π Bonding and π Backbonding Effects*

The study of redox potentials is a valuable tool in understanding π bonding and backbonding stabilization of oxidation states. Lower oxidation states tend to be more strongly stabilized by π backbonding than are higher oxidation states, moving redox potentials to more positive values with increases in the electron acceptor strength of π acid ligands bound to a metal center. Conversely, π bases tend to stabilize higher oxidation states, resulting in negative shifts in redox potentials as the electron-donating strength increases. It needs to be emphasized, however, that redox properties are a function of both oxidation states. Therefore, any deductions made about the strength of π interactions between a ligand and a metal ion on the basis of redox potentials must consider the effects of σ and π interactions in both oxidation states of the redox couple. The importance of this is illustrated in Section III,B.

5. *Spin-Orbit Coupling*

Spin-orbit coupling stabilizes the ground state of the low-spin d^5 electronic configuration of Os(III) and Ru(III). The ground states of the diamagnetic d^6 M(II) complexes are not influenced by spin-orbit coupling. This results in a lowering of the energy of the M(III) oxidation state with respect to M(II). Because the spin-orbit coupling constant is much larger for Os(III) than Ru(III), this will also tend to make Os(III/II) couples more negative than their Ru(III/II) counterparts. However, the spin-orbit coupling constant is dependent on the degree of delocalization of the valence electrons onto the ligands. This, in turn, is dependent on the strengths of σ and π interactions between the ligand and metal ion; a decrease in the spin-orbit coupling constant results in a positive shift in the redox potential.

6. *Solvent Effects*

Solvent effects on the redox potentials can be very large and arise from both nonspecific electrostatic and specific hydrogen-bonding and π-stacking contributions (*574, 575*). These contributions are particularly important for highly charged species or complexes with ligands that undergo strong hydrogen-bonding interactions with the solvent. Therefore, for meaningful comparisons to be made between redox potentials, either they should be measured under the same sets of conditions, or the redox potentials must be corrected for the solvent contributions (see Section III,B). Because analogous Ru and Os complexes have virtually the same size and hydrogen-bonding abilities (*501*), solvent contributions to the electrochemistry will cancel if the electrochemistry is performed under identical conditions.

B. Monomers

The developments in Os pentaammine chemistry described in this review have enabled an extensive library of $E^{\circ\prime}$ values to be obtained, spanning a range of ~2 V (~200 kJ mol^{-1}) (Fig. 7). Table XIV compares the redox potentials of the Os(III/II) complexes with Ru(III/II) analogs versus the appropriate $[M(NH_3)_6]^{3+/2+}$ couples. The data are presented in this manner in order to correct for solvent effects, which can be comparable with those induced by the π effects (*574*). The correction of

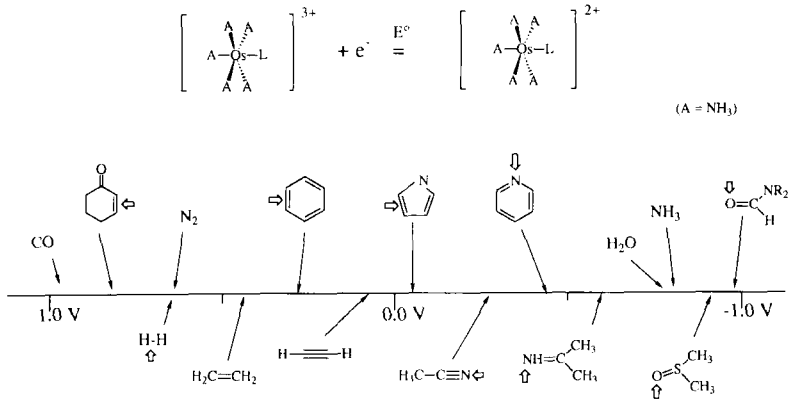


FIG. 7. Redox potentials of $[Os(NH_3)_5L]^{3+/2+}$ couples. In this electrochemical series for pentaammineosmium, the values of $E^{\circ\prime}$ are reported versus NHE as a function of L.

TABLE XIV

COMPARISON OF REDOX POTENTIALS OF $[M(NH_3)_5X]^{n+}$ COMPLEXES VERSUS $[M(NH_3)_6]^{3+/2+}$

Ligand	Ru			Os		
	$E_{\frac{1}{2}}$[a]	Solvent	Ref.	$E_{\frac{1}{2}}$[a]	Solvent	Ref.
SO_2	—	—	—	>1.80	H_2O	*60*
η^2-(*C,C*)-pyH	—	—	—	1.77	dme	*90*
CO	1.35	H_2O	*71*	1.70	H_2O	*83*
η^2-(*C,O*)-Ph_2CO	—	—	—	~1.6	dme	*177*
η^2-(*C,C*)-furan	—	—	—	1.46	an	*179*
η^2(*C,C*)-lut	—	—	—	⩾1.39	dme	*85*
η^2-(*C,C*)-$MeCH_2C{=}C(OMe)Me$	—	—	—	1.37	ac	*168*
η^1-N_2	1.05	H_2O	*576*	1.36	H_2O	*576*
η^1-(*S*)-dmso	0.95	H_2O	*577*			
	0.89	dmso	*68*	~1.35	dmso	*68*
η^2-(*C,C*)-cyclohexene	—	—	—	1.34	an	*432*
η^2-(*C,C*)-$PhCF_3$	—	—	—	1.34	nmp	*75*
η^1-(*N*)-Mepz	0.82	H_2O	*578*	1.33	H_2O	*68*
η^2-(*C,C*)-lutidine	—	—	—	1.30	dme	*90*
η^2-(alkene)-$CH_2{=}CHPh$	0.93	H_2O	*71*	1.27	H_2O	*71*
η^2-(*C,C*)-naphthalene	—	—	—	1.25	H_2O	*172*
η^2-$CH_2{=}CH_2$	0.88	H_2O	*579*	1.25	ac	*120*
η^2-(*C,C*)-thiophene	—	—	—	1.24	an	*179*
η^2-(*C,C*)-$CH_2{=}CHCH{=}CH_2$	0.89	H_2O	*70*	1.22	H_2O	*70*
η^2-(*C,C*)-$MeCH{=}C(OH)Me$[b]	—	—	—	1.21	ac	*168*
η^2-(*C,O*)-Me_2CO	0.203	*ac*	*182*	~1.2	dme	*177*
η^2-(*C,O*)-CH_3CHO	—	—	—	~1.2	dme	*177*
η^2-(*C,O*)-Ph(Bu^t)CO	—	—	—	~1.2	dma	*177*
η^2-(*C,C*)-Ph(Bu^t)CO	—	—	—	1.17	nmp	*177*
η^2-$CH_2{=}CH(CH_2)_2CH{=}CH_2$	0.80	H_2O	*70*	1.15	H_2O	*70*
η^2-$CH_2{=}CHCH_3$	0.78	H_2O	*70*	1.13	H_2O	*70*
η^2-(*C,C*)-$PhOCH_3$	—	—	—	1.11	nmp	*75*
η^2-(*C,C*)-C_6H_6	—	—	—	1.10	nmp	*75*
η^2-(*arene*)-$PhC{\equiv}CPh$	—	—	—	~1.10	ac	*171*
η^2-(*C≡C*)-$PhC{\equiv}CPh$	—	—	—	1.05	ac	*171*
η^2-(*arene*)-$CH_2{=}CHPh$[c]	—	—	—	~1.0	H_2O	*71*
η^2-(*C,C*)-$PhNH_2$	—	—	—	1.00	ac	*175*
η^2-$HC{\equiv}CH$	—	—	—	0.95	ac	*171*
η^2-(*C,C*)-$PhNMe_2$	—	—	—	0.90	ac	*175*
η^1-(*S*)-thiophene	0.55	H_2O	*580*	~0.95	an	*120*
η^1-(N)-NCC_6F_5	—	—	—	0.94	dme	*176*
η^1-(N)-$NCC_{14}H_9$[d]	—	—	—	0.75	dme	*176*
η^2-$CH_3C{\equiv}CCH_3$	—	—	—	0.74	ac	*168*

TABLE XIV *(Continued)*

Ligand	Ru			Os		
	$E_{\frac{1}{2}}$[a]	Solvent	Ref.	$E_{\frac{1}{2}}$[a]	Solvent	Ref.
η^2-(*C,C*)-pyrrole	—	—	—	0.74	an	*179*
η^1-(*N*)-pyrazine	0.44	H_2O	*581*	0.69	H_2O	*60*
η^1-(*N*)-NCCH=CH_2	0.46	H_2O	*582*	0.68	dme	*176*
η^1-(*N*)-NCPh	0.44	H_2O	*582*	0.66	dme	*176*
η^1-pyridazine	—	—	—	0.57	H_2O	*60*
$NCCH_3$	0.324	an	*182*	0.56	dme	*176*
	0.38	H_2O	*582*			
η^1-(*N*)-isn	0.33	H_2O	*582*	0.54	H_2O	*60*
$NCBu^t$	—	—	—	0.52	dme	*176*
η^1-(*N*)-pyrimidine	0.37	H_2O	*583*	0.52	H_2O	*60*
η^1-(*N*)-NMe_2Ph	—	—	—	0.46	ac	*175*
η^1-(*N*)-3-pic	—	—	—	0.45	dme	*90*
η^1-(*N*)-pyridine	0.25	H_2O	*582*	0.45	dme	*90*
				0.39	H_2O	*60*
η^1-(*C*)-lutidinium	—	—	—	0.35	dme	*85*
η^1-(*O*)-Me_2CO	0.061	ac	*182*	0.32	ac	*177*
η^1-(*N*)-NH=CHMe	—	—	—	0.31	acet	*194*
η^1-(*N*)-NH_2Ph	0.16	H_2O	*583*	0.30	ac	*175*
η^1-(*N*)-imidazole	0.06	H_2O	*584*	0.29	dme	*90*
η^1-(*N*)-NH=CMe_2	—	—	—	0.23	ac	*194*
η^1-(*N*)-$NCSe^-$	—	—	—	0.17	H_2O	*198*
η^1-(*N*)-NCS^-	0.08	H_2O	*581*	0.16	H_2O	*197*
				0.12	H_2O	*198*
dme	—	—	—	~0.1	dme	*90*
dmf	0.061	dmf	*182*	~0.2	dmf	*68*
OH_2	0.02	H_2O	*582*	0.05	H_2O	*69*
NH_3	0.000			0.00		
η^1-(*O*)-dmso	−0.001	dmso	*182*	~0.0	dmso	*68*
	−0.04	H_2O	*577*			
Cl^-	−0.09	H_2O	*582*	−0.07	H_2O	*199*
Br^-	−0.08	H_2O	*585*			
I^-	—	—	—	+0.01	H_2O	*199*

[a] V; potential versus appropriate $[M(NH_3)_6]^{3+/2+}$ couple. The redox potentials of the hexaammine complexes are +0.05 and −0.78 V, respectively, versus NHE in water.

[b] The complexes of the cis and trans ligands have the same redox potentials.

[c] The presence of this couple was not recognized in the original paper, but it is clearly present in Fig. 6 of Ref. *71* as a small response at potentials more negative than the main response that is due to the $[Os(NH_3)_5(\eta^2\text{-}(alkene)\text{-}CH_2{=}CHPh)]^{3+/2+}$ couple. As can be seen from its position, its redox potential is consistent with an η^2-arene structure.

[d] 9-Anthracenecarbonitrile.

the solvent contribution enables meaningful comparisons of the effects of π backbonding and π bonding, both within the Os series, and between the Ru and Os series of complexes. Such comparisons show the extent of stabilization of the M(II) oxidation state, with respect to the M(III) oxidation state, when an ammine ligand is replaced by a π acid or a π base. Because the remaining five ligands are innocent with respect to π interactions (except hyperconjugation), the effect of the π acceptance or donation is amplified to the maximum extent, enabling both subtle differences in ligands and the considerable effect on the electronic distribution within the ligand to be assessed. The latter is very important in understanding the new chemistry that has been outlined in Section V.

Table XIV (*60, 68–71, 75, 83, 85, 90, 120, 168, 171, 172, 175–177, 179, 182, 194, 197–199, 432, 576–585*) shows that, in general, the shift in $[M(NH_3)_5L]^{3+/2+}$ redox potentials from the $[M(NH_3)_6]^{3+/2+}$ couple is larger by 30–50% for Os compared to Ru. This does not, however, give a true indication of the relative extent of π backbonding in the M(II) oxidation states because π backbonding is also important for Os(III), but not for Ru(III) (*67, 586*). Therefore, the use of redox potentials alone underestimates the relative strengths of π bonding in analogous Ru and Os complexes. There are other problems in using redox potentials to quantify π backbonding, even if the relevant contributions of the two oxidation states to shifts in redox potentials could be evaluated. This is because π backbonding in Os(III) decreases the spin-orbit coupling constant, thereby providing a destabilizing effect, which partially offsets the stabilization of Os(III) by stronger metal–ligand bonding. Nonetheless, the electrochemical data establish that π backbonding is much more significant in Os(II) complexes than in Ru(II) analogs. This is rationalized in terms of better spatial and energy overlaps between the metal d orbitals and the ligand π^* orbitals for Os(II), as opposed to Ru(II) (*67*).

By contrast, π bonding will tend to stabilize the M(III) oxidation state with respect to the M(II) oxidation state, thereby leading to negative shifts in redox potentials. This may be important in understanding the much larger shifts in the Os(III/II) couples, compared to Ru(III/II) couples with imidazole, aldehyde, and ketone ligands. These ligands tend to be better π donors than most of the other ligands in Table XIV, and therefore would tend to provide π stabilization of the M(III) oxidation state, which will make the shifts in the M(III/II) oxidation states less positive than would otherwise be the case. Because the energy overlap is greater between π orbitals and Ru(III) d orbitals compared to Os(III), this would result in much less positive shifts for the Ru(III/II) couple.

Given the shifts of over a volt in M(III/II) redox potentials that can be achieved by changing one ligand in the coordination sphere, it is not surprising that a large range of stable oxidation states, from 0 with strong π acceptors [e.g., $[Os(PMe_3)_5]$ (*15*)] to VIII with strong π donors [e.g., $[OsO_4]$], are observed. A simple example of the change in redox potential that can be achieved even with the addition of a moderate π acid is the redox potentials of $[Os(NH_3)_6]^{3+/2+}$ and of $[Os(bpy)_3]^{3+/2+}$, which differ by over 1.5 V. This makes $[Os(NH_3)_6]^{2+}$ a strong reductant, whereas $[Os(bpy)_3]^{3+}$ is a strong oxidant, even though both complexes are surrounded by six N donors. Similarly, the oxidation of the bpy complex to the Os(IV) species (*587*) occurs at a potential ~2 V more positive than that for the hexaammine complex (*83*).

Conversely, the stabilization of Os(IV) by ~ 1 V per deprotonation in $[Os(en)_3]^{n+}$ (*204, 205*) and the stabilization of higher oxidation states by deprotonation of aqua ligands (*325*) illustrate well the large effects brought about by π donation.

C. Dinuclear and Polynuclear Complexes

1. *Comparison of K_{com} Values for Dinuclear Ruthenium and Osmium Complexes*

Table XV (*80, 427, 518, 536, 537, 542, 544, 552, 588–591*) summarizes redox potential data and derived comproportionation constants for Os complexes and their Ru analogs. Although the number of Os complexes that have been prepared, and hence for which data are known, is much less extensive, some clear patterns emerge. The first is that the values of K_{com} for the ammine complexes of Os are approximately the square of the value of the Ru analogs. This dramatic difference is not solely due to stabilization of the mixed-valence ion, but rather to a variety of factors that require consideration. The first of these is the extent of spin-orbit coupling and π backbonding stabilization of the Os(III)–Os(III) dimers, compared to the Ru(III)–Ru(III) dimers. Unlike the Ru(III)–Ru(III) dimers, which are paramagnetic, many of the Os dimers are diamagnetic or exist as an equilibrium between a low-lying triplet excited state and a singlet ground state (Section IV,B,1,c). The latter is a manifestation of the degree of π backbonding and/or direct metal–metal bonding, which enables the metal ions to couple more strongly with respect to the analogous Ru(III) complexes. In the absence of coupling interactions, the triplet states of both the Ru(III) and Os(III) dimers will be stabilized by spin-orbit coupling with respect to the singlet states, but the effect will be significantly greater for the latter. The fact that most of the +6 ions have a diamagnetic ground

TABLE XV

COMPARISON OF REDOX POTENTIALS AND COMPROPORTIONATION CONSTANTS FOR SYMMETRICALLY SUBSTITUTED DINUCLEAR OSMIUM AND RUTHENIUM COMPLEXES AT 20°C

Complex	$E_{\frac{1}{2}}(1)^{a,b}$	$E_{\frac{1}{2}}(2)^{a,c}$	K_{com}	Ref.
$[A_5RupzRuA_5]^{n+}$	0.772	0.376	6.6×10^6	*80*[d]
$[A_5OspzOsA_5]^{n+}$	0.324	−0.438	1.0×10^{13}	*80*[d]
$[A_5RuN_2RuA_5]^{n+}$	0.73	~1.2	$\sim 10^8$	*536*[d]
$[A_5OsN_2OsA_5]^{n+}$	−0.16	1.05	10^{21}	*426*[d]
$[A_5RuNCCNRuA_5]^{n+}$	0.71	≥1.2	$\geq 10^{13}$	*588*[d]
$[A_5OsNCCNOsA_5]^{n+}$	0.37_4	~1.3	$\geq 10^{22}$	*542*[d]
$[A_5Ru(4,4'\text{-bpy})RuA_5]^{n+}$	0.121	0.041	2.3×10^1	*589*[e]
$[A_5Os(4,4'\text{-bpy})OsA_5]^{n+}$	−0.257	−0.415	6.1×10^2	*537, 544*[d]
$[\{(bpy)_2Ru\}_2(bpz)]^{n+}$	2.26	1.76	3.0×10^8	*549*[g]
$[\{(bpy)_2Os\}_2(bpz)]^{n+}$	1.96	1.24	1.6×10^{12}	*549*[g]
$[\{(bpy)_2Ru\}_2(bibzim)]^{n+}$	1.30	1.01	8.2×10^4	*552*[g]
$[\{(bpy)_2Os\}_2(bibzim)]^{n+}$	0.82	0.64	1.1×10^3	*552*[g]
$[\{(bpy)_2Ru\}_2(adc\text{-}Me)]^{n+}$	1.23	0.67	3.1×10^9	*549*[g]
$[\{(bpy)_2Os\}_2(adc\text{-}Me)]^{n+}$	0.79	0.45	5.8×10^5	*549*[g]
$[\{(bpy)_2ClRu\}_2(dppm)]^{n+}$	1.06	0.92	2.3×10^2	*590*[g]
$[\{(bpy)_2ClOs\}_2(dppm)]^{n+}$	0.67	0.54	1.6×10^2	*591*[g]
[(oep)RuRu(oep)]	0.62	−0.11	4×10^{12}	*518*[f]
[(oep)OsOs(oep)]	0.09	−0.53	5×10^{10}	*518*[f]

[a] V versus NHE.
[b] M_2^{6+}/M_2^{5+} couple.
[c] M_2^{5+}/M_2^{4+} couple.
[d] 0.1 *M* HCl.
[e] 1 *M* HCl.
[f] dme; V versus Ag/AgCl.
[g] an; V versus SCE.

state, whereas the analogous Ru complexes have triplet ground states, illustrates the much larger degree of π backbonding interactions in the Os complexes. Therefore, the + 6/+ 5 redox potentials are less positive than they would be in the absence of Os(III) π backbonding. This means that the values of K_{com} underestimate the degree of stabilization of the mixed-valence Os complexes compared with their Ru analogs. For this reason and other factors that influence redox potentials (Section III,A), the use of K_{com} values to quantify the degree of intermetallic interaction must be treated with caution. This is well illustrated by the fact that the values of K_{com} for $[(NH_3)_5Os(\mu\text{-L})Os(NH_3)_5]^{n+}$ (L = N_2 or NCCN) are 10 orders of magnitude larger than those for $[(oep)MM(oep)]^{m+}$. Because the latter have direct metal–metal bonds,

the interactions must be greater than with the decaammine complexes (Table XV).

The differences in the abilities of the M(III) and M(II) ions to act as π donors and π acceptors have also been used to rationalize the differences in the values of K_{com} for analogous $[(bpy)_2M(\mu\text{-}L)M(bpy)_2]^{n+}$ complexes (M = Ru or Os). When L is a good π donor, K_{com} is larger for Ru than for Os, but when L is a good π acceptor, the opposite is the case (*549*).

2. *Solvent Effects on the Stabilization of Electronic Isomers of Mixed-Valence Ions*

As a consequence of the solvent dependence of the redox potentials alluded to in Section III,A,6, the ground electronic state of mixed-valence ions with dissimilar redox centers can be controlled by the appropriate choice of solvent. An eloquent example of the design of electronic isomers utilizes the *cis*-$[(bpy)_2ClOspzRu(NH_3)_5]^{4+}$ ion. Os^{III}–Ru^{II} is the ground electronic state in CD_3NO_2 and CD_3CN, but in d_6-dmso, Os^{II}–Ru^{III} is the ground-state electronic configuration (*541*).

D. Polymers

A considerable amount of work has been performed on electrodes coated with $\{cis\text{-}[Os(bpy)_2(vpy)_2]^{2+}\}_n$ and $\{[Os(bpy)_2(vbpy)]^{2+}\}_n$ polymers in order to delineate the controlling factors of electron transfer rates within such polymers (e.g., *566*, *592*). Similar work has been performed on nafion polymers in which $[Os(bpy)_3]^{2+}$ has been incorporated (e.g., *593*, *594*). Such electrodes have been used for the electrocatalytic oxidation of organic and biological substrates in sensor applications (e.g., *595*, *596*). There have been many other studies using such electrodes, but they will not be discussed here.

IV. Spectroscopic and Magnetic Properties of Coordination Complexes

A. Monomers

1. *Osmium(III) Ammine and Amine Complexes*

Magnetic circular dichroism (MCD) spectra of $[Os(NH_3)_6]^{3+}$ (*193*), $[Os(NH_3)_5L]^{3+}$ (*428*, *597*), $[Os(NH_3)_5X]^{2+}$ (*597*), and *cis*- and *trans*-$[Os(NH_3)_4Cl_2]^{2+}$ (*543*) have been studied from 4 K to room temperature,

and in a range of different media (KCl and KBr disks, PVA films, nafion films, and single crystals). The near-IR region of the spectra, where the intra-t_2 electronic transitions are observed, is of particular interest because of the vibrational fine structure.

Low-temperature polarized single-crystal studies of the near-IR transitions of Os(III) ammine complexes have also been studied. These include $[Os(NH_3)_6](ClO_4)_2Cl \cdot KCl$ (*193*), $[Os(en)_3]_2Cl_6 \cdot KCl \cdot 6H_2O$ (*193*), $[Os(NH_3)_5X]SiF_6$ (*193*), $[Os(NH_3)_5Cl]Cl_2$ (*598*), and $[Os(NH_3)_5Cl](S_2O_6)$ (*598*). In some systems it is possible to find the two origins, which can be assigned to the two transitions in Fig. 8 (*428*), but in many others the spectra are not amenable to simple analyses and the second origin is inferred from EPR spectroscopy. There are also some inconsistencies in the evaluation of the energy differences in the spin-orbit states from optical and EPR spectroscopy. It is conceivable that these inconsistencies are due to the quenching of the low-symmetry splittings by vibronic activity in the first excited (pseudo) Γ_8 state (*193*).

There are also charge-transfer characteristics within the electronic transitions between the spin-orbit states of the pentaammine complexes. This is evidenced by order of magnitude increases in the intensities of these transitions when an ammine or aqua ligand is replaced by a π-base (e.g., Cl^-) or a π-acid (e.g., N heterocycle) (*67*).

Detailed studies of the solvent dependencies of the charge-transfer transitions in the UV/Vis region of $[Os(NH_3)_5(Mepz)]^{3+}$ and a variety of

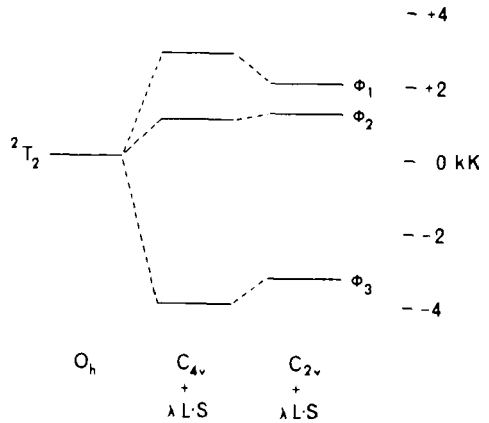


FIG. 8. State energy level diagram of Os(III) (Δ = 1290, β = 160, and λ = 3200 cm^{-1}). Reprinted with permission from the *Journal of Physical Chemistry,* Ref. *428*. Copyright 1984, American Chemical Society.

$[Ru(NH_3)_5(L)]^{n+}$ complexes have been used as an aid to assign the various transitions that occur in this region (*599*).

2. *Tris(2,2'-bipyridine)osmium(II) and Related Complexes*

In order to gain an appreciation of the problems that arise in interpreting the electronic spectroscopy of $[Os(bpy)_3]^{2+}$ and related complexes, it is necessary to understand the controversies in the analogous Ru spectroscopy. More papers on the spectroscopy and photochemistry of $[Ru(bpy)_3]^{2+}$ have been published than for any other compound (*223, 600, 601*). The research in this area, together with complexes with other N-heterocyclic ligands, has been covered in recent reviews (*222–224, 600–604*). This extensive literature has arisen because of the inherently interesting spectroscopy and photophysics of these complexes and their potential uses in solar energy conversion. Though interest in potential practical applications has waned, controversy still rages about the most appropriate descriptions of the electronic structures of the initially formed and lowest energy triplet states of these complexes. This controversy is well summarized in two recent reviews (*600, 601*). The strongest evidence available is that, upon excitation, the initial excited state has a structure in which all of the bpy ligands are equivalent (i.e., the electron is delocalized over all three of the ligands). This excited state then relaxes to one in which the unpaired electron is localized on only one of the bpy ligands (*600, 605–607*).

The literature on the analogous Os spectroscopy and photochemistry is nowhere near as extensive. A major reason for this is the much shorter lifetimes of the triplet excited states, which are a consequence of the much greater degree of spin-orbit coupling in the Os(III)-bpy^- excited state, in comparison with its Ru analog. The larger spin-orbit coupling in Os(III) increases the mixing of the triplet and singlet states, thereby providing a more efficient pathway for intersystem crossing and, hence, shorter lifetimes of the excited states. At a time when the possibility of solar energy applications was driving the research in this area, this made the study of the Os complexes much less attractive compared to their Ru analogs. Also, the chemistry is more difficult and expensive than that of Ru. Despite this, there is a quite extensive and rapidly growing literature on the spectroscopy and photochemistry of $[Os(bpy)_3]^{2+}$ and related complexes. The literature to 1988 has been covered in recent reviews (*223, 224*). Like the Ru chemistry, controversies regarding the electronic structures of the excited states have raged. However, the most appropriate descriptions of the initially formed excited state of D_3 systems appear to be a delocalized structures.

When the symmetry is reduced by replacement of a bpy ligand by another bidentate, the symmetry restrictions are relaxed and the initially formed excited state is expected to be localized (*600, 601*). The rates of nonradiative decay of a large range of Os(II)–polypyridine have been calculated successfully in terms of a modified "energy gap law" in which low-frequency modes are explicitly considered (*148*).

The charge transfer that occurs on photoexcitation changes the pK_a values of substituents on bpy or related ligands. Because the substituents become more basic as a result of the MLCT nature of the triplet states, excited-state proton transfers can occur. There have been many studies of such reactions of Ru complexes, but few on analogous Os complexes until recently (*233*).

3. *Nitrido and Oxo Complexes*

A feature of the numerous Os(VI) complexes is the presence of highly vibronically coupled charge-transfer spectra in the UV/Vis region, even at room temperature. The emission spectra are also highly structured and the charge-transfer excited states are sufficiently long-lived to undergo both outer-sphere and atom-transfer quenching reactions. A detailed review of this area is beyond the goals of this article, but some representative publications are given (*107, 114, 211, 212, 608*).

B. Dimers

1. *Ammine Complexes*

a. Os_2^{4+} Dimers. Little work has been performed on the decaammine $Os(II)_2$ complexes, because they are very air sensitive and their electronic absorption spectra are not as rich as their oxidized counterparts. Their spectra are dominated by intense MLCT bnads in the visible region. In all cases, the MLCT bands are more intense and are at lower frequencies than in their oxidized counterparts. Complexes that have been studied to date are those with N_2, NCCN, and pz (*80, 536, 543*).

b. Os_2^{5+} Dimers. MCD and EPR spectra have been measured on the mixed-valence $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$ ion in nafion film, and in an ethylene glycol/water glass, respectively. The position of the three absorption bands in the NIR are consistent with both the predictions made using the delocalized electronic coupling model (*609*) and the published absorption spectra in water (Fig. 9) (*80*). The remarkable

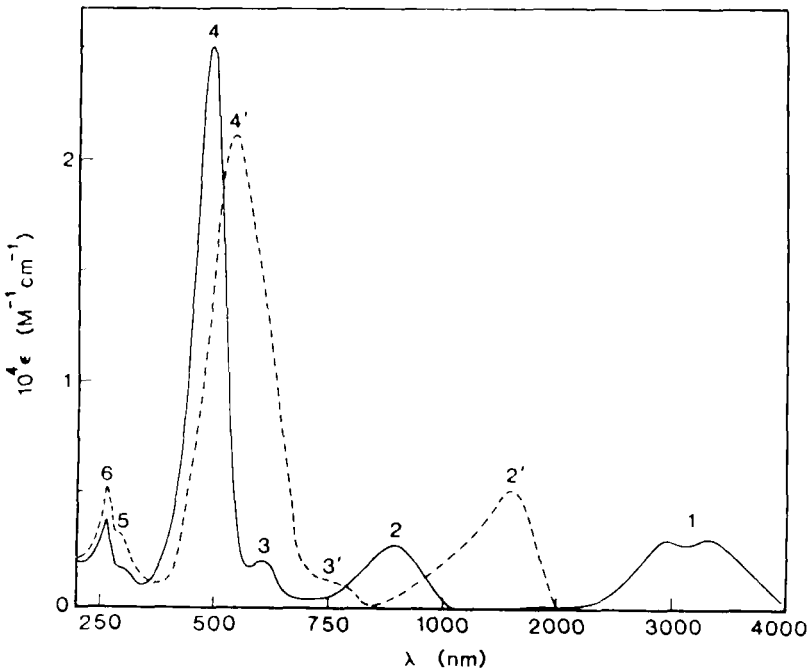


FIG. 9. Ultraviolet, visible (0.1 *M* HCl), near-infrared (O.1 *M* DCl/D_2O), and infrared (KBr) absorption spectra of the electronic transitions of $[(NH_3)_5OspzOs(NH_3)_5]^{5+}$ (solid line) and $[(NH_3)_5RupzRu(NH_3)_5]^{5+}$ (dashed line). The numbers refer to analogous transitions in Ru and Os complexes. The value of ϵ_{max} for transition 1 is approximate because the absorption intensity has been measured in a KBr disk. Reprinted with permission from *Inorganic Chemistry*, Ref. *80*. Copyright 1988, American Chemical Society.

feature of this complex is the intense electronic transitions observed in the IR region of the spectrum. These are an order of magnitude more intense than the N—H stretches that occur at the same frequencies. The normal intra-t_2 bands that occur in the NIR region of mononuclear and dinuclear Os(III) complexes, and trapped-valence Os(III)–Os(II) dimers, e.g., *cis*-$[(NH_3)_4(N_2)Os(pz)Os(NH_3)_5]^{5+}$, are absent in the symmetric mixed-valence ion, which supports a delocalized electronic structure (*80*).

The delocalized electronic coupling model also quantifies the MCD, absorption, and EPR spectra of the N_2 complex $[(NH_3)_5Os(N_2)$-$Os(NH_3)_5]^{5+}$ (*610*), which is delocalized and has a particularly rich electronic absorption spectrum (Fig. 10) (*426, 536, 610*).

$[(NH_3)_5Os(4,4'\text{-bpy})Os(NH_3)_5]^{5+}$ has a weak and broad intervalence

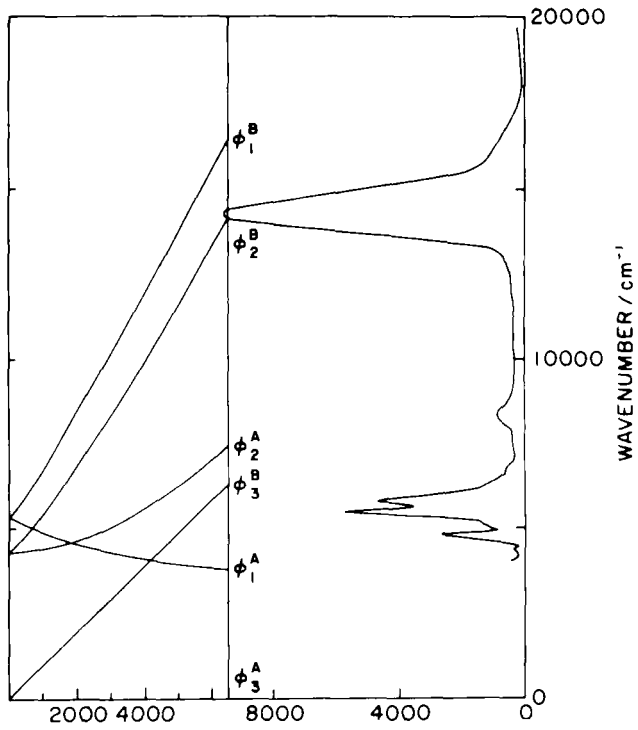


FIG. 10. Calculated energy level scheme for $[(NH_3)_5Os(N_2)Os(NH_3)_5]^{5+}$ as a function of W for a value of $\Delta = 1800\ cm^{-1}$ and $\lambda = 3000\ cm^{-1}$. The observed 8 K absorption spectrum is shown on the right-hand side. Reprinted with permission from the *Journal of the American Chemical Society*, Ref. *610*. Copyright 1985, American Chemical Society.

transition on the edge of the charge-transfer bands. This, together with the presence of normal intra-t_2 Os(III) transitions in the NIR spectrum, indicates that this is a trapped valence Os(III)–Os(II) dimer (*542*).

Resonance Raman spectroscopy is also being used both to aid the assignment of their electronic spectra and to delineate the degree of electronic delocalization (*611*).

c. Os_2^{6+} Dimers. The MCD spectra of $[(NH_3)_5Os(4,4'\text{-bpy})Os(NH_3)_5]^{6+}$ exhibit normal C term behavior down to 4 K, whereas the temperature dependence of the MCD spectra of the pz complex does not because of a temperature-dependent equilibrium between the singlet ground state and the low-lying triplet excited state. The intensity of the C terms actually decreases with decreasing temperature due to the depopulation of the excited triplet state. Such changes in population of

these two states are also evident in the temperature dependence of the electronic absorption spectra (Fig. 11) (*428*). By contrast, the μ-N_2 complex is diamagnetic, even at room temperature, and no C terms are observed (*426*). Thus, the extent of coupling between the metal ions increases in the order 4,4′-bpy < pz < N_2. The much weaker coupling in the Ru analogs (4,4′-bpy and pz) is apparent from the fact that they are triplets even down to 1 K, whereas the N_2 complex is too unstable to measure.

2. *Bpy and Related Complexes*

The relatively long lifetimes of the excited states of these complexes have made them particularly attractive in the study of electron and energy-transfer quenching of excited states through organic bridges. In addition, the more positive redox potentials of these ions, compared with their pentaammine counterparts, mean that the mixed-valence ions are not air sensitive, thus facilitating spectroscopic measurements.

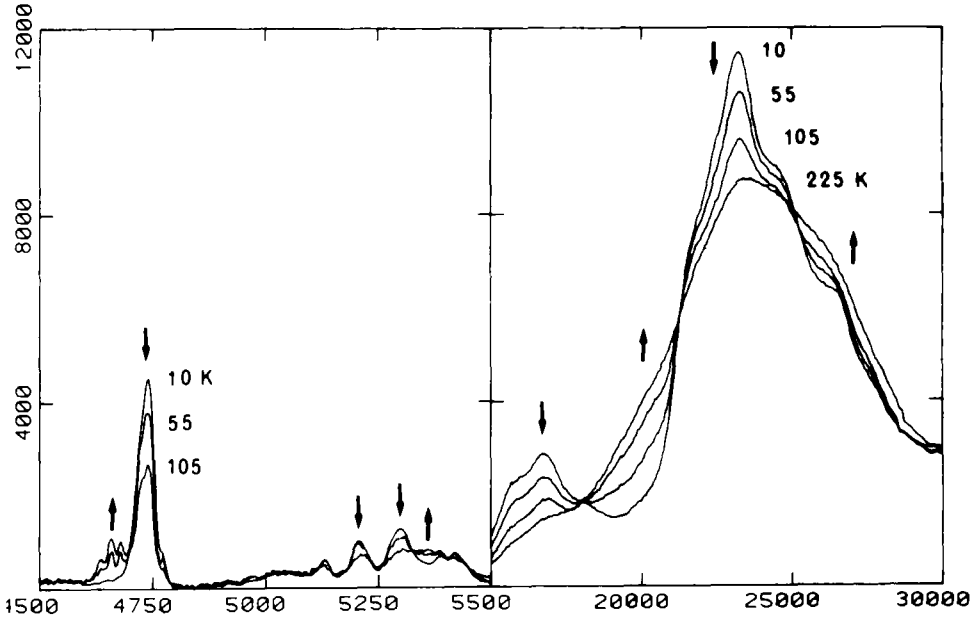


FIG. 11. Absorption spectra of $[(NH_3)_5OspzOs(NH_3)_5]^{6+}$ at various temperatures in PVA. The arrows indicate the direction of intensity change with increasing temperature. Reprinted with permission the from *Journal of Physical Chemistry*, Ref. *428*. Copyright 1984, American Chemical Society.

For these reasons, and the relative ease with which the complexes are prepared, an increasing number of studies have been performed on the photophysical and photochemical properties of such complexes. Though most of the studies in this area have been performed on dinuclear ruthenium complexes, an increasing number of Ru/Os and Os/Os dimers have been studied in recent years (*228, 541–552*) and this subject has been reviewed (*222*).

3. *μ-Nitrido Os(IV) Complexes*

In addition to intense charge-transfer bands that trail into the visible region, these diamagnetic complexes have weaker d–d transitions at lower energies. The presence of these previously unrecognized transitions, and other properties, are rationalized by the MO description shown in Fig. 12, where the d–d transitions are indicated (*47*).

C. Polymers

1. *Porphyrin Polymers*

The intervalence transitions of doped $[M(oep)(L\text{-}L)]_n^{m+}$ polymers (M = Fe, Ru, or Os and L-L = pz, dabco, or 4,4′-bpy) have been studied. The metal–metal coupling and the intensity of the intervalence transition increase in the order dabco < 4,4′-bpy < pz, and the energy of the intervalence band decreases in the same order. Within a series with the same bridging ligand, the strength of metal–metal coupling and the intensity of the intervalence transition increase in the order Fe < Ru < Os, and the energies of intervalence bands decrease in the same order. With $[Os(oep)pz]_n^{m+}$, an intense and relatively sharp electronic transition is observed at ~2000 cm^{-1} in the IR (*563–565*), which is reminiscent of a similar transition in $[(NH_3)_5Os(pz)Os(NH_3)_5]^{5+}$ (Section IV,B,1,b).

2. *Bpy Polymers*

The photophysics and photochemical properties of polymers containing Os–polypyridine or Os/Ru and Os/Zn copolymers are an area of increasing interest. Recent applications include photochemical ligand loss as a basis for imaging and microstructure formation (*612*) and the storage of photochemical redox equivalents in polystyrene polymers, derivatized with bpy (*613*). Long-range energy transfer has also been studied (*569*).

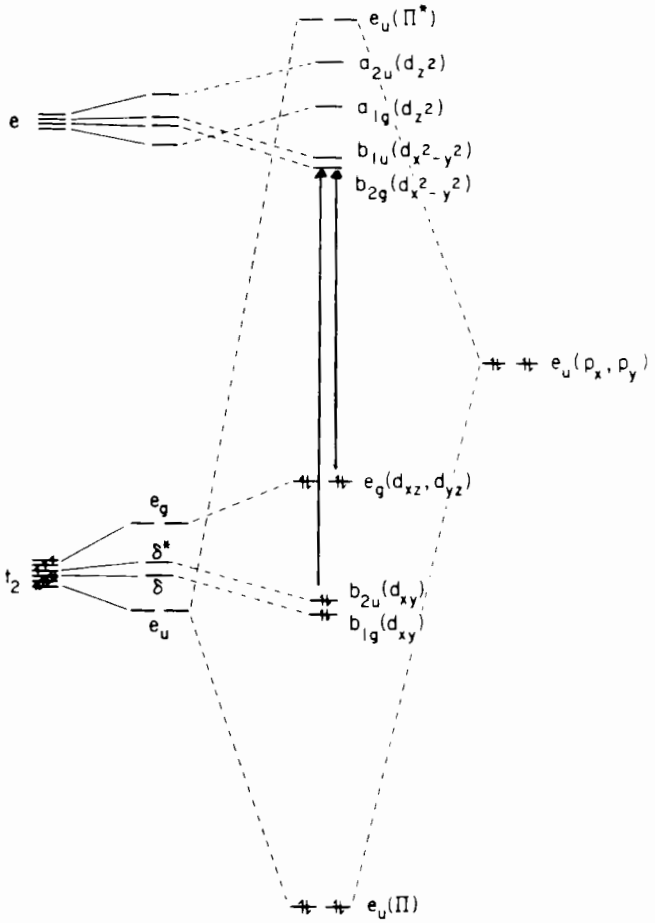


FIG. 12. Qualitative molecular orbital description of bonding within the $Os^{IV}-N^{3-}-Os^{IV}$ moiety. The d–d transitions are indicated by arrows. Reprinted with permission from *Inorganic Chemistry*, Ref. *47*. Copyright 1989, American Chemical Society.

V. Reactivity of Coordination Complexes

A. Addition Reactions of Osmium(VIII)

The kinetics and thermodynamics of the addition reactions of amine and N-heterocyclic ligands to $[OsO_4]$ have been studied using UV/Vis and NMR spectroscopies. With py, 4-pic, and bpy, the kinetics are too fast to be studied without using stopped-flow techniques, whereas the

kinetics of tmen, bpds, phen, and imidazoles in water are monitored by conventional mixing techniques. These are the first studies of such kinetics, and as expected for associative reactions, the activation enthalpies are low (15–60 kJ mol^{-1}) (*335, 336*).

B. Substitution Reactions

Although there have been few studies performed on the substitution kinetics of pentaammineosmium complexes, compared to other pentaammine complexes, the importance of π-bonding and π-backbonding effects on the stabilization of metal–ligand bonds in different oxidation states is amply illustrated in Table XVI (*65, 67, 83, 199, 536, 576, 614–617*). Thus, though N_2 bound to M(II) complexes is inert toward substitution, it is labile when bound to M(III) complexes. Similar observations are made for the $[Os(NH_3)_5(\eta^2\text{-benzene})]^{3+/2+}$ complexes in acetonitrile, for which the specific rates for substitution are 3.5×10^2 and 3.5×10^{-5} sec^{-1}, respectively, for the +3 and +2 ions (*75*). By contrast, M(III) complexes are much more inert than M(II) complexes when the leaving group is a π-donor ligand such as Cl^-.

Another important factor that separates π-acceptor ligands in traditional organometallic complexes, as compared to pentaammine com-

TABLE XVI

Spontaneous Aquation Rates of Pentaammineosmium(III/II) and Analogous Pentaammineruthenium(III/II) Complexes[a]

	k (sec^{-1})			
Ligand	Ru(II)	Ru(III)	Os(II)	Os(III)
N_2	2×10^{-6}[b]	70[c]	$<10^{-8}$[d]	2×10^{-2}[c]
Cl^-	6.3[e]	9.3×10^{-7}[f]	0.2[g]	$\sim 10^{-8}$[h]
$CF_3SO_3^-$	—	93[i]	—	8.8×10^{-4}[j]

[a] 25°C.
[b] Ref. *614*.
[c] Refs. *536* and *576*.
[d] Ref. *615*.
[e] Ref. *616*.
[f] Ref. *617*.
[g] Ref. *199*.
[h] Ref. *83*.
[i] Ref. *65*.
[j] Ref. *67*.

plexes, is the relative lability of the ligand. Thus, alkene (Section II,C,2,h) and N_2 (Section II,C,4,j) ligands bound to Os(II) phosphine complexes tend to be rather easily displaced, but are much more inert when bound to $[Os(NH_3)_5]^{2+}$. This is because in the latter, other ligands are not competing for metal π electrons. Such a phenomenon also manifests itself in the greater sensitivity of the electrochemistry of $[Os(NH_3)_5L]^{n+}$ complexes to the nature of L (Section III,B) and the often unusual reactivities of coordinated ligands (Section V,D and V,E).

Though few studies have been performed on the mechanisms of substitution of Os(III) and Os(II) complexes, some deductions can be made about probable mechanisms. In the case of Os(III), with charged leaving groups such as Cl^-, it is expected that the preferred mechanism will be one in which bond breaking substantially precedes bond making (i.e., predominantly dissociatively activated). By contrast, reactions will be more associative with neutral leaving groups, although it is difficult to ascertain where they are expected to occur along the continuum of interchange mechanisms (*618, 619*). In the case of substitution of $[Os(NH_3)_5(\eta^2\text{-benzene})]^{2+}$, the rate constant only varies slightly with the nature of the incoming ligand (L = isn, py, CH_3CN, acetone, CH_3COPh) in d_6-acetone at 25°C (*75*). This is a strong indication of an I_d mechanism for the substitution reactions, which is to be expected for a sterically crowded d^6 complex.

Aqua exchange in $[Os(\eta^6\text{-}C_6H_6)(OH_2)_3]^{2+}$ has been subjected to detailed mechanistic studies, along with the Ru analog. The volumes of activation are small and positive. This has been taken as an indication of an interchange mechanism that is near the middle of the continuum, but that is more dissociatively than associatively activated (*620*).

C. Electron Transfer Reactions

1. Intermolecular Electron Transfer

Electron self-exchange reactions of $[Os(L\text{-}L)_3]^{3+/2+}$ (L-L = phen, 4,7-Me_2phen, 3,5,6,8-Me_4phen, or 3,4,7,8-Me_4phen) were studied by ^1H NMR line broadening. There are two pathways, one involving the +3 ion, and the other involving the PF_6^- ion pair of the +3 ion. Rate constants are $\sim 10^5$ and $\sim 10^6\ M^{-1}\ sec^{-1}$, respectively (*621*).

The reversibility of the $[Os(bpy)_3]^{3+/2+}$ couple makes it useful for the determination of the electron self-exchange rates of other couples by application of the Marcus cross-reaction equation. Recently, this has been applied to the oxidation of SO_3^{2-} to SO_4^{2-} (*622*). The new rate constant for this reaction of $1.63 \times 10^7\ M^{-1}\ sec^{-1}$ is consistent with the

expectations of Marcus theory, but three orders of magnitude greater than that determined previously (*623*). Other self-exchange rates that have been determined using $[Os(bpy)_3]^{3+/2+}$, $[Os(phen)_3]^{3+/2+}$, and related couples include $V(O)(OH)^{2+/+}$ (aq) (*624*) and $[Mn(edta)]^{1-/2-}$ (*625*). The rate of electron transfer from $[Fe(CN)_6]^{2-}$ to $[Os(bpy)_3]^{3+}$, in the presence of reversed micelles, has been used as a probe of coalescence of the reversed micelles (*626*).

2. *Intramolecular Electron Transfer*

As indicated in Section III,A, the Os(III/II) redox potentials are generally much more negative than analogous Ru(III/II) redox potentials. This has important implications in the study of intramolecular electron transfer through organic chains and, in particular, through polypeptides. This is an area that has been under intensive study in Ru chemistry because of the desire to understand such electron transfer, so important in many biological processes (*427, 429*). These processes have been studied by monitoring the rate of intramolecular electron transfer from Ru(II) or Os(II) to Co(III), or Os(II) to Ru(III). Os(II) is a much stronger reductant than Ru(II), and Os(II) π backbonding is also much stronger. Because all other factors, such as inner- and outer-sphere reorganizational energy terms, are approximately equal, the rates of intramolecular electron transfer are much faster in the Os(II) complexes, compared with their Ru(II) analogs (Table XVII). This is an important recent development because it extends the range over which intramolecular electron transfer is observable and also illustrates the importance of conformational changes of the polypeptide backbone in

TABLE XVII

COMPARISONS OF THE RATES OF INTRAMOLECULAR ELECTRON TRANSFER AT 25°C THROUGH ORGANIC MOLECULES IN Co(III)/Ru(II), Co(III/Os(II), AND Ru(III)/Os(II) DIMERS [a]

Complex		$k(sec^{-1})$	
M(III)LM'(II)	Co(III)/Ru(II)	Co(III/Os(II)	Ru(III)/Os(II)
isn	1.2×10^{-2}	2.4×10^{5}	$>5 \times 10^{9}$
proisn	1.04×10^{-3}	2.9×10^{2}	3.1×10^{6}
$(pro)_2$isn	6.4×10^{-6}	0.6	3.7×10^{4}
$(pro)_3$ isn	5.6×10^{-5}	0.08	3.2×10^{2}
$(pro)_4$isn	1.4×10^{-4}	0.09	0.5

[a] Refs. *429* and *430*.

affecting the rate of intramolecular electron transfer. Thus, for the Ru complexes, the addition of a third or more prolines to the polypeptide chain results in a increase in the rate of intramolecular electron transfer. This has been attributed to a cis–trans isomerization of the proline groups, which enables the Co(III) center to get nearer to the Ru(II) center than is the case for the complexes with only two proline groups (*427*). The kinetic behavior observed for the Os analogs differs in that the rates of intramolecular electron transfer are much faster than the rate of cis–trans isomerization of the proline chains. This results in the rate of intramolecular electron transfer decreasing as the chain length increases.

More recently the same reactions have been monitored for Ru(III)–Os(II) analogs. These complexes are generated by the reduction of the Ru(III)–Os(III) dimers by e^- (aq) or CO_2^- (aq) radicals in pulse radiolysis experiments (*429*). Because of the much lower inner-sphere reorganizational energy terms for the $[Ru(NH_3)_5L]^{3+/2+}$ couples compared with Co(III/II) analogs, the rates of intramolecular electron transfer in the Ru(III)–Os(II) dimers are much larger than those of Co(III)–Os(II) dimers (*429*).

Upon deprotonation, $[(trpy)(bpy)Os^{III}(4,4'\text{-bpy})Ru^{II}(OH_2)(bpy)_2]^{5+}$ and $[(trpy)(bpy)Os^{III}(4,4'\text{-bpy})Ru^{III}(OH)(bpy)_2]^{5+}$ undergo rapid intramolecular electron transfer to form $[(trpy)(bpy)Os^{II}(4,4'\text{-bpy})Ru^{III}(OH)(bpy)_2]^{4+}$ and $[(trpy)(bpy)Os^{II}(4,4'\text{-bpy})Ru^{IV}(O)(bpy)_2]^{4+}$, respectively, but no details have been given about the rates (*228*). Fast intramolecular electron transfer from the excited states of $[Os(trpy)_2]^{2+}$ complexes with donor or acceptor substituents have also been observed (*229*).

D. Linkage Isomerizations

As indicated earlier, a dramatic difference is observed in the chemistry of Os(II) and Os(III), the former gaining stabilization from π acids and the latter from σ and π donors and to a lesser extent π acids. This difference is most amplified when the ligand set is predominantly saturated, e.g., pentaammineosmium. In this configuration, the electron-rich Os(II) must depend entirely on the sixth ligand for stabilization through π backbonding.

The sharp contrast in the chemical nature of Os(II) and Os(III) often results in a linkage isomerization of an ambidentate ligand accompanying such a redox change. To date, such isomerizations have been reported solely for the pentaammine moiety. Typically, through electrochemical measurements, a cyclic process is observed: the oxidation of a species Os(II)–AB to Os(III)–AB is proceeded by an intramolecular

isomerization to Os(III)–BA. Subsequently, the latter species is reduced, at some new potential to Os(II)–BA, which then reisomerizes to Os(II)–AB, thus completing the cycle. Some ligands have several different binding sites, and in these cases three or more isomers can be observed. The thermodynamically stable Os(III)–BA complex normally binds the ligand via the best σ donor and, in this respect, forms typical coordination complexes. By contrast, the thermodynamically favored Os(II)–AB complex binds the ligand normally in an η^2 fashion typical of organometallic compounds. Of particular significance in these systems are the thermodynamic parameters obtained that relate the relative affinities of the metal for the bond sites A and B.

1. $\eta^1 \leftrightarrow \eta^2$ *Linkage Isomerizations for Aldehydes and Ketones*

First reported in 1986 (*181*), the complex $[Os(NH_3)_5(acetone)]^{2+}$ and related aldehyde and ketone complexes (*177*) were the first examples of linkage isomerizations on Os(III/II). In acetone solution, a detailed electrochemical and chemical investigation revealed that the substitutionally inert complex, $[Os(NH_3)_5(\eta^2\text{-acetone})]^{2+}$, is in facile equilibrium with the η^1 form, the former being favored by 21 kJ mol^{-1}. Upon oxidation, the Os—C bond is ruptured, but the Os—O bond remains intact, even in good donor solvents such as dma. Reduction of the η^1–acetone–Os(III) species occurs at a potential of ~750 mV negative of that of the η^2 form in acetone. Subsequent $\eta^1 \rightarrow \eta^2$ isomerization of the ketone occurs with a specific rate of 6×10^3 sec^{-1} at 20 ± 2°C.

Of the variety of aldehydes and ketones investigated (*177*), all were found to be η^2 coordinated to $[Os(NH_3)_5]^{2+}$ except for the bulky pinacolone. However, it is unclear whether this is a thermodynamic or kinetic limitation.

At the time of its original report (*627*), the labile complex $[Ru(NH_3)_5(acetone)]^{2+}$ was considered to contain an O-bound ketone. However, recent studies (*182–184*) revealed both η^2 and η^1 bonding modes in solution. In this case the former mode of binding is favored by 7 kJ mol^{-1}. Astonishingly, even in the case of Ru(III), a significant population of π-bound acetone is present. However, this type of η^2 binding is clearly more stable relative to the η^1 mode in Os(II) complexes compared to the Ru(II) analogs in a variety of ketone ligands (*177*, *181–184*).

2. η^2-C=S *to* η^2-C=Se *Linkage Isomerization Reactions of CSSe, and* η^2-(C=S) *to* η^1-(C) *Reactions of* $S{=}CSMe^-$

Given the facile linkage isomerization reactions for a large number of η^2-bound ligands coordinated to $[Os(NH_3)_5]^{2+}$, it is astonishing that

there is no low-energy pathway for the η^2-C,S to η^2-C,Se linkage isomerization of [Os(η^2-CSSe)(CO)(CNR)(PPh_3)]. Both linkage isomers are kinetically stable and the η^2-C,S isomer is converted to the η^2-C,Se linkage isomer only by a set of addition and elimination reactions (*152, 628*). The η^2-(S,C) to η^1-(C) linkage isomerizations of coordinated $SCSMe^-$ are also induced by addition reactions (*152*) (Section II,C,2,e).

3. *Linkage Isomerizations with Arenes and Heterocycles*

A series of $[Os(NH_3)_5(\eta^2\text{-arene})]^{2+}$ complexes has been investigated in order to determine the effect of substituent on the stability of the Os–arene bond (*75*). As part of this study, information was gained regarding the ability of the substituent to direct the metal to a specific π-bond site within the ring. Surprisingly, both electron-donating and electron-withdrawing groups were found to direct the metal to the 2,3-η^2 position relative to this substituent. Bulky groups, on the other hand, tended to direct the metal to the 3,4-η^2 position relative to the bulky group. In cases in which steric effects can be discounted, the free energies of 2,3-$\eta^2 \rightarrow$ 3,4-η^2 isomerizations range from 0 to 10 kJ mol^{-1}. All of the substituted benzene complexes exhibit migration around the ring, with specific rates ranging from 1 sec^{-1} (L = anisole) to 10^4 sec^{-1} (L = benzene), at room temperature. For monosubstituted benzene ligands, electron-donating substituents were most effective at retarding this rate (*75*). As observed for the η^2-arene complexes, η^2-heterocyclic complexes often show migration around the ring at ambient temperature. The only cases in which such isomerizations have not been observed are when the ligand is η^2-furan or η^2-thiophene (*90*).

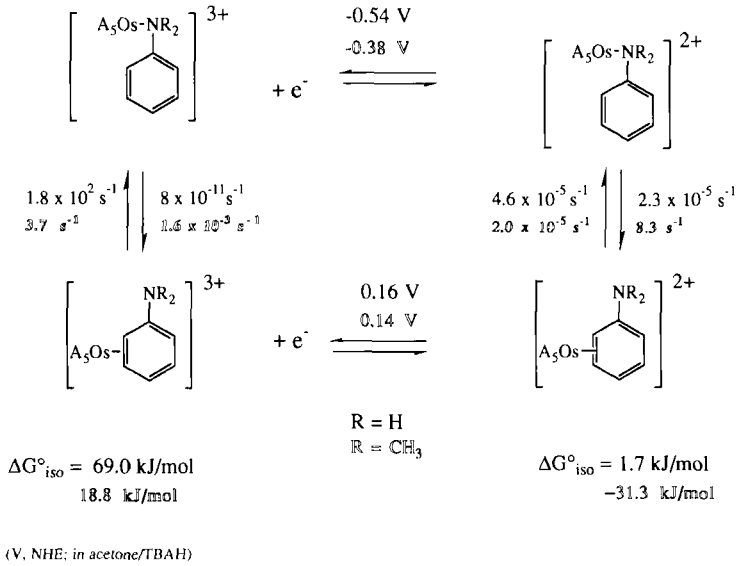
Oxidation of these materials often resulted in a linkage isomerization of the organic ligand from the ring to a basic site of the substituent. Examples include arene-to-amine (anilines) (*175*), arene-to-ketone (phenones) (*177*), arene-to-ether (anisole) (*120*), and arene-to-alkyne (diphenylacetylene) (*497*) isomerizations. In the case of the 2,2-dimethylpropiophenone (*177*), a sequence of one-electron oxidations and reductions resulted in the Os complex isomerizing from an arene to an η^1-ketone to an η^2-ketone, then back to the ring to form an Os—η^2-C,C bond. Although most of these reactions were not investigated in any detail, in two cases, aniline and *N,N*-dimethylaniline, a complete kinetic and thermodynamic analysis has been undertaken (Scheme 14) (*175*).

For aniline, an equilibrium with K_{eq} close to unity exists between the N-bound and 2,3-C,C-η^2-bound isomers of Os(II). The one-electron oxidation of the latter isomer ($E^{\circ\prime}$ = 0.16 V versus NHE in acetone) is followed by an arene-to-nitrogen linkage isomerization, proceeding

with a specific rate constant of 180 sec^{-1} at 20 ± 2°C. Initially, on reduction of $[Os(NH_3)_5(N\text{-aniline})]^{3+}$ (−0.54 V), no change in coordination geometry occurs, but with time, rearrangement to the ring isomer occurs with a specific rate constant of 4.6×10^{-5} sec^{-1} at 20 ± 2°C. The data indicate free energies of N → π isomerization for Os(III) and Os(II) of 69 and 16.7 kJ mol^{-1}, respectively, at 20 ± 2°C.

Similar experiments with the *N,N*-dimethylaniline analog reveal that the addition of the two methyl groups destabilizes the N-bound form by 33 kJ mol^{-1} on Os(II) and >50 kJ mol^{-1} for Os(III). The increased sensitivity to steric effects for Os(III) is thought to be a result of the increased demand for electron density by this higher oxidation state. The differences in isomerization energy for both oxidation states are reflected almost entirely in the rate constants of isomerization from nitrogen-bound to arene-bound complexes.

Heterocyclic complexes of pentaammineosmium(II) have also been reported for pyridinium (*85*), 2,6-lutidine (*85*), 2,6-lutidinium (*85*), pyrrole (*179*), furan (*179*), and thiophene (*179*), in which the organic ligand is dihapto coordinated via a C=C bond (*90*). These ligands are thought to rearrange upon oxidation to coordinate through the heteroatom.



SCHEME 14. Kinetics and thermodynamics of the linkage isomerization reactions of $[Os(NH_3)_5(NR_2Ph)]^{3+/2+}$

Only for lutidine has this been confirmed, wherein the isomerizations occur with specific rate constants of $\geq 10^3$ sec^{-1} ($\eta^2 \rightarrow \eta^1$) and 36 ± 10 sec^{-1} ($\eta^1 \rightarrow \eta^2$) for the Os(III) and Os(II) complexes, respectively. It is worth noting that the resulting complex, $[Os(NH_3)_5(N\text{-}2,6\text{-lutidine})]^{3+}$, cannot be made by conventional, substitution-based, synthetic methods for Os(III), and is likely to be the only reported example of this molecule bonding to a transition metal through nitrogen.

When pentaammineosmium(II) complexes of pyridinium salts or 2,6-lutidine are allowed to stand, an activation of the C4—H bond is observed, yielding σ-bound pyridinium complexes (*85*). Such C—H activation is unusual for aromatic heterocycles with six-membered rings and has not been observed for Os(II) complexes of arenes. Its nearest parallel is the C—H bond activation that accompanies the linkage isomerization of N-bound imidazole to the C-bound isomers of Ru(II) ammine complexes (*441*). It is remarkable that the latter type of isomerization has not as yet been observed in analogous Os chemistry, and the former has not been observed in Ru chemistry. Thus, $[Os^{II}(NH_3)_5(N\text{-im})]^{2+}$ has been prepared, but it does not undergo isomerization to $[Os^{II}(NH_3)_5(C\text{-im-H})]^{+}$ over 2 days (*90*) under conditions that facilitate the isomerization of the Ru(II) analog (*441*). This is not due to any inherent instability of the C-bound imidazole complexes, because $[Os^{II}(NH_3)_5(C\text{-diMeim-H})]^{2+}$ is readily prepared (*90*). This again highlights some fundamental differences in the reactivity of Os and Ru complexes.

4. S ↔ O Linkage Isomerizations with Dimethyl Sulfoxide

As earlier reported for Ru (*577*), $[Os(NH_3)_5(dmso)]^{2+}$ preferentially binds the ligand via the S atom (*67, 120, 200*), an action that allows for considerable π back-donation. Upon oxidation of this species (0.36 V, NHE) a linkage isomerization ensues with a specific rate of ≤ 0.1 sec^{-1}, in which the sulfoxide ligand shifts from sulfur to oxygen coordination. The reduction potential of $[Os(NH_3)_5(O\text{-dmso})]^{3+}$ (−0.90 V, NHE) is dramatically shifted due both to stabilization of Os(III) and to destabilization of Os(II), as compared to sulfur coordination. The cycle is completed by an O → S isomerization on Os(II) at a specific rate of >100 sec^{-1}.

5. S-Sulfinato to O-Sulfinato Linkage Isomerizations

$[OsCl\{(S)\text{-}SO_2C_6H_4Me\text{-}4\}(CO)(PPh_3)_2]$ undergoes CO addition with concomitant linkage isomerization to form $[OsCl\{(O)\text{-}OS(O)C_6H_4Me\text{-}4\}(CO)_2(PPh_3)_2]$ (*434*).

E. Reactions of Ligands on Osmium

1. *Atom-Transfer Reactions*

Reports of atom-transfer reactions for complexes of Os in high oxidation states chiefly appear in three areas: hydride transfer, oxotransfer, and nitrogen transfer.

a. Hydrogen Atom Transfer. In general, H^- and H_2 complexes are uncommon for polypyridine and polyamine systems lacking Os—C or Os—P bonds, although a few examples are known. The chemistry of hydride and dihydrogen complexes containing Os—C and Os—P bonds are covered in a number of reviews (*4, 8–10*) and will not be discussed further here. Recently, $[OsA_4(H)_2]^{2+}$ complexes were observed to undergo reductive coupling in the presence of π acids or halides (X^-) to form $[OsA_4(H_2)(\pi \text{ acid})]^{2+}$ and $[OsA_4(H_2)X]^{2+}$, respectively (*89*). Such activity has been observed for both *cis*- and *trans*-dihydride configurations. Similar reactions probably occur in the elimination of H_2 from $[Os(L\text{-}L)(PPh_3)_2(CO)(H)_2]^{2+}$ (L-L = bpy, 4,4′-Me_2bpy, or 5,5′-Me_2bpy) on treatment with CF_3SO_3H to form $[Os(L\text{-}L)(PPh_3)_2(CO)(OSO_2CF_3)]^+$ (*19*). $[Os(NH_3)_5(H_2)]^{2+}$ has been shown to transfer dihydrogen to acetone upon the one-electron oxidation to Os(III) (*201*). $[Os(NH_3)_5(H_2)]^{3+}$ is stable only in strongly acidic media, and is thought to readily deprotonate to form the Os(III) hydride, $[Os(NH_3)_5H]^{2+}$, the species suspected of being the active reducing agent for the ketone.

b. Oxygen Atom Transfer. These are extremely numerous in Os(VIII) chemistry, in which oxo-transfer reactions of $[OsO_4]$, $[Os(O)_n(NR)_{4-n}]$, and their adducts with N-donor ligands are widely used in organic chemistry, interactions with DNA, and biological fixing and staining (Section II,C,6,b). The cis dihydroxylation reactions with alkenes, acetylenes, arenes, and unsaturated heterocycles have been known for many years in organic chemistry. Literally hundreds of different osmate esters have been prepared by these atom-transfer reactions, although a much smaller number have been characterized prior to hydrolysis of the *cis*-diol. Despite the long history of the applications of these reactions to organic chemistry, it is only recently that the mechanisms have been elucidated, particularly for those reactions that are asymmetric, promoted by N heterocycles or light, and/or are catalytic. It is not possible to detail all of these advances here, but they are well documented in recent reviews and papers (*35, 36, 327–332, 334–336*). Recent studies on the mechanisms of oxo-transfer reactions to other organic and inorganic substrates are summarized in Table IX.

Such reactions are not only interesting in their own right but are germane to the synthesis of many Os complexes.

The reverse reactions, in which Os(VI) complexes undergo an oxo atom transfer with organic substrates, are also very important. They are the key steps in the regeneration of the catalyst in the Os(VIII)-catalyzed cis-dihydroxylation reactions of organic N oxides (*27, 35, 329, 390, 391, 394*). Although the trigonal-planar $[Os^{VI}(NAr)_3]$ (Ar = 2,3-$Pr^i_2C_6H_3$) is air-stable, it undergoes an atom-transfer reaction with Me_3NO to give $[Os^{VIII}(O)(NAr)_3]$ (*22*).

Oxotransfer is well documented for complexes of Ru(IV) → Ru(VI) (*629, 630*). In addition to oxotransfer to organic substrates, Ru complexes have been shown to be electrocatalysts for the oxidation of water (*631*). Though not as strong oxidizing agents as their Ru analogs, Os(VI) complexes have also been reported to undergo oxo-transfer reactions. *cis-* and *trans*-$[Os(bpy)_2(O)_2]^{2+}$ react with two equivalents of PPh_3 to give either the *cis-* or *trans*-$[Os(bpy)_2(OPPh_3)_2]^{2+}$, respectively (*415*). Similar activity is shown by the porphyrin complex, $[Os(oep)(O)_2]$ (*218*), the complex containing the tetradentate amide/pyridine ligand, *trans*-$[Os(bpbH_2)(O)_2]$ (*283*), and the macrocyclic complex, *trans*-$[Os(14\text{-tmc})(O)_2]$ (*39*). Indeed, oxo-transfer reactions of dioxoOs(VI) complexes with PPh_3 are standard preparative methods for the syntheses of Os(II), Os(III), and Os(IV) complexes. Oxo complexes of Os(VI) in saturated ligand environments are less reactive than with bpy or porphyrinato ligands, but have been shown to be powerful photooxidants (*107, 114*). Similarly, the oxo-bridged dimers of Os are not sufficiently oxidizing to oxidize water to dioxygen (*554*). *trans*-$[Os(bpbH_2)(O)_2]$ also reacts with cyclohexene to form cyclohexenol (*283*).

c. *Nitrogen Atom Transfer.* Although not as numerous as oxo-transfer reactions, the nitrogen atom-transfer reactions of $[Os^{VIII}(O)_n(NR)_{4-n}]$ with unsaturated substrates such as alkenes have received recent attention in organic synthesis. These reactions result in Os(VI) imido complexes that ultimately yield diamines and aminoalcohols (*22, 35, 208*). Other atom-transfer reactions of Os(VIII) include the reaction of $[Os(O)(NAr)_3]$ with PR_3 to form $[Os^{IV}(NAr)_2(PR_3)_2]$, OPR_3, and $ArNPR_3$ (*22*), and $[Os(O)_3(NBu^t)]$ with mesMgBr to give $[Os^{VI}(O)_2(mes)_2]$ and $mesNH_2$ (*30*).

In the late 1970s, Buhr and Taube demonstrated a nitrido coupling reaction in which treatment of $[Os(NH_3)_5(CO)]^{2+}$ by Ce(IV) generated $[\{Os(NH_3)_4(CO)\}_2(\mu\text{-}N_2)]^{4+}$ in high yield (*58*). Work in this area has recently been extended to complexes of aromatic nitrogen ligands:

when *trans*-$[Os(py)_2Cl_3N]$ is heated in py for several hours, N_2 is eliminated in good yield concurrent with the formation of $[Os(py)_3Cl_3]$ (*42, 226*). Experiments with substituted pyridines indicate that coupling is triggered by substitution of the heterocycle into a coordination position trans to the nitrido group. Similar coupling reactions occur with $[Os^{VI}(NH_3)_4N]$ under UV/Vis irradiation in acetonitrile to form the mixed-valence *trans,trans*-$[Os_2(\mu\text{-}N_2)(NH_3)_8(NCCH_3)_2]^{5+}$ complex (*269*). Such reactions are not only of fundamental interest, but they are also the reverse reactions involved in nitrogen fixation. A knowledge of the factors that affect the coupling reaction may lead to the rational design of nitrogen-fixing reactions.

$[Os^{VI}(N)Cl_3(pic)_2]$ and $[Os^{VI}(N)Cl_2(trpy)]^+$ undergo atom-transfer reactions with CN^- to form $[Os^{IV}(pic)_2(NCN)Cl_3]^-$ and $[Os^{IV}(tryp)(NCN)Cl_2]$, and with N_3^- to form $[Os^{II}(pic)_2(N_2)Cl_3]^-$ and $[Os^{II}(trpy)(N_2)Cl_2]$, respectively (*632*). $[Os^{V}(trpy)(bpy)(N)]^{2+}$ is believed to undergo an atom transfer with H_2O to form $[Os^{II}(trpy)(bpy)(NH_2O)]$ in the oxidative conversion of $[Os^{II}(trpy)(bpy)(NH_3)]^{2+}$ to $[Os^{V}(trpy)(bpy)(NO)]^{3+}$ (*43*).

Although not strictly atom-transfer reactions, because there are no changes in formal oxidation states, the nucleophilic substitution reactions of the nitrido complexes are parallel reactions. The nitrido ligands of $[Os(N)R_4]^-$ are alkylated readily to give $[Os(NR')R_4]$, and the kinetics of the reaction between $[Os(N)(CH_2SiMe_3)_4]^-$ and MeI have been studied (*155*). This illustrates that even in the Os(VI) oxidation state, N^{3-} retains some nucleophilic characteristics. Whether it acts as a nucleophile or electrophile depends critically on the nature of the other ligands and the substrate with which it reacts. Even though this ligand can act as nucleophile when bound to Os(VI), it is not as good a nucleophile as RS^-, because $[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]^-$ is preferentially methylated at the sulfur to form $[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2SMe)]$ (*156*).

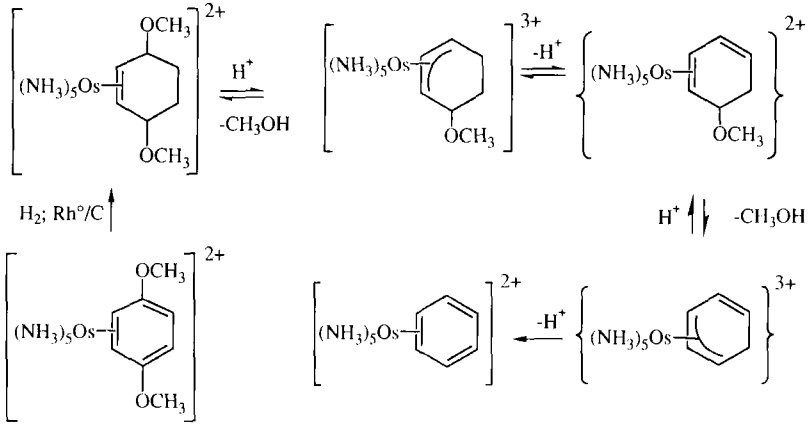
d. Halogen Atom Transfer. Rapid halide atom transfer occurs in the system $[Os^{II}(cp)_2]/[Os^{IV}(cp)_2I]^+$, although much slower than the analogous Ru chemistry. There are two independent reaction pathways. One is first order in both reactions and is the only pathway available in polar solvents, and the other is first order with respect to the Os(II) complex and zero order with respect to the Os(IV) complex. This second pathway is only observed at low concentrations of Os and in weakly polar solvents. The rate constants of the overall second-order reactions vary by over an order of magnitude in going from dmso ($3.5\ M^{-1}\ sec^{-1}$) to acetone ($78.3\ M^{-1}\ sec^{-1}$) at 20°C, although the acti-

vation enthalpies and entropies show a much bigger variation. The cross-reaction $[Ru(cp)_2Cl]^+/[Os(cp)_2]$ has also been studied (*633, 634*).

2. Ligand-Centered Reactions on Osmium(IV)

a. Allyl Complexes. As is common for most η^3-allyl complexes of higher oxidation states (*180*), $[Os^{IV}(NH_3)_5(\eta^3\text{-allyl})]^{3+}$ readily undergoes nucleophilic attack to give substituted $[Os^{II}(NH_3)_5(\eta^2\text{-olefin})]^{2+}$ complexes (*180*). Suitable nucleophiles include PPh_3, py, and MeO^-. The cyclic allyl complex, $[Os(NH_3)_5(C_6H_9)]^{3+}$, reacts with base to generate an Os(II) 1,3-cyclohexadiene species. The tendency of allyl complexes to deprotonate is markedly enhanced when the product is aromatic, hence, even in acidic media, $[Os(NH_3)_5$(3,6-dimethoxycyclohexene)$]^{2+}$ eliminates two equivalents of methanol to generate $[Os(NH_3)_5(\eta^2\text{-benzene})]^{2+}$. This sequence is shown in Scheme 15, starting from the hydrogenation of *p*-dimethoxybenzene (*180*).

b. Oxidative Dehydrogenation. The Os(IV) oxidation state is also important in oxidative dehydrogenation reactions. $[Os^{IV}(en)(en\text{-}H)_2]^{2+}$ (*204, 205*) is an intermediate in the oxidative dehydrogenation reaction of $[Os(en)_3]^{3+}$. The reaction proceeds by base-catalyzed disproportionation of the Os(III) compound to Os(II) and deprotonated Os(IV) complexes. Such disproportionation is facilitated by the stabilization of Os(IV) by π bonding between the deprotonated amines and the electron-deficient Os(IV) center (*204, 205*). The subsequent intra-



SCHEME 15. Reactions of $[Os(NH_3)_5(\eta^3\text{-allyl})]^{3+}$ complexes.

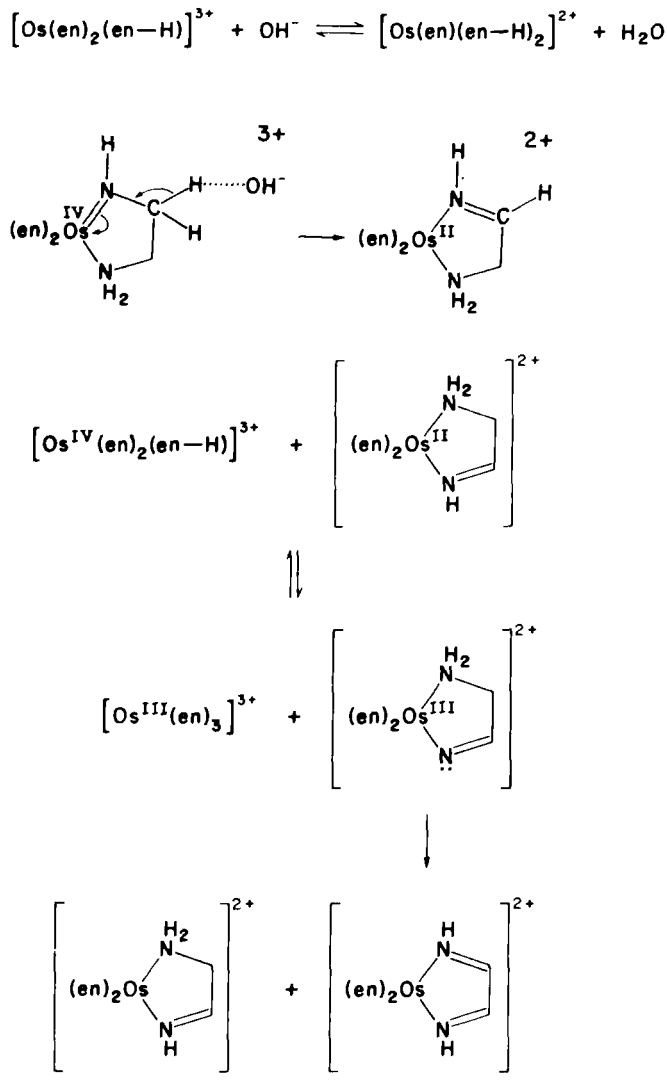
molecular two-electron transfer to produce $[Os(en)_2(enim)]^{2+}$ is driven by the π backbonding stabilizing of Os(II). The reaction continues in air via a series of oxidations, disproportionations, and intramolecular redox reactions to produce $[Os(en)(diim)_2]^{2+}$ as the air-stable product (*204, 205*). This chemistry is summarized in Schemes 11 and 16. Parallel chemistry is observed for $[Ru(en)_3]^{3+}$, but the Ru(IV) intermediates are too unstable to be characterized and the aerial oxidation stops at $[Ru(en)_2(diim)]^{2+}$ (*635*). The extent of oxidation depends on the ability of O_2 to oxidize $[M^{II}(en)_2(diim)]^{2+}$ to the M(III) counterpart. The Ru(II) complex has a more positive redox potential than does its Os(II) counterpart and hence is not easily oxidized to Ru(III) in order that the disproportionation and subsequent oxidative dehydrogenations can occur to give $[Ru(en)(diim)_2]^{2+}$.

Similar reactions occur in the oxidative dehydrogenation reactions of $[Os(bpy)_2(ampy)]^{2+}$ to $[Os(bpy)_2(impy)]^{2+}$ and related ligand oxidations (*256*) that parallel the well-studied Ru chemistry (*636*). Such reactions are also used in the synthesis of $[(NH_3)_5Os(NCCN)Os(NH_3)_5]^{5+}$ from $[(NH_3)_5Os(NH_2CH_2CH_2NH_2)Os(NH_3)_5]^{6+}$ (*542*), and the oxidations both of amines to nitriles and of alcohols to aldehydes and ketones in $[Os(NH_3)_5L]^{n+}$ complexes (*637*). Os(II) carbonyl complexes are also prepared from the oxidative dehydrogenation of methanol, to form $[Os(PPr^i_3)_3(CO)(H)(Cl)]$ (*18*). $MCl_3 \cdot xH_2O$ reacts with the tetradentate ligand, picstien, in air to give *trans*-[M(picstiendii)Cl_2] (M = Ru or Os) in which the diamine ligand has undergone an oxidative dehydrogenation reaction to form a M(II) diimine complex (*638*).

c. Ligand Deprotonation. Base-catalyzed disproportionations of $[Os(NH_3)_5(N\text{-heterocycle})]^{3+}$ complexes present a problem in the direct synthesis of these complexes from the reaction $[Os(NH_3)_5(O\text{-}SO_2CF_3)]^{2+}$ with excess ligand. Upon deprotonation and disproportionation of the Os(III) complex, it is presumed that amido ligand further deprotonates to form imido or nitrido Os(IV) species. These doubly or triply deprotonated ammine ligands both stabilize the higher oxidation states and labilize cis ammine ligands to substitution, resulting in multiple cis substitution of the N heterocycles (*68*).

3. Ligand-Centered Reactions on Osmium(III)

For Os(III), the origin of most ligand-centered reactions is due to the Lewis acidic nature of the metal ion. This effect raises the acidity of $[Os(NH_3)_6]^{3+}$ significantly ($pK_a \approx 16$) (*87*). Hence, trace amounts of this material in an acetone solution of $[Os(NH_3)_6]^{2+}$ act to catalyze the



SCHEME 16. Mechanism of oxidative dehydrogenation of $[Os^{IV}(en)_2(en\text{-}H)]^{3+}$ produced from the disproportionation of $[Os(en)_3]^{3+}$. Reprinted with permission from the *Journal of the American Chemical Society*, Ref. *204*. Copyright 1982, American Chemical Society.

formation of the imine species $[Os(NH_3)_5\{NHC(CH_3)_2\}]^{2+}$, wherein the imine acts to stabilize the electron-rich Os(II) center (*194*).

The acidity of the Os(III) ammine complexes is enhanced considerably by replacement of an ammine ligand by N-heterocyclic, imine, or

other π-acid ligands. This is due to the transferral of electron density from the π-donor ligand, NH_2^-, to the π^* orbital of the π-acid ligand, via the Os(III) center. This aids considerably in catalyzing reactions that proceed via base-catalyzed disproportionation reactions (Sections V,E,1,c and V,E,2.

Although Os(III) is a Lewis acid, it undergoes stronger π backbonding than does Ru(III) (*196, 426, 586*). For example, acid hydrolysis of $[Ru(NH_3)_5(NCMe)]^{3+}$ gives $[Ru(NH_3)_5(NHCOMe)]^{2+}$ (or its protonated analog at low pH values) with a specific rate constant of 1.2×10^{-5} sec^{-1} at 25°C. This rate is independent of pH and ionic strength, which is indicative of OH_2 being the nucleophile (*639*). The analogous chemistry occurs for Os(III), but at a much slower rate ($k \ll 1 \times 10^{-5}$ sec^{-1} at 25°C) (*67, 119*). A similar significant stabilization is apparent in the acid hydrolysis of the cyanogen-bridged complexes. Thus, hydrolysis of the cyanogen ligand in $[(NH_3)_5Ru(NCCN)Ru(NH_3)_5]^{5+}$ gives $[(NH_3)_5Ru(NHCOCN)Ru(NH_3)_5]^{4+}$ with a specific rate constant of 7.0×10^{-3} sec^{-1} at 25°C (*588, 640*). By contrast, the same reaction at the mixed-valence Os complex occurs with a specific rate constant of $\sim 2 \times 10^{-4}$ sec^{-1} at 25°C (*542*). The acid hydrolyses of the cyanogen ligand bound to both of the +6 ions is too fast to be measured using conventional cyclic voltammetry (up to 50 V sec^{-1} at 25°C). The Os_2^{4+} and Ru_2^{4+} ions are both very resistant to nucleophilic attack at the cyanogen ligand, due to the very substantial degree of transferral of π electron density by π backbonding. In summary, bonding of nitriles to Os(III) activates them to nucleophilic attack, but this activation appears to be moderated by a greater degree of π backbonding for Os(III), compared to Ru(III). Of course the results can also be interpreted in terms of stronger π bonding of the nitriles to Ru(III) than Os(III). This would also activate the nitriles to a greater extent when bound to the former, but the balance of evidence strongly points to π backbonding deactivation by Os(III) as the major source of the differences in reactivities. Confirmation of this awaits crystal structures of isomorphous complexes. If π bonding activation is the most important factor, the Ru-N(nitrile) bond will be shortened with respect to the anologous Os-N bond, whereas the converse will be true if π backbonding deactivation is most important.

A further demonstration of the Lewis acidity of Os(III) is the aldol condensation reaction of $[Os(NH_3)_5(\eta^1\text{-acetone})]^{3+}$, to form the diacetone alcohol complex (*67, 90*). The catalysis of this reaction can occur in one of two ways. Either Os(III) catalyzes the deprotonation of a methyl group of the bound acetone ligand to produce a nucleophile for attack at a second acetone ligand, or the Os(III) center polarizes the C=O bond of

the acetone ligand, which facilitates the attack of a $CH_3COCH_2^-$ nucleophile. The kinetics and mechanisms were not studied in detail and isotopic labeling experiments would be required to distinguish between these two possibilities or one in which both forms of activation are occurring. Similar reactions occur with the Co(III) (*90*) and Ru(III) (*182–184*) analogs.

There is also other evidence for the activation toward nucleophilic attack of ligands coordinated to Os(III). One example is the formation of $[Os^{III}(NH_3)_5(N\text{-Etpz})]^{4+}$ as a by-product in the reaction of $[Os(NH_3)_5(O\text{-}SO_2CF_3)]^{2+}$ with pz in triethylphosphate. The by-product is thought to occur via the nucleophilic attack of $[Os(NH_3)_5(pz)]^{3+/2+}$ on the $[Os(NH_3)_5\{OP(OEt)_3\}]^{3+}$ intermediate (*68, 80*). If the $[Os(NH_3)_5(pz)]^{3+}$ complex is the nucleophile, then it is a further indication of the importance of π backbonding in the Os(III) complex. In fact, it has been shown that the pyrazine ligand bound to Os(III) is surprisingly basic for a diazine coordinated to a M(III) center. Dissolution of yellow $[Os(NH_3)_5(pz)]^{3+}$ in 0.1 *M* HCl results in an immediate color change to the dark brown $[Os^{III}(NH_3)_5(pzH)]^{4+}$ ion (*66, 67*).

4. *Ligand-Centered Reactions on Osmium(II)*

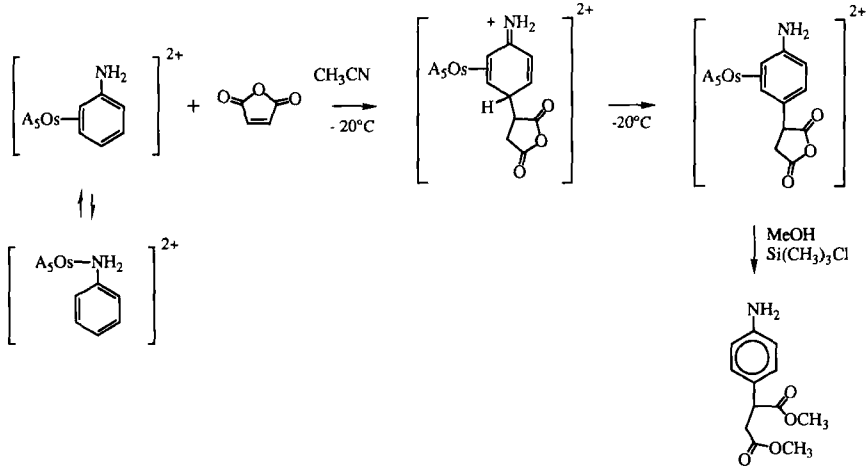
a. Protonations. The vast majority of ligand-centered reactivity on Os(II) ammine complexes is attributed to the strong tendency of this metal ion to undergo π backbonding with π-acid ligands. Perhaps the most fundamental demonstration of this is the enhancement in proton affinity reported for various organic bases upon coordination to the metal. A striking example is the pyrazine complex $[Os(NH_3)_4Cl(pz)]^+$ (*77*), which is greater than seven orders of magnitude *more* basic than for the free ligand. Such increases in basicity are also observed for the $[M(NH_3)_5(pz)]^{2+}$ complexes (*60, 67*). The fact that the increase in basicity is 6.8 pK_b units when M = Os, but only 1.9 pK_b units when M = Ru, quantifies the much greater π basicity of Os(II), compared to Ru(II) (*60*). In contrast, $[Os(NH_3)_5(3,4\text{-}\eta^2\text{-lutidine})]^{2+}$, in which the heterocycle is dihapto bound (*85*), shows virtually no change in proton affinity upon ligation. However, dihapto coordination of aromatic molecules can also result in a thermodynamic protonation site that differs from the free ligand, e.g., free pyrrole, which protonates preferentially at the 2-position ($pK_a \approx -4$), protonates at the 4-position in $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-pyrrole})]^{2+}$, but at considerably higher pH values (>4) (*430*). Similarly, $[Os(NH_3)_5(\eta^2\text{-aniline})]^{2+}$ and related complexes show enhanced basicity at the para-position of the ring, an observation which suggests that the ligand possesses a considerable dienamine character

(*431*). Finally, upon treatment with acid, both diene and allyl ether complexes of $[Os(NH_3)_5]^{2+}$ yield Os(IV) η^3-allyl species, the latter reaction proceeding by the elimination of alcohol (*180*).

b. Alkylations. Reactions analogous to the protonation of π-acid ligand bound to Os ammine complexes have been observed with other electrophiles. The pyrazine complexes, $[Os(NH_3)_5(pz)]^{2+}$ and $[Os(NH_3)_4(N_2)(pz)]^{2+}$, and other diazine complexes are N-methylated by the reaction of CH_3I in dmso (*195*). $[Os(NH_3)_5(\eta^2\text{-pyrrole})]^{2+}$ complexes are methylated at the 4-position or the N-position by CH_3OTf in dme (*85*), and 2,3,-η^2-coordinated phenol is methylated at the oxygen (*178*). When this phenol complex or the aniline derivative is treated with maleic anhydride, a Michael reaction is observed exclusively at the para position, and in high yield (*178, 431*). For the aniline complex, oxidative work-up followed by esterification in MeOH results in dimethyl (4-aminophenyl)succinate ester, free of ortho-substituted contaminants (Scheme 17) (*431*).

cis-$[Os(bpy)_2(CN)_2]$ is methylated with MeI or benzylated with $PhCH_2Br$ in MeCN to give the isonitrile complexes, *cis*-$[Os(bpy)_2(CNR)_2]^{2+}$ (R = Me or $PhCH_2$) (*97*).

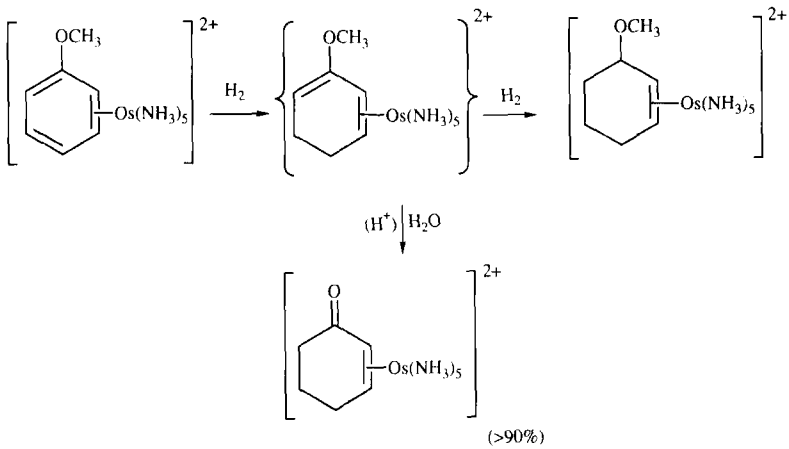
c. Arene Activation. One of the most significant outcomes of the formation of stable $[Os(NH_3)_5(\eta^2\text{-arene})]^{2+}$ complexes is the manifestation of dienelike reactivity in the organic ligand. $[Os(NH_3)_5(\eta^2\text{-benzene})]^{2+}$ is readily hydrogenated under 1 atm of hydrogen at 20°C to



SCHEME 17. Reaction of $[Os(NH_3)_5(\eta^2\text{-aniline})]^{3+}$ to give dimethyl (4-aminophenyl)succinate ester.

the cyclohexene analog in the presence of a Pd^0 catalyst (*432*). When the reaction is carried out under D_2 in CD_3OD, all of the deuterium is incorporated at a common ring face. Thus, the metal serves to activate the arene, protect the olefin product from further hydrogenation, and direct the stereochemistry of the reaction. Such a hydrogenation can be carried out on substituted benzene complexes as well (*169*). For the case of the 2,3-η^2-anisole species, hydrogenation in dry methanol yields the 3-methoxycyclohexene isomer in high yield. When this reaction is repeated in aqueous methanol with a trace of acid, the major product is a 2-cyclohexene-1-one-complex, i.e., the hydrolysis product of a 2-methoxy-1,3-diene intermediate (Scheme 18). The dihapto coordination of arenes also results in their activation toward additional metalation, even by weaker π-bases such as $[Ru(NH_3)_5]^{2+}$ (*172*).

One of the most exciting findings concerning η^2-arene activation is the enhancement of nucleophilic character at the ortho and para positions of phenols, phenyl ethers, and anilines (*178, 431*). As mentioned above in the context of alkylations, Michael additions readily occur at the para position of phenol and aniline. The action of the methylnitrillium ion on anisole or phenol in CH_3CN leads to the formation of 4-methoxy- and 4-hydroxyacetophenone imines in excellent yields (*178*). When a methyl group occupies the para position, imine formation takes place exclusively ortho to the electron-donating substituent. The redistribution in electron density upon coordination of these arenes is significant enough that the complexes $[Os(NH_3)_5(o\text{-cresol})]^{2+}$ and



SCHEME 18. Preparation of a 2-cyclohexene-1-one complex from a 2,3-η^2-anisole complex.

$[Os(NH_3)_5(m\text{-cresol})]^{2+}$ exist primarily as the 2,5-cyclohexadien-1-one tautomers under equilibrium conditions in methanol (*178*).

d. Activation of N-Heterocycles. The reduction of $[Os^{III}(NH_3)_5(N\text{-heterocycle})]^{3+}$ complexes by Zn(Hg) in acidic solution initially produces the Os(II) analogs. However, the charge-transfer bands of these complexes slowly disappear upon further reduction and this is attributed to hydrogenation of the ligands (*60*). Given the recent work on hydrogenation of the arenes discussed previously (*169, 172, 432*) and the formation of η^2-bound N-methylated complexes (*85*), a likely mechanism is as follows. Following reduction to Os(II), the complex is protonated to form the diazenium complex, which rearranges to form an equilibrium concentration of the η^2 linkage isomer. This isomer would be expected to be susceptible to hydrogenation in chemistry that parallels that observed for the η^2-arenes (*169*).

e. Addition Reactions. $[Os(NH_3)_5(\eta^2\text{-pyrrole})]^{2+}$ is 2,3-$\eta^2 \leftrightarrow$ 3,4-η^2 fluxional at room temperature and shows markedly different reactivity toward cycloaddition to maleic anhydride than is observed for the free ligand (*179*). Whereas pyrrole itself is quite resistant to this dienophile and undergoes a Michael addition only at high temperatures, the complex readily forms a mixture of exo and endo cycloaddition products at room temperature. The reaction is thought to proceed through a dipolar cycloaddition in which the active intermediate is an azomethine ylide stabilized by metal coordination at the 3,4-positions. By contrast, no reaction is observed when $[Os(NH_3)_5(\text{pyrrole})]^{2+}$ is replaced by the furan analog, even though cycloaddition to maleic anyhydride readily occurs with the free ligand.

Alkyne complexes of Os(II) are observed to undergo addition of water and methanol across the alkyne bond, resulting in stable vinyl alcohol and vinyl ether complexes, respectively (*168*). When an aqueous solution of $[Os(NH_3)_5(CH_3C{\equiv}CCH_3)]^{2+}$ is allowed to stand, the initial product observed is the *cis*-2-hydroxy-2-butene complex. Over a period of several days, this species equilibrates with its trans stereoisomer, the latter being slightly favored in aqueous solution ($K_{eq} = 1.5$).

The Os(II) alkene complexes $[OsCl(NO)(R_2C{=}CR_2)(PPh_3)_2]$ are quite reactive toward addition of $OSNSO_2C_6H_4Me$-4 (Section II,C,2,f) (*163, 164*).

Elliott and Shepherd (*70*) have investigated the effect of Os(II) coordination on dienes and report that the metal acts as a protecting group for electrophilic addition of bromine. Thus, the action of bromine on $[Os(NH_3)_5\{\eta^2\text{-}1,2\text{-}(1,3\text{-butadiene})\}]^{2+}$ is thought to result in the 3,4-dibromo-1-butene analog.

f. Condensation of Acetone. The reduction of *cis*-$[Os(NH_3)_4(O-SO_2CF_3)_2]^+$ in acetone results in the substitution-inert $[Os(NH_3)_4(daa)]^+$ complex (daa = diacetone alcohol). The fact that the complex is substitution inert shows that one site is occupied by a η^2-ketone group. The other site is expected to be occupied by the deprotonated alcohol, although the coordination mode has not been positively identified. It appears that this reaction occurs via an intramolecular condensation of *cis*-acetone ligands, but the details of the mechanism are uncertain and the condensation may have occurred prior to reduction of the Os(III) complex *cf.* Section V,E,3 (*81, 89*).

g. Dehydration Reactions. The propensity of Os(II) to bind strong π acceptor ligands drives a number of dehydration reactions. These include the dehydration of formate to carbon monoxide (*119*), hydrogen sulfite to sulfur dioxide (*197*), and oximes to nitriles (*195*). The former, in particular, is a rapid reaction and must also involve a linkage isomerization reaction because the formate ligand is initially O bound, whereas the product has the C-bound carbonyl ligand. A likely intermediate is the η^2-*C,O*-formic acid complex, by analogy with the preferred linkage isomers of ketones and aldehydes. As shown in the following section, such an intermediate is expected to activate the ligand to dehydration by analogy with the elinination reaction of the η^2-*C,O*-acetaldehyde complex. A second possible intermediate is the C-bound formate isomer.

Upon reoxidation of the Os(II) complexes, hydration of the ligands bound to Os(III) is much slower than the dehydration of the ligands bound to Os(II). Thus, reversible redox couples are found for the oxidation of the Os(II) dehydration products. Though the SO_2 and nitrile ligand will hydrate in the Os(III) oxidation state, the latter forms amides and is quite slow. In the case of the CO complex, the Os(III) complex is too labile for any appreciable CO hydration to occur within the lifetime of the complex.

Similar dehydration reactions are observed at Ru(III), but they are somewhat slower (*195, 641–643*), which is consistent with the smaller degree of stabilization of the products by π backbonding and, by implication, the transition states/intermediates in the reactions.

h. Other Elimination Reactions. Though Os chemistry parallels Ru chemistry in the dehydration/elimination reactions, Os(II) exhibits other elimination reactions that have no known parallels in pentaammineruthenium(II) chemistry. A particularly surprising reaction is the rapid extrusion of CO from $[Os(NH_3)_5(dmf)]^{2+}$ to form $[Os(NH_3)_5(CO)]^{2+}$ and $NH(CH_3)_2$ (*120*). Other similar reactions that occur

are the elimination of methane from coordinated acetaldehyde to form $[Os(NH_3)_5(CO)]^{2+}$, and the elimination of H_2 from the methylimine complex, $[Os(NH_3)_5(NH{=}CHCH_3)]^{2+}$, to form $[Os(NH_3)_5(NCCH_3)]^{2+}$ (*120*). Similar reactions are used in the preparation of $[Os(H)(X)(CO)(PR_3)_n]$ complexes (Section II,C,2,b), but these require much greater forcing conditions, illustrating the greater degree of π stabilization of the Os(II) π-acid complexes with the pentaammine moiety as opposed to complexes with other π acids, such as phosphines. The pentaammine chemistry also shows the much greater driving force of π-backbonding stabilization of Os(II) compared to RU(II), although facile elimination reactions of $[Ru(NH_3)_5(HON{=}C(R)CH_3)]^{2+}$ to produce $[Ru(NH_3)_5(N{\equiv}CCH_3)]^{2+}$ and ROH have been reported (*644*).

Abbreviations and Trivial Nomenclature

A	ammine or amine
$(aa)_2en$	*N,N*-bis(acetylacetone) ethylenediimine = 3,3′-(1,2-ethanediylnitrilo) bis(1-methyl-1-butanonato)
abn	aminobenzonitrile
ac	acetone
acac	acetylacetonato(1−) = 2,4-pentanedionato(1−)
Acdhqd	acetyldihydroquinidine
acet	acetaldehyde
AcOH	acetic acid
adc-Me	1,2-diacetylhydrazido(2−)
ampy	2-(aminomethyl)pyridine
an	acetonitrile
[9]aneS_3	1,4,7-trithiacyclononane
[14]aneS_4	1,4,8,11-tetrathiacyclotetradecane
[14]aneN_4	1,4,8,11-tetraazacyclotetradecane
[15]aneN_4	1,4,8,12-tetraazacyclopentadecane
[16]aneN_4	1,5,9,13-tetraazacyclohexadecane
[18]aneS_6	1,4,7,10,13,16-hexathiacyclooctadecane
anisole	methoxybenzene
$(ba)_2en$	*N,N′*-bis(benzoylacetone) ethylenediimine = 3,3′-(1,2-ethanediylnitrilo)-bis(1-phenyl-1-butanonato)

bbpe	*trans*-1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethene
bibzim	2,2′-bis(benzimidazolate)(2−)
bim	2,2′-biimidazolato(2−)
bimH	2,2′-biimidazolato(1−)
bpa	1,2-bis(4-pyridyl)ethane
$bpbH_2$	*N*,*N*′-bis(2′-pyridinecarboxamide)-1,2-benzene
bpb	*N*,*N*′-bis[2′-pyridinecarboxamido(1−)]-1,2-benzene
bpds	4,7-diphenyl-1,10-phenanthroline disulfonate
bpt	3,5-bis(pyridin-2-yl)-1,2,4-triazolate(1−)
bptz	3,6-bis(2-pyridyl)-1,2,4,5-tetraazine
bpy	2,2′-bipyridine
4,4′-bpy	4,4′-bipyridine
bsd	2,1,3-benzoselenadiazole
bta	benzotriazolato(1−)
btd	2,1,3-benzothiadiazole
Bu^n	*n*-butyl = 1-butyl
Bu^t	*tert*-butyl = 2-(2-methylpropyl)
$(Bu^i)_2$en	*N*,*N*′-bis(isobutyrylacetone) ethylenediimine = 3,3′-(1,2-enthanediylnitrilo)bis(1-(2-butyl)-1-butanonato)
4-Bu^tpy	4-*tert*-butylpyridine = 4-[2-(2-methylpropyl)]pyridine
3-Bu^t-saltmen	*N*,*N*′-(1,1,2,2-tetramethylethylene)bis-(3-*tert*-butylsalicylideneaminato)(2−)
chd	1,2-cyclohexanediol
chp	6-chloro-2-hydroxypyridinato(1−)
4-cinn	*N*-(4-pyridyl)cinnamamide
ClBzdhq	(4-chlorobenzoyl)dihydroquinine
ClBzdhqd	(4-chlorobenzoyl)dihydroquinidine
cod	1,5-cyclooctadiene
cp	cyclopentadienyl
o-cresol	2-methylphenol
p-cresol	4-methylphenol
$crMe_3$	*meso*-1,2,6,10,11-pentamethyl-2,6,10-triaza[11](2,6)-pyridinophane

CT	charge transfer
Ctmen	2,3-dimethylbutane-2,3-diamine
Ctmen-H	2,3-dimethylbutane-2,3-diaminato(1−)-*N*
Ctmen-2H	2,3-dimethylbutane-2,3-diaminato(2−)-*N*,*N*′
cym	cymene = 1-methyl-4-(1′-methylethyl)benzene
CV	cyclic voltammetry
daa	diacetone alcohol = 4-hydroxy-4-methylpenta-2-one
dabco	1,4-diazabicyclo[2.2.2]octane
dabcoMeps/dvp	dabco-methylated polystyrene/divinylbenzene copolymer
das	*cis*-1,2-bis(dimethylarsino)benzene
dbcat	3,5-di-*tert*-butylcatechol
dca	dicyanoamide(1−)
1,2-dcb	1,2-dicyanobenzene
1,3-dcb	1,3-dicyanobenzene
1,4-dcb	1,4-dicyanobenzene
dcbpy	2,2′-bipyridine-4,4′-dicarboxylate(2−)
dcpe	1,2-bis(dicyclohexylphosphino)ethane
ddq	dichlorodicyanobenzoquinone
depe	1,2-bis(diethylphosphino)ethane
dhc	*cis*-1,2-dihydrocatecholate(2−) = *cis*-5,6-dihydroxy-1,3-cyclohexadienate(2−)
dhdhp	*cis*-9,10-dihydro-9,10-dihydroxyphenanthrenato(2−)
diaa	di(4-anisyl)amine = bis(4-methoxyphenyl)amine
diim	ethanediimine
diMeim	*N*,*N*′-dimethylimidazolinium
diMeim-H	*N*,*N*′-dimethylimidazolinium ion deprotonated at the 2-position
dma	*N*,*N*-dimethylacetamide
dmcdhqd	dimethylcarbamoyl dihydroquinidine
dme	1,2-dimethoxyethane
dmf	*N*,*N*-dimethylformamide
dmpe	1,2-bis(dimethylphosphino)ethane
dmps	2,3-dimercaptopropanesulfonate(3−)
dmso	dimethyl sulfoxide

dpae	1,2-bis(diphenylarsino)ethane
dpb	1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12, 18-tetramethyl)porphyrinato(2-)] biphenylene
dpp	2,3-bis(2′-pyridyl)pyrazine
dppe	1,2-bis(diphenylphosphino)ethane
dppene	*cis*-1,2-bis(diphenylphosphino)ethene
dppm	bis(diphenylphosphino)methane
dppmO	(diphenylphosphinomethyl)diphenylphosphine oxide
dppmS	(diphenylphosphinomethyl)diphenylphosphine sulfide
dpq	2,3-bis(2′-pyridyl)quinoxaline
ehba	2-ethyl-2-hydroxybutanoato(2−)
en	1,2-ethanediamine
en-H	1,2-ethanediaminato(1−)
enim	2-aminoethan-1-imine
EPR	electron paramagnetic resonance
Etpz	*N*-ethylpyrazinium
Fc	ferrocene
Fc^+	ferricenium
fhp	6-fluoro-2-hydroxypyridinato(1−)
gn	glutaronitrile
glyc	glycolate(2−)
H_2chba	3,5-dichloro-2-hydroxybenzamide
H_4chba-dcb	1,2-bis(2-hydroxy-3,5-dichlorobenzamido)-4,5-dichlorobenzene
H_4chba-Et	1,2-bis(2-hydroxy-3,5-dichlorobenzamido)ethane
H_4chba-ethylene	*cis*-1,2-bis(2-hydroxy-3,5-dichlorobenzamido)ethylene
H_4chba-*t*-1,2-diEtO-Et	1,2-bis(2-hydroxy-3,5-dichlorobenzamido)-*trans*-1,2-diethoxyethane
H_4chba-*t*-1,2-diHO-Et	1,2-bis(2-hydroxy-3,5-dichlorobenzamido)-*trans*-1,2-dihydroxyethane
H_4chba-*t*-1-OH-2-MeO-Et	1,2-bis(2-hydroxy-3,5-dichlorobenzamido)-*trans*-1-hydroxy-2-methoxyethane
hhch	*cis*,*cis*,*cis*,*cis*,*trans*,*trans*-1,2,3,4,5,6-hexahydroxycyclohexanate(6−)
hmt	hexamethylenetetraamine
hp	2-hydroxypyridinate(1−)

Hpy	pyridinium
HpyS	pyridinium-2-thiolate
H_2dpd	1-[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrinato(2−)]-8-[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]biphenylene
H_4dpd	1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethyl)porphyrin]biphenylene
H_2fo-chba	*N*-formyl-3,5-dichloro-2-hydroxybenzamide
H_4hba-b	1,2-bis(2-hydroxybenzamido)benzene
im	imidazole
impy	2-(carboxyimine)pyridine
isn	*iso*-nicotinamide = 4-(carboamide) pyridine
4-lutdm	4-(2,6-lutidinium)
malt	maltolato(1−) = 3-hydroxy-2-methyl-1-oxacyclohexa-2,5-dien-4-onato(1−)
Mb	myoglobin
MCD	magnetic circular dichroism
4,4′-Me_2bpy	4,4′-dimethyl-2,2′-bipyridine
5,5′-Me_2bpy	5,5′-dimethyl-2,2′-bipyridine
Me_4bpy	4,4′,5,5′-tetramethyl-2,2′-bipyridine
MeOdhqd	methoxydihydroquinidine
4,7-Me_2phen	4,7-dimethyl-1,10-phenanthroline
3,5,6,8-Me_4phen	3,5,6,8-tetramethyl-1,10-phenanthroline
3,4,7,8-Me_4phen	3,4,7,8-tetramethyl-1,10-phenanthroline
Mepy	*N*-methylpyridinium(1+)
Me_2PymS	4,6-dimethylpyrimidine-2-thiolato(1−)
Me_2PymSH	4,6-dimethylpyrimidine-2-thiol
Mepz	*N*-methylpyrazinium
mes	mesityl = 2,4,6-trimethylphenyl
mix	*meso*-porphyrinato(2−) IX-dicarboxylic acid
mix-dme	*meso*-porphyrinato(2−) IX-dimethyl ester
MO	molecular orbital
m.p.	melting point

mv^{2+}	methyl viologen = *N,N'*-dimethyl-4,4'-bipyridinium(2+)
NBu^t	*tert*-butylimide = 2-methylpropan-2-imide
nd	2,3-naphthalenediolato(2−)
$(NEt)_2bpy$	4,4'-bis(diethylamino)-2,2'-bipyridine
neopentyl	2,2-dimethylpropyl
NIR	near-infrared
nmp	*N*-methylpyrrolidine
NQR	nuclear quadrapole resonance
Ntmen	*N,N,N',N'*-tetramethyl-1,2-ethanediamine
oep	octaethylporphyrinato(2−)
oep^+	octaethylporphyrinato(1−) radical
oep^-	octaethylporphyrinato(3−) radical
OTf	triflate = trifluoromethanesulfonate
Pc	phthalocyanato(2−)
pda	1,2-phenylenediaminato(2−)
Ph	phenyl
phen	1,10-phenanthroline
phenba	*N,N'*-1,2-phenylenebis[2-acetyl-1-amino-1-buten-3-onato(1−)]
4-pic	4-picoline = 4-methylpyridine
picstien	3,4-diphenyl-1,6-bis(2'-pyridyl)-2,5-diazahexane
picstiendii	3,4-diphenyl-1,6-bis(2'-pyridyl)-2,5-diazahexan-1,5-diene
Pr^i	*iso*-propyl = 2-propyl
Pro	proline
ptz	phenothiazine
pvp	polyvinyl pyridine
py	pyridine
pyca	pyridine-2-carboxylato(1−)
pycaH	pyridine-2-carboxylic acid
pyO	pyridine *N*-oxide
pyr	pyrimidine
pyS	pyridine-2-thiolato(1−)
pySH	pyridine-2-thiol
pySSpy	2,2'-bis(pyridyl) disulfide

pz	pyrazine
pzH	pyrazinium(1+)
qncd	quinuclidine
salen	*N,N'*-ethylenebis(salicylideneaminato)(2−)
5-SO_3^--bpy	2,2′-bipyridine-5-sulfonate(1−)
tatd	1,3,5,7-tetraazatricyclo[3.3.1.$1^{3,7}$]decane
tcne	tetracyanoethene
tet*a*	*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
tetraphos	3,6-diphenyl-1,8-bis(diphenylphosphino)-3,6-diphosphaoctane
thch	*cis,trans,trans*-3,4,5,6-tetrahydroxycyclohex-1-enato(4−)
thf	tetrahydrofuran
thio	thiourea
ththa	*cis,trans,trans*-1,2,3,4-tetrahydro-1,2,3,4-tetrahydroxyanthracenate(4−)
14-tmc	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
15-tmc	1,4,8,12-tetramethyl-1,4,8,12-tetraazacyclopentadecane
16-tmc	1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane
tmp	*meso*-tetramesitylporphyrinato(2−)
o-tolyl	2-tolyl = 2-methylphenyl
tpp	*meso*-tetraphenylporphyrinato(2−)
triflate	trifluoromethanesulfonate
triflato	trifluoromethanesulfonato
trop	tropolonato(−)
trpy	2,2′:6′,2″-terpyridine
tterpy	4′-phenyl-2,2′:6′,2″-terpyridine
vbpy	4-vinyl-4′-methyl-2,2′-bipyridine
vpy	4-vinylpyridine
XPS	X-ray photoelectron spectroscopy
p-Xtpp	*meso*-tetra(4-Xphenyl)porphyrinato(2−)
X-tterpy	4′-(4‴-Xphenyl)-2,2′:6′,2″-terpyridine
2-xylyl	2,6-dimethylphenyl

ACKNOWLEDGMENTS

The authors would like to thank Zai-Wei Li, Henry Taube, Andreas Ludi, Kim Finnie, Elmars Krausz, and David Ware for supplying the results of certain studies prior to publication. PAL is grateful for funding from the Australian Research Council for some aspects of the work described and for a CSIRO Postdoctoral Fellowship, which enabled the development of the Os triflato chemistry at Stanford University.

REFERENCES

1. Tennant, S., *Philos. Trans. R. Soc. London* **94,** 411 (1804).
2. Griffith, W. P., *in* "Comprehensive Coordination Chemistry" (G. Wilkinson, R. D. Gillard, and J. A. McCleverty, eds.), Vol. 4, Chapter 46, pp. 519–633. Pergamon, Oxford, 1987.
3. Bretherick, L., "Hazards in the Chemical Laboratory," 3rd ed., p. 422. The Royal Society of Chemistry, London, 1981.
4. Adams, R. D., and Selegue, J. P., *in* "Comprehensive Organometallic Chemistry" (G. Wilkinson, F. G. A. Stone, and E. W. Abel, eds.), Vol. 4, Chapter 33 pp. 967–1064. Pergamon, Oxford, 1982.
5. "Gmelin's Handbuch der Anorganischen Chemie," 8th ed., Vol. 66. Verlag Chemie, Berlin, 1939.
6. "Gmelin's Handbuch der Anorganischen Chemie, Supplement Volume, 'Osmium'," Vol. 1, No. 66. Springer-Verlag, Berlin, 1980.
7. Robinson, S. D., *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.* **83,** 310 (1987); **84,** 227 (1988); **85,** 219 (1989).
8. Shapley, P. A., *J. Organomet. Chem.* **351,** 145 (1988).
9. Shapley, P. A., *J. Organomet. Chem.* **318,** 409 (1987).
10. Keister, J. B., *J. Organomet. Chem.* **318,** 297 (1987).
11. Le Bozec, H., Touchard, D., and Dixneuf, P. H., *Adv. Organomet. Chem.* **29,** 163 (1989).
12. Roper, W. R., *NATO ASI Ser., Ser. C* **269,** 27 (1989).
13. Kallmann, S., *Talanta* **34,** 677 (1987).
14. Singh, S., Mathur, S. P., Thakur, R. S., and Katyal, M., *Acta Cienc. Indica [Ser.] Chem.* **13,** 40 (1987).
15. Ermer, S. P., Shinomoto, R. S., Deming, M. A., and Flood, T. C., *Organometallics* **8,** 1377 (1989).
16. Martins, S., Jr., and Vugman, N. V., *Chem. Phys Lett.* **141,** 548 (1987).
17. Elliott, G. P., McAuley, N. M., and Roper, W. R., *Inorg. Synth.* **26,** 184 (1989).
18. Esteruelas, M. A., and Werner, H., *J. Organomet. Chem.* **303,** 221 (1986).
19. Sullivan, B. P., Lumpkin, R. S., and Meyer, T. J., *Inorg. Chem.* **26,** 1247 (1987).
20. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 5th ed., Chapter 17, pp. 632–633. Wiley, New York.
21. Tooze, R. P., Stavropoulos, P., Motevalli, M., Hursthouse, M. B., and Wilkinson, G., *J. Chem. Soc., Chem. Commun.* p. 1139 (1985).
22. Anhaus, J. T., Kee, T. P., Schofield, M. H., and Schrock, R. R., *J. Am. Chem. Soc.* **112,** 1642 (1990).
23. Arnold, J., Wilkinson, G., Hussain, B., and Hursthouse, M. B., *J. Chem. Soc., Chem. Commun.* p. 1349 (1988).

23a. Dengel, A. C., and Griffith, W. P., *Inorg. Chem.* **30,** 869 (1991).
24. Danopoulos, A. A., Wong, A. C. C., Wilkinson, G., Hursthouse, M. B., and Hussain, B., *J. Chem. Soc., Dalton Trans.* p. 315 (1990).
25. Che, C. M., Lam, M. H. W., Wang, R. J., and Mak, T. C. W., *J. Chem. Soc., Chem. Commun.* p. 820 (1990).
26. Marshman, R. W., Bigham, W. S., Wilson, S. R., and Shapley, P. A., *Organometallics* **9,** 1341 (1990).
27. Sivik, M. R., Gallucci, J. D., and Paquette, L. A., *J. Org. Chem.* **55,** 391 (1990).
28. Shapley, P. A. B., Own, Z. Y., and Huffman, J. C., *Organometallics* **5,** 1269 (1986).
29. Pearlstein, R. M., Blackburn, B. K., Davis, W. A., and Sharpless, K. B., *Angew. Chem.* **102,** 710 (1990); *Angew Chem., Int. Ed. Engl.* **29,** 639 (1990).
30. McGilligan, B. S., Arnold, J., Wilkinson, G., Hussain-Bates, B., and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* p. 2465 (1990).
31. Longley, C. J., Savage, P. D., Wilkinson, G., Hussain, B., and Hursthouse, M. B., *Polyhedron* **7,** 1079 (1988).
32. Stravopoulos, P. G., Edwards, P. G., Behling, T., Wilkinson, G., Motevalli, M., and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* p. 169 (1987).
33. Edwards, C. F., Griffith, W. P., and Williams, D. J., *J. Chem. Soc., Chem. Commun.* p. 1523 (1990).
34. Katti, K. V., Roesky, H. W., and Rietzel, M., *Z. Anorg. Allg. Chem.* **553,** 123 (1987).
35. Griffith, W. P., *Transition Met. Chem. (London)* **15,** 251 (1990).
36. Griffith, W. P., and White, A. D., *Proc. Indian Natl. Sci. Acad., Part A* **52,** 804 (1986).
37. Dobson, J. C., Takeuchi, K. J., Pipes, D. W., Geselowitz, D. A., and Meyer, T. J., *Inorg. Chem.* **25,** 2357 (1986).
38. Mosseri, S., Neta, P., Hambright, P., Sabry, D. Y., and Harriman, A., *J. Chem. Soc., Dalton Trans.* p. 2705 (1988).
39. Che, C., and Poon, C., *Pure Appl. Chem.* **60,** 1201 (1988).
40. Che, C. M., Chung, W. C., and Lai, T. F., *Inorg. Chem.* **27,** 2801 (1988).
41. Pipes, D. W., Bakir, M., Vitols, S. E., Hodgson, D. J., and Meyer, T. J., *J. Am. Chem. Soc.* **112,** 5507 (1990).
42. Ware, D. C., Ph.D. Thesis, Stanford University, Stanford, California (1986).
43. Murphy, W. R., Jr., Takeuchi, K., Barley, M. H., and Meyer, T. J., *Inorg. Chem.* **25,** 1041 (1986).
44. Barner, C. J., Collins, T. J., Mapes, B. E., and Santarsiero, B. D., *Inorg. Chem.* **25,** 4322 (1986).
45. Cleare, M. J., and Griffith, W. P., *J. Chem. Soc. A,* p. 1117 (1970).
46. Kim, S. H., Moyer, B. A., Azan, S., Brown, G. M., Olins, A. L., and Allison, D. P., *Inorg. Chem.* **28,** 4648 (1989).
47. Lay, P. A., and Taube, H., *Inorg. Chem.* **28,** 3561 (1989).
48. Dwyer, F. P., and Hogarth, J. H., *J. Proc. R. Soc. N.S.W.* **84,** 117 (1951).
49. Dwyer, F. P., and Hogarth, J. H., *J. Proc. R. Soc. N.S.W.* **85,** 113 (1952).
50. Watt, G. W., and Vaska, L., *J. Inorg. Nucl. Chem.* **5,** 304 (1958).
51. Watt, G. W., and Vaska, L., *J. Inorg. Nucl. Chem.* **5,** 308 (1958).
52. Watt, G. W., and Vaska, L., *J. Inorg. Nucl. Chem.* **6,** 246 (1958).
53. Watt, G. W., and Vaska, L., *J. Inorg. Nucl. Chem.* **77,** 66 (1958).
54. Allen, A. D., and Stevens, J. R., *J. Chem. Soc., Chem. Commun.* p. 1147 (1967).
55. Allen, A. D., and Stevens, J. R., *Can. J. Chem.* **50,** 3093 (1972).
56. Bottomley, F., and Tong, S. B., *Inorg. Synth.* **16,** 9 (1976).
57. Elson, C. M., Gulens, J., and Page, J. A., *Can. J. Chem.* **49,** 297 (1971).
58. Buhr, J. D., and Taube, H., *Inorg. Chem.* **18,** 2208 (1979).

59. Lay, P. A., Magnuson, R. H., and Taube, H., *Inorg. Synth.* **24,** 269 (1986).
60. Sen, J., and Taube, H., *Acta Chem. Scand., Ser. A* **A33,** 125 (1979).
61. Allen, A. D., and Stevens, J. R., *Can. J. Chem.* **51,** 92 (1973).
62. Taube, H., *Pure Appl. Chem.* **51,** 901 (1979).
63. Taube, H., *Comments Inorg. Chem.* **1,** 127 (1981).
64. Dixon, N. E., Jackson, W. G., Lancaster, M. J., Lawrance, G. A., and Sargeson, A. M., *Inorg. Chem.* **20,** 470 (1981).
65. Dixon, N. E., Lawrance, G. A., Lay, P. A., and Sargeson, A. M., *Inorg. Chem.* **23,** 2940 (1984).
66. Lay, P. A., Magnuson, R. H., Sen. J., and Taube, H., *J. Am. Chem. Soc.* **104,** 7658 (1982).
67. Lay, P. A., Magnuson, R. H., and Taube, H., *Inorg. Chem.* **28,** 3001 (1989).
68. Lay, P. A., Magnuson, R. H., and Taube, H., *Inorg. Chem.* **27,** 2848 (1988).
69. Gulens, J., and Page, J. A., *J. Electroanal. Chem., Interfacial Electrochem.* **55,** 239 (1974).
70. Elliott, M. G., and Shepherd, R. E., *Inorg. Chem.* **27,** 3332 (1988).
71. Elliott, M. G., Zhang, S., and Shepherd, R. E., *Inorg. Chem.* **28,** 3036 (1989).
72. Zhang, S., and Shepherd, R. E., *Inorg. Chim. Acta* **163,** 237 (1989).
73. Finn, M. G., and Harman, W. D., unpublished results.
74. Harman, W. D., and Taube, H., *Inorg. Chem.* **26,** 2917 (1987).
75. Harman, W. D., Sekine, M., and Taube, H., *J. Am. Chem. Soc.* **110,** 5725 (1988).
76. Scheidegger, H., Armor, J. N., and Taube, H., *J. Am. Chem. Soc.* **90,** 3263 (1968).
77. Magnuson, R. H., and Taube, H., *J. Am. Chem. Soc.* **97,** 5129 (1975).
78. Magnuson, R. H., and Taube, H., *J. Am. Chem. Soc.* **94,** 7213 (1972).
79. Magnuson, R. H., Ph.D. Thesis, Stanford University, Stanford, California (1974).
80. Lay, P. A., Magnuson, R. H., and Taube, H., *Inorg. Chem.* **27,** 2364 (1988).
81. Li, Z.-W., Lay, P. A., Taube, H., and Harman, W. D., *Inorg. Chem.*, in press.
82. Svetlov, A. A., and Sinitsyn, N. M., *Zh. Neorg. Khim.* **31,** 2902 (1986); *Russ. J. Inorg. Chem. (Engl. Transl.)* **31,** 1667. (1986).
83. Buhr, J. D., Winkler, J. R., and Taube, H., *Inorg. Chem.* **19,** 2416 (1980).
84. Lay, P. A., unpublished results.
85. Cordone, R., and Taube, H., *J. Am. Chem. Soc.* **109,** 8101 (1987).
86. Hall, J. P., and Griffith, W. P., *Inorg. Chim. Acta* **48,** 65 (1981).
87. Buhr, J. D., and Taube, H., *Inorg. Chem.* **19,** 2425 (1980).
88. Harman, W. D., Gebhard, M., and Taube, H., *Inorg. Chem.* **29,** 567 (1990).
89. Li, Z.-W., and Taube, H., work in progress.
90. Cordone, R., Ph.D. Thesis, Stanford University, Stanford, California (1988).
91. Buchler, J. W., *in* "The Porphyrins" (D. Dolphin, ed.), Vol. 1, p. 463. Academic Press, New York, 1978.
92. Buchler, J. W., Kokisch, E., and Smith, P. D., *Struct. Bonding (Berlin)* **34,** 79 (1978).
93. Che, C. M., and Poon, C. K., *Pure Appl. Chem.* **60,** 495 (1988).
94. Lay, P. A., Sargeson, A. M., and Taube, H., *Inorg. Synth.* **24,** 291 (1986).
95. Ware, D. C., Lay, P. A., and Taube, H., *Inorg. Synth.* **24,** 299 (1986).
96. Takeuchi, K. J., Thompson, M. S., Pipes, D. W., and Meyer, T. J., *Inorg. Chem.* **23,** 1845 (1984).
97. Kober, E. M., Caspar, J. V., Sullivan, B. P., and Meyer, T. J., *Inorg. Chem.* **27,** 4587 (1988).
98. Popov, A. M., and Egorova, M. B., *Zh. Obschch. Khim.* **58,** 1673 (1988); *Chem. Abstr.* **109,** 242938y (1988).
99. Dwyer, F. P., and Hogarth, J. W., *Inorg. Synth.* **5,** 206 (1957).

100. Bould, J., Greenwood, N. N., and Kennedy, J. D., *J. Organomet. Chem.* **249,** 11 (1983).
101. Bould, J., Crook, J. E., Greenwood, N. N., and Kennedy, J. D., *J. Chem. Soc., Chem. Commun.* p. 951 (1983).
102. Beckett, M. A., Greenwood, N. N., Kennedy, J. D., and Thornton-Pett, M., *J. Chem. Soc., Dalton Trans.* p. 795 (1986).
103. Elrington, M., Greenwood, N. N., Kennedy, J. D., and Thornton-Pett, M., *J. Chem. Soc., Dalton Trans.* p. 2277 (1986).
104. Brown, M., Greenwood, N. N., and Kennedy, J. D., *J. Organomet. Chem.* **309,** C67 (1986).
105. Hosmane, N. S., and Sirmokadam, N. N., *Organometallics* **3,** 1119 (1984).
106. Alcock, N., Jasztal, M. J., and Wallbridge, M. G. H., *J. Chem. Soc., Dalton Trans.* p. 2793 (1987).
107. Yam, V. W. W., and Che, C. M., *New J. Chem.* **13,** 707 (1989).
108. Weigard, W., Nagel, U., and Beck, W., *Z. Naturforsch., B: Chem. Sci.* **43,** 328 (1988).
109. Matsumura-Inoue, T., Ikemoto, I., and Umezawa, Y., *J. Electroanal. Chem. Interfacial Electrochem.* **209,** 135 (1986).
110. Afanas'ev, M. L., Kubarev, Yu. G., and Zeer, E. P., *Sovrem. Metody YaMR EPR Khim. Tverd. Tela [Mater. Vses. Koord. Soveshch.], 4th, 1985* pp. 63–65. Akad. Nauk SSR, Inst. Khim. Fiz., Chernogolovka, USSR., *Chem. Abstr.* **104,** 99844d (1986).
110a. Xu, X. L., and Hulliger, F., *J. Solid State Chem.* **80,** 120 (1989).
110b. Gentil, L. A., Nauaza, A., Olabe, J. A., and Rigoiti, G. E., *Inorg. Chim. Acta* **179,** 89 (1991).
111. Oyama, N., Ohsaka, T., Yamamoto, N., Matsui, J., and Hatozaki, O., *J. Electroanal. Chem. Interfacial Electrochem.* **265,** 297 (1989).
111a. Vogler, A., and Kunkely, H., *Inorg. Chim. Acta* **150,** 3 (1988).
112. Opekar F., and Beran, P., *Electrochim. Acta* **22,** 249 (1977).
113. Sartori, C., Preetz, W., *Z. Anorg. Allg. Chem.* **572,** 151 (1989).
114. Yam, V. W. W., and Che, C., *Coord. Chem. Rev.* **97,** 93 (1990).
115. Sartori, C., and Preetz, W., *Z. Naturforsch., A: Phys. Sci.* **43,** 239 (1988).
116. Thomas, N. C., *Coord. Chem. Rev.* **93,** 225 (1989).
117. Bruns, M., and Preetz, W., *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **41B,** 25 (1986).
118. Lay, P. A., and Taube, H., unpublished results (1982).
119. Lay, P. A., and Taube, H., *Inorg. Chem.*, to be submitted.
120. Harman, W. D., Ph.D. Thesis, Stanford University, Stanford, California (1987).
121. Moers, F. G., and Langhout, J. P., *Recl. Trav. Chim., Pays. Bas* **91,** 591 (1972).
122. Vaska, L., *J. Am. Chem. Soc.* **86,** 1943 (1964).
123. Ahmad, N., Robinson, S. D., and Uttley, M. F., *J. Chem. Soc., Dalton Trans.* p. 843 (1972).
124. Meyer, U., and Werner, H., *Chem. Ber.* **123,** 697 (1990); Werner, H., Meyer, U., Peters, K., and von Schnering, H. G., *ibid.* **122,** 2097 (1989).
125. Esteruelas, M. A., Sola, E., Oro, L. A., Werner, H., and Meyer, U., *J. Mol. Catal.* **45,** 1 (1988).
126. Harding, P. A., Robinson, S. D., and Henrick, K., *J. Chem. Soc., Dalton Trans.* p. 415 (1988).
127. Bohle, D. S., Clark, G. R., Rickard, C. E. F., and Roper, W. R., *Chem. Aust.* **54,** 293 (1987).
128. Werner, H., Esteruelas, M. A., Meyer, U., and Wrackmeyer, B., *Chem. Ber.* **120,** 11 (1987).

129. Alteparmakian, V., and Robinson, S. D., *Inorg. Chim. Acta* **116,** L37 (1986).
130. Bohle, D. S., Rickard, C. E. F., and Roper, W. R., *J. Chem. Soc., Chem. Commun.* p. 1594 (1985).
131. Bohle, D. S., and Roper, W. R., *Organometallics* **5,** 1607 (1986).
132. Bohle, D. S., Jones, T. C., Rickard, C. E. F., and Roper, W. R., *Organometallics* **5,** 1612 (1986).
133. Conway, C., Kemmitt, R. D. W., Platt, A. W. G., Russell, D. R., and Sherry, L. J. S., *J. Organomet. Chem.* **292,** 419 (1985).
134. Sanchez-Delgado, R. A., Thewalt, U., Valencia, N., Andriollo, A., Marquez-Silva, R. L., Puga, J., Schoellhorn, H., Klein, H. P., and Fontal, B., *Inorg. Chem.* **25,** 1097 (1986).
135. Sanchez-Delgado, R. A., Valencia, N., Marquez-Silva, R., Andriollo, A., and Medina, M., *Inorg. Chem.* **25,** 1106 (1986).
136. Mura, P., Olby, B. G., and Robinson, S. D., *J. Chem. Soc., Dalton Trans.* p. 2101 (1985).
137. Sanchez-Delgado, R. A., Andriollo, A., Gonzalez, E., Valencia, N., Leon, V., and Espidel, J., *J. Chem. Soc., Dalton Trans.* p. 1859 (1985).
138. Lundquist, E. G., Huffman, J. C., and Caulton, K. G., *J. Am. Chem. Soc.* **108,** 8309 (1986).
139. Buchler, J. W., and Rohbock, K., *J. Organomet. Chem.* **65,** 223 (1974).
140. Che, C.-M., Poon, C.-K., Chung, W.-C., and Gray, H. B., *Inorg. Chem.* **24,** 1277 (1985).
141. Collman, J. P., and Garner, J. M., *J. Am. Chem. Soc.* **112,** 166 (1990).
142. Kadish, K. M., *Prog. Inorg. Chem.* **34,** 435 (1986).
143. Che, C. M., and Chung, W. C., *J. Chem. Soc., Chem. Commun.* p. 386 (1986).
144. Che, C. M., Chiang, H. J., Margalit, R., and Gray, H. B., *Catal. Lett.* **1,** 51 (1988).
145. Coombe, V. T., Heath, G. A., Stephenson, T. A., Whitelock, J. D., and Yellowlees, L. J., *J. Chem. Soc., Dalton Trans.* p. 947 (1985).
146. Collins, T. J., Coots, R. J., Furutani, T. T., Keech, J. T., Peake, G. T., and Santarsiero, B. D., *J. Am. Chem. Soc.* **108,** 5333 (1986).
147. Megehee, E. G., and Meyer, T. J., *Inorg. Chem.* **28,** 4084 (1989).
148. Kober, E. M., Caspar, J. V., Lumpkin, R., and Meyer, T. J., *J. Phys. Chem.* **90,** 3722 (1986).
149. Bruce, M. R. M., Megehee, E., Sullivan, B. P., Thorp, H., O'Toole, T. R., Downard, A., and Meyer, T. J., *Organometallics* **7,** 238 (1988).
150. Herberhold, M., and Hill, A. F., *J. Organomet. Chem.* **377,** 151 (1989).
151. Clark, G. R., Marsden, K., Rickard, C. E. F., Roper, W. R., and Wright, L. J., *J. Organomet Chem.* **338,** 393 (1988).
152. Herberhold, M., Hill, A. F., McAuley, N., and Roper, W. R., *J. Organomet. Chem.* **310,** 95 (1986).
153. Herberhold, M., and Hill, A. F., *J. Organomet. Chem.* **315,** 105 (1986).
154. Zhang, N., Mann, C. M., and Shapley, P. A., *J. Am. Chem. Soc.* **110,** 6591 (1988).
155. Shapley, P. A., and Own, Z. Y., *J. Organomet. Chem.* **335,** 269 (1987).
156. Zhang, N., Wilson, S. R., and Shapley, P. A., *Organometallics* **7,** 1126 (1988).
157. Zhang, N., and Shapley, P. A., *Inorg. Chem.* **27,** 976 (1988).
158. Own, Z. Y. B., Ph.D. Thesis, University of Illinois, Chicago (1986).
159. Marshman, R. W., and Shapley, P. A., *J. Am. Chem. Soc.* **112,** 8369 (1990).
160. Arnold, J., Wilkinson, G., Hussain, B., and Hursthouse, M. B., *Organometallics* **8,** 1362 (1989).
161. Stavropolous, P., Savage, P. D., Tooze, R. P., Wilkinson, G., Hussain, B., Motevalli, M., and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* p. 557 (1987).

162. Arnold, J., Wilkinson, G., Hussain, B., and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* p. 2149 (1989).
163. Herberhold, M., Hill, A. F., Clark, G. R., Rickard, C. E. F., Roper, W. R., and Wright, A. H., *Organometallics* **8,** 2483 (1989).
164. Herberhold, M., and Hill, A. F., *J. Organomet. Chem.* **395,** 315 (1990).
165. Harper, T. G. P., Shinomoto, R. S., Deming, M. A., and Flood, T. C., *J. Am. Chem. Soc.* **110,** 7915 (1988).
166. Clark, G. R., Greene, T. R., and Roper, W. R., *Aust. J. Chem.* **39,** 1315 (1986).
167. Cordone, R., Harman, W. D., and Taube, H., *J. Am. Chem. Soc.* **111,** 2896 (1989).
168. Harman, W. D., Dobson, J. C., and Taube, H., *J. Am. Chem. Soc.* **111,** 3061 (1989).
169. Harman, W. D., Schaefer, W. P., and Taube, H., *J. Am. Chem. Soc.* **112,** 2682 (1990).
170. Collman, J. P., Brothers, P. J., McElwee-White, L., and Rose, E., *J. Am. Chem. Soc.* **107,** 6110 (1985).
171. Harman, W. D., Wishart, J. F., and Taube, H., *Inorg. Chem.* **28,** 2411 (1989).
172. Harman, W. D., and Taube, H., *J. Am. Chem. Soc.* **110,** 7555 (1988).
173. Harman, W. D., and Taube, H., *J. Am. Chem. Soc.* **109,** 1883 (1987).
174. Hasegawa, T., Sekine, M., Schaefer, W. P., and Taube, H., *Inorg. Chem.* **30,** 449 (1991).
174a. Taube, H., and Sekine, M., unpublished results.
175. Harman, W. D., and Taube, H., *J. Am. Chem. Soc.* **110,** 5403 (1988).
176. Sekine, M., Harman, W. D., and Taube, H., *Inorg. Chem.* **27,** 3604 (1988).
177. Harman, W. D., Sekine, M., and Taube, H., *J. Am. Chem. Soc.* **110,** 2439 (1988).
178. Harman, W. D., Hipple, W. G., and Kopach, M. E., in preparation.
179. Cordone, R., Harman, W. D., and Taube, H., *J. Am. Chem. Soc.* **111,** 5969 (1989).
180. Harman, W. D., Hasegawa, T., and Taube, H., *Inorg. Chem.* **30,** 453 (1991).
181. Harman, W. D., Fairlie, D. P., and Taube, H., *J. Am. Chem. Soc.* **108,** 8223 (1986).
181a. Esteuruelas, M. A., Valero, C., Oro, L. A., Meyer, U., and Werner, H., *Inorg. Chem.* **30,** 1159 (1991).
182. Powell, D. W., Ph.D. Thesis, University of Sydney (1990).
183. Lay, P. A., and Powell, D. W., *in* "Proceedings of the Seventh Australian Electrochemistry Conference (Electrochemistry: Current and Potential Applications)" (T. Tran, and M. Skyllas-Kazacos, eds.), pp. 237–240. Royal Australian Chemical Institute, Electrochemical Division, Sydney, 1988.
184. Powell, D. W., and Lay, P. A., *Inorg. Chem.*, submitted for publication.
185. Gieren, A., Ruiz-Perez, C., Huebner, T., Herberhold, M., and Hill, A. F., *J. Chem. Soc., Dalton Trans.* p. 1693 (1988).
186. Hanack, M., and Vermehren, P., *Inorg. Chem.* **29,** 134 (1990).
187. Amendola, P., Antoniutti, S., Albertin, G., and Bordignon, E., *Inorg. Chem.* **29,** 318 (1990).
188. Albertin, G., Antoniutti, S., and Bordignon, E., *J. Chem. Soc., Dalton Trans.* p. 2353 (1989).
189. Barratt, D. S., Glidewell, C., and Cole-Hamilton, D. J., *J. Chem. Soc., Dalton Trans.* p. 1079 (1988).
190. Clark, G. R., Rickard, C. E. F., Roper, W. R., Salter, D. M., and Wright, L. J., *Pure Appl. Chem.* **62,** 1039 (1990).
191. Holmes-Smith, R. D., Stobart, S. R., Vefghi, R., Zaworotko, M. J., Jochem, K., and Cameron, T. S., *J. Chem. Soc., Dalton Trans.* p. 969 (1987).
192. Hu, X., *Gaodeng Xuexiao Huaxue Xuebao* **11,** 1 (1990); *Chem. Abstr.* **113,** 90295d (1990).
192a. Esteruelas, M. A., Oro, L. A., and Valero, C., *Organometallics* **10,** 462 (1991).

193. Finnie, K., and Krausz, E. R., unpublished results (1989).
194. Harman, W. D., and Taube, H., *Inorg. Chem.* **27,** 3261 (1988).
195. Lay, P. A., and Taube, H., unpublished results.
196. Johnson, A., and Taube, H., *J. Indian Chem. Soc.* **66,** 503 (1989).
197. Buhr, J. D., Ph.D. Thesis, Stanford University, Stanford, California (1978).
198. Preetz, W., and Buetje, K., *Z. Anorg. Allg. Chem.* **557,** 112 (1988).
199. Gulens, J., and Page, J. A., *J. Electroanal. Chem. Interfacial Electrochem.* **67,** 215 (1976).
200. Lay, P. A., Gulyas, P., Harman, W. D., and Taube, H., in preparation.
201. Harman, W. D., and Taube, H., *J. Am. Chem. Soc.* **112,** 2261 (1990).
202. Dwyer, F. P., and Hogarth, J. W., *J. Am. Chem. Soc.* **75,** 1008 (1953).
203. Dwyer, F. P., and Hogarth, J. W., *J. Am. Chem. Soc.* **77,** 6152 (1955).
204. Lay, P. A., Sargeson, A. M., Skelton, B. W., and White, A. H., *J. Am. Chem. Soc.* **104,** 6161 (1984).
205. Lay, P. A., McLaughlin, G. M., and Sargeson, A. M., *Aust. J. Chem.* **40,** 1267 (1987); Lay, P. A., Ph.D. Thesis, Australian National University, Canberra (1981).
206. Patel, A., Ludi, A., Bürgi, H.-B., Raselli, A., and Bigler, P., *Inorg. Chem.* (submitted for publication).
207. Malin, J. M., Schlemper, E. O., and Murmann, R. K., *Inorg. Chem.* **16,** 615 (1977).
208. Griffith, W. P., McManus, N. T., and White, A. D., *J. Chem. Soc., Dalton Trans.* p. 1035 (1986).
209. Harbron, S. K., and Levason, W., *J. Chem. Soc., Dalton Trans.* p. 633 (1987).
210. Che, C.-M., and Cheng, W. K., *J. Am. Chem. Soc.* **108,** 4644 (1986).
211. Wong, K.-Y., and Anson, F. C., *J. Electronanal. Chem. Interfacial Electrochem.* **237,** 69 (1987).
211a. Yam, V. W.-W., and Che, C.-M., *J. Chem. Soc., Dalton Trans.* 3741 (1990).
212. Che, C. M., and Cheng, W.-K., *J. Chem. Soc., Chem. Commun.* p. 1519 (1986).
213. Che, C. M., Cheng, W.-K., Lai, T.-F., Poon, C.-K., and Mak, T. C. W., *Inorg. Chem.* **26,** 1678 (1987).
214. Che, C. M., Leung, W. H., and Chung, W. C., *Inorg. Chem.* **29,** 1841 (1990).
215. Nasri, H., and Scheidt, W. R., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C46,** 1096 (1990).
216. Buchler, J. W., and Smith, P. D., *Chem. Ber.* **109,** 1465 (1976).
217. Che, C. M., Lai, T. F., Tong, W. F., and Marsh, R. E., unpublished results.
218. Che, C. M., Lai, T. F., Chung, W. C., Schaefer, W. P., and Gray, H. B., *Inorg. Chem.* **26,** 3907 (1987).
219. Groves, J. T., and Quinn, R., U.S. Pat. 4,822,899 A18 (1989); *Chem. Abstr.* **112,** 7351e (1990).
220. Collman, J. P., McDevitt, J. T., Yee, G. T., Leidner, C. R., McCullough, L. G., Little, W. A., and Torrance, J. B., *Proc. Natl. Acad. Sci. U.S.A.* **83,** 4581 (1986).
221. Bolt, N. J., Goodwill, K. E., and Bocian, D. F., *Inorg. Chem.* **27,** 1188 (1988).
222. Meyer, T. J., *Pure Appl. Chem.* **58,** 1193 (1986); **62,** 1003 (1990).
223. Yersin, H., Braun, D., Hensler, G., and Gallhuber, E., *NATO ASI Ser., Ser. C* **288,** 195 (1989).
224. Constable, E. C., *Adv. Inorg. Chem.* **34,** 1 (1989).
225. Constable, E. C., *Adv. Inorg. Chem. Radiochem.* **30,** 69 (1986).
226. Ware, D. W., and Taube, H., *Inorg. Chem.* (in press).
227. Garcia, M. P., López, A. M., Esteruelas, M. A., Lahoz, F. J., and Oro, L. A., *J. Chem. Soc., Dalton Trans.* p. 3465 (1990).
228. Neyhart, G. A., and Meyer, T. J., *Inorg. Chem.* **25,** 4807 (1986); Loeb, L. B., Neyhart,

G. A., Worl, L. A., Danielson, E., Sullivan, B. P., and Meyer, T. J., *J. Phys. Chem.* **93,** 717 (1989).

229. Collin, J. P., Guillerez, S., and Sauvage, J. P., *J. Chem. Soc., Chem. Commun.* p. 776 (1989).

230. Collin, J.-P., Guillerez, S., and Sauvage, J.-P., *Inorg. Chem.* **29,** 5009 (1990).

231. Della Ciana, L., Dressick, W. J., Sandrini, D., Maestri, M., and Ciano, M., *Inorg. Chem.* **29,** 2792 (1990).

232. Kalyanasundaram, K., and Nazeeruddin, M. K., *J. Chem. Soc., Dalton Trans.* p. 1657 (1990).

233. Kalyanasundaram, K., and Nazeeruddin, M. K., *Inorg. Chim. Acta* **171,** 213 (1990).

234. Cipriano, R. A., Levason, W., Mould, R. A. S., Pletcher, D., and Webster, M., *J. Chem. Soc., Dalton Trans.* p. 2609 (1990); Blake, A. J., Heath, G. A., Smith, G., Yellowlees, L. J., and Sharp, D. W. A., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44,** 1836 (1988).

235. El-Hendawy, P. A. M., Griffith, W. P., Tahu, F. I., and Moussa, M. N., *J. Chem. Soc., Dalton Trans.* p. 901 (1989).

236. Herrmann, W. A., Thiel, W. R., and Kuchler, J. G., *Chem. Ber.* **123,** 1945 (1990).

237. Figge, R., Patt-Siebel, V., Conradi, E., Mueller, U., and Dehnicke, K., *Z. Anorg. Allg. Chem.* **558,** 107 (1988).

238. Kanishcheva, A. S., Mikhailov, Yu. N., Sinitsyn, M. N., Svetlov, A. A., Kokunov, Yu. V., and Buslaev, Yu. A., *Dokl. Akad. Nauk SSSR* **308,** 381 (1989); Sinitsyn, M. N., Svetlov, A. A., Kokunov, Yu. V., Fal'kengof, A. T., Larin, G. M., Minin, V. V., and Buslaev, Yu. A., *ibid.* **293,** 1144 (1987).

239. Bobkova, E. Yu., Svetlov, A. A., Rogalevich, N. L., Novitskii, G. G., and Borkovskii, N. B., *Zh. Neorg. Khim.* **35,** 981 (1990); *Russ. J. Inorg. Chem. (Engl. Transl.)* **35,** 549 (1990); Salomov, A. S., Mikhailov, Yu. N., Kanishcheva, A. S., Svetlov, A. A., Sinitsyn, N. M., Porai-Koshits, M. A., and Parpiev, N. A., *Zh. Neorg. Khim.* **33,** 2608 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)* **33,** 1496 (1988).

240. Pandey, K. K., Sharma, R. B., and Pandit, P. K., *Inorg. Chim. Acta* **169,** 207 (1990).

241. Pandey, K. K., Ahuja, S. R., and Goyal, M., *Indian J. Chem., Sect. A* **24A,** 1059 (1985).

242. Bottomley, F., Hahn, E., Pickardt, J., Schumann, H., Mukaida, M., and Kakihana, H., *J. Chem. Soc., Dalton Trans.* p. 2427 (1985).

243. Bobkova, E. Yu., Svetlov, A. A., Rogalevich, N. L., Novitskii, G. G., Borkovskii, N. B., and Sinitsyn, M. N., *Zh. Neorg. Khim.* **35,** 979 (1990); *Russ. J. Inorg. Chem. (Engl. Transl.)* **35,** 546 (1990).

244. Svetlov, A. A., Sinitsyn, N. M., and Kravchenko, V. V., *Zh. Neorg. Khim.* **35,** 336 (1990); *Russ. J. Inorg. Chem. (Engl. Transl.)* **35,** 189 (1990).

245. Sinitsyn, M. N., Svetlov, A. A., Kanishcheva, A. S., Mikhailov, Yu. N., Sadikov, G. G., Kokunov, Yu. V., and Buslaev, Yu. A., *Zh. Neorg. Khim.* **34,** 2795 (1989); *Russ. J. Inorg. Chem. (Engl. Transl)* **34,** 1599 (1989).

246. Pandey, K. K., Nehete, D. T., Tewari, S. K., Rewari, S., and Bharduraj, R., *Polyhedron* **7,** 709 (1988).

247. Nikol'skii, A. B., Popov, A. M., Simonenko, N. G., Khoninzhii, V. V., and Egorova, M. B., *Zh. Obshch. Khim.* **58,** 930 (1988); *J. Gen. Chem. USSR (Engl. Transl.)* **58,** 825 (1988).

248. Herberhold, M., and Hill, A. F., *J. Organomet. Chem.* **363,** 371 (1989).

248a. Mingos, D. M. P., Sherman, D. J., and Bott, S. G., *Transition Met. Chem. (London)* **12,** 471 (1987).

249. Stershic, M. T., Keefer, L. K., Sullivan, B. P., and Meyer, T. J., *J. Am. Chem. Soc.* **110,** 6884 (1988).

250. Vorob'eva, N. E., Pavlov, P. T., and Zhivopistsev, V. P., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* **32,** 33 (1989); *Chem. Abstr.* **112,** 234900b (1990).
251. Gowda, H. S., Ahmed, S. M., and Raj, J. B., *Indian J. Chem., Sect. A* **29A,** 95 (1990).
252. Vorob'eva, N. E., Zhivopistsev, V. P., and Pavlov, P. T., *Zh. Anal. Khim.* **44,** 467 (1989); *Chem. Abstr.* **112,** 29922u (1990).
253. Vorob'eva, N. E., Zhivopistsev, V. P., Zhdanova, T. N., Pavlov, P. T., Veretennikova, O. V., and Berdinskii, I. S., *Otkrytiy, Izobret., Prom. Obraztsy, Tovarnye Znaki* p. 159 (1987); *Chem. Abstr.* **108,** 160580r (1988).
254. Cruz-Garritz, D., Gelover, S., Torrens, H., Leal, J., and Richards, R. L., *J. Chem. Soc., Dalton Trans.* p. 2393 (1988).
255. Armstrong, J. E., and Walton, R. A., *Inorg. Chem.* **22,** 1545 (1983).
256. Lay, P. A., and Sargeson, A. M., unpublished results.
257. Fenske, D., Baum, G., Swidersky, H. W., and Dehnicke, K., *Z. Naturforsch., B: Chem. Sci.* **45,** 1210 (1990).
258. Sacksteder, L. A., Demas, J. N., and DeGraff, B. A., *Inorg. Chem.* **28,** 1787 (1989).
259. Perkins, T. A., Pourreau, D. B., Netzel, T. L., and Schanze, K. S., *J. Phys. Chem.* **93,** 4511 (1989).
260. Popov, A. M., Egorova, M. B., Khorunzhii, V. V., and Drobachenko, A. V., *Zh. Neorg. Khim.* **33,** 2319 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)* **33,** 1324 (1988).
261. Bohle, D. S., Clark, G. R., Rickard, C. E. F., Roper, W. R., and Taylor, M. J., *J. Organomet. Chem.* **348,** 385 (1988).
262. Kravchenko, E. A., Burstev, M. Yu., Morgunov, V. G., Sinitsyn, M. N., Kokunov, Yu. V., and Buslaev, Y. A., *Koord. Khim.* **13,** 1520 (1987).
263. Kravchenko, E. A., Burstev, M. Yu., Sinitsyn, M. N., Svetlov, A. A., Kokunov, Yu. V., and Buslaev, Yu. A., *Dokl. Akad. Nauk SSSR* **294,** 130 (1987).
264. Droege, M. W., Harman, W. D., and Taube, H., *Inorg. Chem.* **26,** 1309 (1987).
265. Danopoulos, A. A., and Wilkinson, G., *Polyhedron* **9,** 1009 (1990).
265a. Danopoulos, A. A., Wilkinson, G., Hussain-Bates, B., and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* 269 (1991).
266. Che, C.-M., Lam, M. H.-W., and Mak, T. C. W., *J. Chem. Soc., Chem. Commun.* p. 1529 (1989).
267. Nath, N., and Singh, L. P., *Rev. Roum. Chim.* **31,** 489 (1986).
268. Nefedov, V. I., Trishkina, E. M., Sinitsyn, M. N., Svetlov, A. A., Kokunov, Yu. V., and Buslaev, Yu. A., *Dokl. Akad. Nauk SSSR* **291,** 614 (1986).
269. Che, C. M., Lam, H. W., Tong, W. F., Lai, T. F., and Lau, T. C., *J. Chem. Soc., Chem. Commun.* p. 1883 (1989).
270. Che, C. M., Lau, T. C., Lam, H. W., and Poon, C. K., *J. Chem. Soc., Chem. Commun.* p. 114 (1989).
271. Ta, N. C., *Synth. React. Inorg. Met.-Org. Chem.* **16,** 1357 (1986).
272. Sartori, C., and Preetz, W., *Z. Anorg. Allg. Chem.* **565,** 23 (1988).
273. Cockman, R. W., and Peacock, R. D., *J. Flourine Chem.* **30,** 469 (1986).
274. Buetje, K., and Preetz, W., *Z. Naturforsch., B: Chem. Sci.* **43,** 371 (1988).
275. Buetje, K., and Preetz, W., *Z. Naturforsch., B: Chem. Sci.* **43,** 382 (1988).
276. Bhattacharyya, R., and Saha, A. M., *Transition Met. Chem. (London)* **12,** 85 (1987).
277. Bütje, K., and Preetz, W., *Z. Naturforsch., B: Chem. Sci.* **43,** 574 (1988).
278. Kukushkin, V. Yu., Egorova, M. B., and Popov, A. M., *Koord. Khim.* **13,** 1507 (1987).
279. Sinitsyn, N. M., Kokunova, V. N., and Svetlov, A. A., *Zh. Neorg. Khim.* **33,** 2340 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)* **33,** 1336 (1988).
280. Che, C.-M., Cheng, W.-K., and Mak, T. C. W., *Inorg. Chem.* **27,** 250 (1988).
281. Che, C.-M., Cheng, W.-K., and Mak, T. C. W., *Inorg. Chem.* **25,** 703 (1986).
281a. Lynch, W. E., Lintvedt, R. L., and Shui, X. O., *Inorg. Chem.* **30,** 1014 (1991).

282. Lahiri, G. K., Bhattacharya, S., Ghosh, B. K., and Chakravorty, A., *Inorg. Chem.* **26,** 4324 (1987).
283. Che, C.-M., Cheng, W.-K., and Mak, T. C. W., *J. Chem. Soc., Chem. Commun.* p. 200 (1986).
284. Anson, F. C., Collins, T. J., Gipson, S. L., Keech, J. T., and Krafft, T. E., *Inorg. Chem.* **26,** 1157 (1987).
285. Collins, T. J., and Keech, J. T., *J. Am. Chem. Soc.* **110,** 1162 (1988).
286. Collins, T. J., Lai, T., and Peake, G. T., *Inorg. Chem.* **26,** 1674 (1987).
287. Anson, F. C., Collins, T. J., Coots, R. J., Gipson, S. L., Krafft, T. E., Santarsiero, B. D., and Spies, G. H., *Inorg. Chem.* **26,** 1161 (1987).
288. Anson, F. C., Collins, T. J., Gipson, S. L., Keech, J. T., Krafft, T. E., and Peake, G. T., *J. Am. Chem. Soc.* **108,** 6593 (1986).
289. Anson, F. C., Christie, J. A., Collins, T. J., Coots, R. J., Furutani, T. T., Gipson, S. L., Keech, J. T., Krafft, T. E., Santarsiero, B. D., and Spies, G. H., *J. Am. Chem. Soc.* **106,** 4460 (1984).
290. Christie, J. A., Collins, T. J., Krafft, T. E., Santarsiero, B. D., and Spies, G. H., *J. Chem. Soc., Chem. Commun.* p. 198 (1984).
291. Muller, J. G., and Takeuchi, K. J., *Inorg. Chem.* **26,** 3634 (1987).
292. Olby, B. G., Robinson, S. D., Hursthouse, M. B., and Short, R. C., *Polyhedron* **7,** 1781 (1988).
293. Colson, S. F., and Robinson, S. D., *Polyhedron* **9,** 1737 (1990); *Inorg. Chim. Acta* **149,** 13 (1988).
294. Mahapatra, A. K., Ghosh, B. K., Goswami, S., and Chakravorty, A., *J. Indian Chem. Soc.* **63,** 101 (1986).
295. Mukhopadyay, A., and Ray, S., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C43,** 14 (1987).
296. Ghosh, B. K., Mukherjee, R., and Chakravorty, A., *Inorg. Chem.* **26,** 1946 (1987).
297. Desrosiers, P. J., Shinomoto, R. S., Deming, M. A., and Flood, T. C., *Organometallics* **8,** 2861 (1989).
298. Gotzig, J., Werner, R., and Werner, H., *J. Organomet. Chem.* **290,** 99 (1985).
299. Cappellani, E. P., Maltby, P. A., Morris, R. H., Schweitzer, C. T., and Steele, M. R., *Inorg. Chem.* **28,** 4437 (1989).
300. Mezzetti, A., Del Zotto, A., and Rigo, P., *J. Chem. Soc., Dalton Trans.* p. 2515 (1990).
301. Bautista, M., Earl, K. A., Maltby, P. A., and Morris, R. H., *J. Am. Chem. Soc.* **110,** 4056 (1988).
302. Fanwick, P. E., Fraser, I. F., Tetrick, S. M., and Walton, R. A., *Inorg. Chem.* **26,** 3786 (1987).
302a. Cipriano, R. A., Levason, W., Mould, R. A. S., Pletcher, D., and Webster, M., *J. Chem. Soc., Dalton Trans.* p. 339 (1990).
303. Cotton, F. A., Diebold, M. P., and Matusz, M., *Polyhedron* **6,** 1131 (1987).
304. Robinson, P. D., Hinckley, C. C., and Ikuo, A., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44,** 1491 (1988).
305. Bressan, M., and Morvillo, A. *Stud. Org. Chem.* **33,** 277 (1988).
306. Desrosiers, P. J., Shinomoto, R. S., and Flood, T. C., *J. Am. Chem. Soc.* **108,** 7964 (1986).
307. Bruno, J., Huffman, J. C., Green, M. A., Zubkowski, J. D., Hatfield, W. E., and Caulton, K.G., *Organometallics* **9,** 2556 (1990).
308. Siedle, A. R., Newmark, R. A., and Pignolet, L. H., *Inorg. Chem.* **25,** 3412 (1986).
309. Howard, J. A. K., Johnson, O., Koetzle, T. F., and Spencer, J. L., *Inorg. Chem.* **26,** 2930 (1987).

310. Shinomoto, R. S., Desrosiers, P. J., Harper, T. G. P., and Flood, T. C., *J. Am. Chem. Soc.* **112,** 704 (1990).
310a. Desrosiers, P. J., Shinomoto, R. S., and Flood, T.C., *J. Am. Chem. Soc.* **108,** 1346 (1986).
311. Hinckley, C. C., Matusz, M., and Robinson, P. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44,** 371 (1988).
312. Otruba, J. P., Neyhart, G. A., Dressick, W. J., Marshall, J. L., Sullivan, B. P., Watkins, P. A., and Meyer, T. J., *J. Photochem.* **35,** 133 (1986).
313. Hinckley, C. C., Matusz, M., and Robinson, P. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44,** 1829 (1988).
314. Lay, P. A., Ludi, A., and Taube, H., work in progress.
315. Griffith, W. P., *J. Chem. Soc. A* p. 211 (1969).
316. Scagliarini, G., and Masetti-Zannini, A., *Gazz. Chim. Ital.* **53,** 504 (1923).
317. Svetlov, A. A., Sinitsyn, M. M., and Kravchenko, V. V., *Zh. Neorg. Khim.* **34,** 953 (1989); *Russ J. Inorg. Chem. (Engl. Transl.)* **34,** 535 (1989).
318. Vining, W. J., and Meyer, T. J., *Inorg. Chem.* **25,** 2023 (1986).
319. Cotton, F. A., Dunbar, K. R., and Matusz, M., *Inorg. Chem* **25,** 1589 (1986).
320. Bardin, M. B., Goncharenko, V. P., and Ketrush, P. M., *Zh. Anal. Khim.* **42,** 2013 (1987).
321. Lay, P. A., and Sasse, W. H. F., *Inorg. Chem.* **24,** 4707 (1985).
322. Cotton, F. A., Dunbar, K. R., and Matusz, M., *Inorg. Chem.* **25,** 1585 (1986).
323. Moskvin, L. N., and Shmatko, A. G., *Zh. Neorg. Khim.* **33,** 1229 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)* **33,** 695 (1988).
324. Singh, A. K., Tewari, A., and Sisodia, A. K., *Natl. Acad. Sci. Lett. (India)* **8,** 209 (1985).
325. Pipes, D. W., and Meyer, T. J., *Inorg. Chem.* **25,** 4042 (1986).
326. Filina, G. G., Shcheglov, O. F., and Chebotarev, O. V., *Zh. Vses. Khim. O-va.* **31**(5), 119 (1986); *Mendeleev Chem. J. (Engl. Transl.)* **31**(4), 67 (1986).
327. Nakajima, M., Tomioka, K., and Koga, K., *Yuki Gosei Kagaku Kyokaishi* **47,** 878 (1989); *Chem Abstr.* **112,** 138295n (1990).
328. Lohray, B. B., Kalantar, T. H., Kim, B. M., Park, C. Y., Shibata, T., Wai, J. S. M., and Sharpless, K. B., *Tetrahedrom Lett.* **30,** 2041 (1989).
329. Griffith, W. P., *Platinum Met. Rev.* **33,** 181 (1989).
330. Nakajima, M., Tomioka, K, and Koga, K., *Kagaku (Kyoto)* **42,** 422 (1987); *Chem. Abstr.* **108,** 55141a (1988).
331. Kobs, S. F., Ph.D. Thesis, Ohio State University, Columbus (1986).
332. Singh, H. S., *in* "Organic Synthesis by Oxidation with Metal Compounds" (W. J. Mijs and C. R. H. I. de Jonge, eds.), p. 633. Plenum Press, New York, 1986.
333. Ruegger, U. P., and Tassera, J., *Swiss Chem.* **8,** 43 (1986).
334. Svendsen, J. S., Marko, I., Jacobsen, E. N., Rao, C. P., Bott, S., and Sharpless, K. B., *J. Org. Chem.* **54,** 2263 (1989).
335. Kobs, S. F., and Behrman, E. J., *Inorg. Chim. Acta* **138,** 113 (1987).
336. Kobs, S. F., and Behrman, E. J., *Inorg. Chim. Acta* **128,** 21 (1987).
337. Peschke, T., Wollweber, L., Gabert, A., Augsten, K., and Stracke, R., *Histochemistry* **93,** 443 (1990).
338. Vandeputte, D. F., Jacob, W. A., and Van Grieken, R. E., *J. Histochem. Cytochem.* **38,** 331 (1990).
339. Anderson, L. J., Boyles, J. K., and Hussain, M. M., *J. Lipid Res.* **30,** 1819 (1989).
340. Nandi, K. N., Beal, J. A., and Knight, D. S., *J. Neurosci. Methods* **25,** 159 (1988).
341. Lascano, E. F., and Berria, M. I., *J. Histochem. Cytochem.* **36,** 697 (1988).

342. Hearn, S. A., *J. Histochem. Cytochem.* **35,** 795 (1987).
343. Caceci, T., and Frankum, K. E., *J. Microsc. (Oxford)* **147,** 109 (1987).
344. Van Dort, J. B., Zeelen, J. P., and De Bruijn, W. C., *Histochemistry* **87,** 71 (1987).
345. Krause, C. R., Ichida, J. M., and Dochinger, L. S., *Scanning Electron Microsc.* p. 975 (1986).
346. Tetzlaff, W., and Hofbauer, A., *Histochemistry* **85,** 295 (1986).
347. Derenzini, M., Farabegoli, F., and Marinozzi, V., *J. Histochem. Cytochem* **34,** 1161 (1986).
348. Hosoda, S., and Kojima, K., *Polym. Commun.* **30,** 83 (1989).
349. Kakugo, M., Sadatoshi, H., Yokoyama, M., and Kojima, K., *Macromolecules* **22,** 547 (1989).
350. Friedrich, J., Pohl, M., Elsner, T., and Altrichter, B., *Acta Polym.* **39,** 594 (1988).
351. Palecek, E., Boublikova, P., and Nejedley, K., *Biophys. Chem.* **34,** 63 (1989).
352. Boublikova, P., *Stud. Biophys.* **131,** 185 (1989).
353. Campbell, R. D., and Cotton, R. G. H., Eur. Pat. Appl. EP 329311 A2 23 (1989); *Chem. Abstr.* **112,** 213550x (1990).
354. Hara, T., and Tsukagoshi, K., *Bull. Chem. Soc. Jpn.* **60,** 2031 (1987).
355. Bakhvalova, I. P., Volkova, G. V., and Ivanov, V. M., *Zh. Anal. Khim.* **45,** 496 (1990); *Chem. Abstr.* **113,** 34049q (1990).
356. Csanyi, L. J., Galbacs, Z. M., Nagy, L., and Horváth, I., *Acta Chim. Hung.* **123,** 123 (1986).
357. Csanyi, L. J., Galbacs, Z. M., Nagy, L., and Marek, N., *Transition Met. Chem. (Weinheim, Ger.)* **11,** 319 (1986).
358. Singh, V., *J. Inst. Chem. (India)* **59,** 248 (1987).
358a. Sattar, S., and Kustin, K. *Inorg. Chem.* **30,** 1668 (1991).
359. Sarala, G., Rao, P. J., Sethuram, B., and Rao, T. N., *Transition Met. Chem. (London)* **13,** 113 (1988).
360. Khomutova, E. G., and Khvorostukhina, N. A., *Zh. Anal. Khim.* **41,** 1647 (1986).
361. Jørgensen, K. A., and Hoffmann, R., *J. Am. Chem. Soc.* **108,** 1867 (1986).
362. Shul'man, R. S., Marochkina, L. Ya., Torgov, V. G., Drozdova, M. K., Glukhikh, L. K., and Yatsenko, V. T., *Zh. Neorg. Khim.* **33,** 166 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)* **33,** 91 (1988).
363. Veerasomaiah, P., Reddy, K., Sethuram, B., and Rao, T. N., *J. Indian Chem. Soc.* **66,** 755 (1989).
364. Somaiah, P. V., Reddy, K. B., Sethuram, B., and Rao, T. N., *Indian J. Chem., Sect. A* **27A,** 876 (1988).
365. Singh, A. K., Saxena, S., Saxena, M., Gupta, R., and Mishra, R. K., *Indian J. Chem., Sect. A* **27A** 438 (1988).
366. Singh, B., Singh, A. K., Singh, M. B., and Singh, A. P., *Tetrahedron* **42,** 715 (1986).
367. Singh, B., Singh, A. K., and Singh, A. P., *Natl. Acad. Sci. Lett. (India)* **8,** 111 (1985).
368. Singh, A. K., Sisodia, A. K., Saxena, S., and Saxena, M., *Indian J. Chem., Sect. A* **26A,** 600 (1987).
369. Singh, M. B., Singh, A. P., Singh, A. K., and Singh, B., *Natl. Acad. Sci. Lett. (India)* **9,** 175 (1986).
370. Singh, A. K., Parmar, A., and Sisodia, A. K., *Natl. Acad. Sci. Lett. (India)* **9,** 273 (1986).
371. Misra, R. K., Saxena, S., and Singh, A. K., *Viznana. Parishad Anusandhan. Patrika* **31,** 83 (1989); *Chem. Abstr.* **212,** 118038c (1990).
372. Rao, P. J. P., Sethuram, B., and Rao, T. N., *J. Indian Chem. Soc.* **67,** 101 (1990).
373. Sarala, G., Rao, P. J. P., Sethuram, B., and Rao, T. N., *Indian J. Chem., Sect. A* **26A,** 475 (1987).

374. Swarnalakshmi, N., Uma, V., Sethuram, B., and Rao, T. N., *Indian J. Chem., Sect. A* **26A,** 592 (1987).
375. Naidu, H. M. K., Yamuna, B., and Mahadevappa, D. S., *Indian J. Chem., Sect. A* **26A,** 114 (1987).
376. Hingorani, H., Goyal, H. C., Chandra, G., and Srivastava, S. N., *Rev. Roum. Chim.* **30,** 725 (1985).
377. Mythily, C. K., Rangappa, K. S., and Mahadevappa, D. S., *Indian J. Chem., Sect. A* **29A,** 676 (1990).
377a. Hussain, J., Mishra, S. K., and Sharma, P. D., *J. Chem. Soc., Dalton Trans.* p. 89 (1991).
378. Mangalam, G., and Meenakshisundaram, S., *J. Indian Chem. Soc.* **66,** 368 (1989).
379. Rao, K. L. V., Rao, M. P., Sethuram, B., and Rao, T. N., *Transition Met. Chem. (London)* **14,** 165 (1989).
380. Reddy, K. B., Sethuram, B., and Rao, T. N., *Z. Phys. Chem. (Leipzig)* **270,** 732 (1989).
381. Volkova, T. Ya., Rozovskii, G. I., and Sakharov, A. A., *Liet. TSR Mokslu Akad. Darb., Ser. B* p. 3 (1985); *Chem. Abstr.* **104,** 206679c (1986).
382. Khetawat, G. K., and Menghani, G.D., *J. Indian Chem. Soc.* **64,** 766 (1987).
383. Shukla, R. K., and Anandam, N., *Acta Cienc. Indica [Ser.] Chem.* **11,** 242 (1985).
384. Mishra, P., and Khandual, N. C., *Indian J. Chem., Sect. A* **25A,** 902 (1986).
385. Mishra, P., Mohapatra, R.C., and Khandual, N. C., *J. Indian Chem. Soc.* **63,** 291 (1986).
386. Radhakrishnamurti, P. S., and Tripathy, K. S., *Indian J. Chem., Sect. A* **25A,** 762 (1986).
387. Saroja, P., Rao, M. P., and Kandlikar, S., *Transition Met. Chem. (London)* **15,** 351 (1990).
388. Radhakrishnamurti, P. S., Panda, R. K., and Panigrahi, J. C., *Indian J. Chem., Sect. A* **26A,** 124 (1987).
389. Hamilton, J. G., Mackey, O. N., Rooney, J. J., and Gilheany, D. G., *J. Chem. Soc., Chem. Commun.* p. 1600 (1990).
390. Erdik, E., and Matteson, D. S., *J. Org. Chem.* **54,** 2742 (1989).
391. Wai, J. S. M., Marko, I., Svendsen, J. S., Finn, M. G., Jacobsen, E. N., and Sharpless, K. B., *J. Am. Chem. Soc.* **111,** 1123 (1989).
392. Wallis, J. M., and Kochi, J. K., *J. Am. Chem. Soc.* **110,** 8207 (1988).
393. Corey, E. J., Jardine, P.D., Virgil, S., Yuen, P. W., and Connell, R. D., *J. Am. Chem. Soc.* **111,** 9243 (1989).
394. Jacobsen, E. N., Marko, I., France, M. B., Svendsen, J. S., and Sharpless, K. B., *J. Am. Chem. Soc.* **111,** 737 (1989).
395. Dijkstra, G. D. H., Kellogg, R. M., Wynberg, H., Svendsen, J. S., Marko, I., and Sharpless, K. B., *J. Am. Chem. Soc.* **111,** 8069 (1989).
396. Gupta, S., Ali, V., and Upadhyay, S. K., *Int. J. Chem. Kinet.* **21,** 315 (1989).
397. Gupta, S., Ali, V., and Upadhyay, S. K. *Transition Met. Chem.* (London) **13,** 573 (1988).
398. Dengel, A. C., El-Hendawy, A. M., Griffith, W. P., and White, A. D., *Transition Met. Chem. (London)* **14,** 230 (1989).
399. Shaplygin, I. S., and Lazarev, V. B., *Zh. Neorg. Khim.* **31,** 3181 (1986); *Russ. J. Inorg. Chem. (Engl. Transl.)* **31,** 1827 (1986).
400. Hagen, K., Hobson, R. J., Holwill, C. J., and Rice, D. A., *Inorg. Chem.* **25,** 3659 (1986).
401. Robinson, P. D., Hinckley, C. C., and Kibala, P. A., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44,** 1365 (1988).

402. Hinckley, C. C., Kibala, P. A., and Robinson, P. D., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C43,** 842 (1987).
403. Harbron, S. K., Jewiss, H. C., Levason, W., and Webster, M., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C43,** 37 (1987).
404. Oishi, T., and Hirama, M., *J. Org. Chem.* **54,** 5834 (1989).
405. Arnold, J., Wilkinson, G., Hussain, B., and Hursthouse, M. B., *Polyhedron* **8,** 597 (1989).
406. Hinckley, C. C., Ali, I. A., and Robinson, P. D., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C46,** 697 (1990).
407. El-Hendawy, A. M., *Polyhedron* **9,** 2309 (1990).
408. Hinckley, C. C., and Kibala, P. A., *Polyhedron* **5,** 1119 (1986).
409. Bhattacharya, S., Boone, S. R., Fox, G. A., and Pierpont, C. G., *J. Am. Chem. Soc.* **112,** 1088 (1990).
410. Griffith, W. P., Pumphrey, C. A., and Skapski, A. C., *Polyhedron* **6,** 891 (1987).
411. Haga, M., Isobe, K., Boone, S. R., and Pierpont, C. G., *Inorg. Chem.* **29,** 3795 (1990).
412. El-Hendawy, A. M., Griffith, W. P., and Pumphrey, C. A., *J. Chem. Soc., Dalton Trans.* p. 1817 (1988).
413. Greaves, S. J., and Griffith, W. P., *Polyhedron* **7,** 1973 (1988).
414. El-Hendawy, A. M., Griffith, W. P., O'Mahoney, C. A., and Williams, D. J., *Polyhedron* **8,** 519 (1989).
414a. El-Hendawy, A. M. *Inorg. Chim. Acta* **179,** 223 (1991).
415. Dobson, J. C., and Meyer, T. J., *Inorg. Chem.* **28,** 2013 (1989).
416. Colson, S. F., and Robinson, S. D., *Polyhedron* **8,** 2179 (1989).
417. Queiros, M. A. M., and Robinson, S. D., *Inorg. Chem.* **17,** 310 (1978).
418. Deeming, A. J., Randle, N. P., Hursthouse, M. B., and Short, R. L., *J. Chem. Soc., Dalton Trans.* p. 2473 (1987).
419. Andriollo, A., Esteruelas, M., A., Meyer, U., Oro, L. A., Sanchez-Delgado, R. A., Sola, E., Valero, C., and Werner, H., *J. Am. Chem. Soc.* **111,** 7431 (1989).
420. Esteruelas, M. A., Sola, E., Oro, L. A., Meyer, U., and Werner, H., *Angew. Chem.* **100,** 1621 (1988); *Angew. Chem., Int. Ed. Engl.* **27,** 1563 (1988).
421. Hinckley, C. C., Ikuo, A., and Robinson, P. D., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44,** 1827 (1988).
422. Hinckley, C. C., Matusz, M., Kibala, P. A., and Robinson, P. D., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C43,** 1880 (1987).
423. Kubas, G. J., *Acc. Chem. Res.* **21,** 120 (1988).
424. Dobson, A., Moore, D. S., Robinson, S. D., Hursthouse, M. B., and New, L., *Polyhedron* **4,** 1119 (1985).
425. Packard, A. B., O'Brien, G. M., and Treves, S., *Nucl. Med. Biol.* **13,** 519 (1986).
426. Lay, P. A., Magnuson, R. H., Taube, H., Ferguson, J., and Krausz, E. R., *J. Am. Chem. Soc.* **107,** 2551 (1985).
427. Isied, S. S., *Prog. Inorg. Chem.* **32,** 443 (1984).
428. Dubicki, L., Ferguson, J., Krausz, E. R., Lay, P. A., Maeder, M., and Taube, H., *J. Phys. Chem.* **88,** 3940 (1984).
429. Vassilian, A., Wishart, J. F., van Hemelryck, B., Schwartz, H., and Isied, S. S., *J. Am. Chem. Soc.* **112,** 7278 (1990).
430. Harman, W. D., and Myers, W. H., *J. Am. Chem. Soc.* (in press).
431. Kopach, M. E., Gonzalez, J., and Harman, W. D. Submitted.
432. Harman, W. D., and Taube, H., *J. Am. Chem. Soc.***110,** 7906 (1988).
433. Harding, P. A., Preece, M., Robinson, S. D., and Henrick, K., *Inorg. Chim Acta* **118,** L31 (1986).
434. Herberhold, M., and Hill, A. F., *J. Organomet. Chem.* **353,** 243 (1988).

435. Graziosi, G., Preti, C., Tosi, G., and Zannini, P., *Aust. J. Chem.* **38,** 1675 (1985).
436. Svetlov, A. A., Sinitsyn, N. M., and Kravchenko, V. V., *Zh. Neorg. Khim.* **33,** 1220 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)* **33,** 690 (1988).
437. Ali, R., Higgins, S. J., and Levason, W., *Inorg. Chim. Acta* **84,** 65 (1984).
438. Hope, E. G., Levason, W., Murray, S. G., and Marshall, G. L., *J. Chem. Soc., Dalton Trans.* p. 2185 (1985).
439. Hope, E. G., Levason, W., Webster, M., and Murray, S. G., *J. Chem. Soc., Dalton Trans.* p. 1003 (1986).
440. Blake, A. J., and Schröder, M., *Adv. Inorg. Chem.* **35,** 1 (1990).
441. Tweedle, M. F., and Taube, H., *Inorg. Chem.* **21,** 3361 (1982).
442. Catala, R. M., Cruz-Garritz, D., Hills, A., Hughes, D. L., Richards, R. L., Sosa, P., and Torrens, H., *J. Chem. Soc., Chem. Commun.* p. 261 (1987).
443. Cruz-Garritz, D., Sosa, P., Torrens, H., Hills, A., Hughes, D. L., and Richards, R. L., *J. Chem. Soc., Dalton Trans.* p. 419 (1989).
444. Cruz-Garritz, D., Torrens, H., Leal, J., and Richards, R. L., *Transition Met. Chem. (Weinheim Ger.)* **8,** 127 (1983).
445. Utegulov, R. N., Kamysbaev, D. Kh., Ospanov, Kh. K., and Kozlovskii, E. V., *Koord. Khim.* **14,** 1529 (1988).
446. Herberhold, M., and Hill, A. F., *J. Chem. Soc., Dalton Trans.* p. 2027 (1988).
447. Pekhn'o, V. I., Fokina, Z. A., and Volkov, S. V., *Zh. Neorg. Khim.* **33,** 1214 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)* **33,** 687 (1988).
448. Angelici, R. J., *Coord. Chem. Rev.* **105,** 61 (1990).
449. Bol'shakov, K. A., Sinitsyn, N. M., Pichkov, V. N., Gribanovskaya, M. G., and Rudnitskaya, O. V., *Zh. Neorg. Khim.* **31,** 720 (1986); *Russ. J. Inorg. Chem. (Engl. Transl.)* **31,** 410 (1986).
450. Rudnitskaya, O. V., Lin'ko, I. V., Ivanova, T. M., Pichkov, V. N., Gribanovskaya, M. G., and Linko, R. V. *Zh. Neorg. Khim.* **31,** 3173 (1986); *Russ. J. Inorg. Chem. (Engl. Transl.)* **31,** 1822 (1986).
451. Gribanovskaya, M. G., Rudnitskaya, O. V., Pichkov, V. N., Lipnitskii, I. V., and Nobitskii, G. G., *Koord. Khim.* **15,** 991 (1989).
452. Morelli, B., *Analyst (London)* **111,** 1289 (1986).
453. Morelli, B., *Anal. Lett.* **18,** 2453 (1985).
454. Calderazzo, F., Pampaloni, G., Vitali, D., Collamati, I., Dessy, G., and Fares, V. *J. Chem. Soc., Dalton Trans.* 1965 (1980).
455. Antonov, P. G., Kukushkin, Yu. N., Konnov, V. I., and Kostikov, Yu. P., *Koord. Khim.* **6,** 1585 (1980).
456. Antonov, P. G., and Amantova, I. A., *Zh. Obshch. Khim* **58,** 2523 (1988); *J. Gen. Chem. USSR (Engl. Transl.)* **58,** 2245 (1988).
457. Robinson, P. D., Hinckley, C. C., and Ikuo, A., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C45,** 1079 (1989).
458. Cabeza, J. A., Adams, H., and Smith, A. J., *Inorg. Chim. Acta* **114,** L17 (1986).
459. Cabeza, J. A., and Maitlis, P. M., *J. Chem. Soc., Dalton Trans.* p. 573 (1985).
460. Kinsenyi, J. M., Cabeza, J. A., Smith, A. J., Adams, H., Sunley, G. J., Salt, N. J. S., and Maitlis, P. M., *J. Chem. Soc., Chem. Commun.* p 770 (1985).
461. Kotov, V. Yu., Nikol'skii, A. B., and Popov, A. M., *Vestn. Leningr. Univ., Fiz., Khim.* p. 39 (1985); *Chem. Abstr.* **104,** 80859r (1986).
462. Droege, M. W., and Taube, H., *Inorg. Chem.* **26,** 3316 (1987).
463. Bond, A. M., and Martin, R. L., *Coord. Chem. Rev.* **54,** 23 (1984).
464. Cole-Hamilton, D. J., and Stephenson, T. A., *J. Chem. Soc., Dalton Trans.* p. 2396 (1976).
465. Craciunescu, D. G., Parrondo-Iglesias, E., Alonso, M. P., Molina, C., Doadrio-Lopez,

A., Gomez, A., Mosquerra, R. M., Ghirvu, C., and Gaston de Iriarte, E., *An. R. Acad. Farm.* **54,** 16 (1988).

465a. Pramanik, A., Bag, N., Ray, D., Lahiri, G. K., and Chakravorty, A., *Inorg. Chem.* **30,** 410 (1991).

465b. Pramanik, A., Bag, N., Ray, D. Lahiri, G. K., and Chakravorty, A., *J. Chem. Soc., Chem. Commun.* p. 139 (1991).

466. Mukherjee, R. M., and Shastri, B. B. S., *Indian J. Chem., Sect. A* **29A,** 809 (1990).

467. McQueen, E. W. D., Blake, A. J., Stephenson, T. A., Schröder, M., and Yellowlees, L. J., *J. Chem. Soc., Chem. Commun.* p. 1533 (1988).

468. Sharma, C. L., and Narvi, S. S., *J. Indian Chem. Soc.* **62,** 397 (1985).

469. Lomakina, L. N., Ivanov, V. M., and Belyaeva, V. K., *Koord. Khim.* **14,** 1098 (1988).

470. Chakrabarty, A. K., *Indian J. Chem., Sect. A.* **27A,** 366 (1988).

471. Olby, B. G., and Robinson, S. D., *Inorg. Chim. Acta* **165,** 153 (1989).

472. Singh, A. K., Roy, B., and Singh, R. P., *J. Indian Chem. Soc.* **62,** 316 (1985).

473. Andzhaparaidze, D. I., and Akimov, V. K., *Izv. Akad. Nauk Gruz. SSR, Ser. Khim.* **14,** 179 (1988); *Chem. Abstr.* **111,** 4950t (1989).

474. Akhond, M., Safavi, A., and Massoumi, A., *Anal. Lett.* **20,** 29 (1987).

475. Morelli, B., *Analyst (London)* **112,** 1395 (1987).

476. Heath, G. A., Moock, K. A., Sharp, D. W. A., and Yellowlees, L. J., *J. Chem. Soc., Chem. Commun.* p. 1503 (1985).

477. Sun, I. W., Ward, E. H., and Hussey, C. L., *J. Electrochem. Soc.* **135,** 3035 (1988).

478. Rybakov, V. B., Aslanov, L. A., Volkov, S. V., and Pekhn'o, V. I., *Koord. Khim.* **15,** 700 (1989).

479. Thiele, G., Wochner, H., and Wagner, H., *Z. Anorg. Allg. Chem.* **530,** 178 (1985).

480. Alyoubi, A. O., Greenslade, D. J., Forster, M. J., Preetz, W., *J. Chem. Soc., Dalton Trans.* p. 381 (1990).

481. Preetz, W., and Groth, Th., *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **41B,** 885 (1986).

482. Bakhvalova, I. P., and Volkova, G. V., *Zh. Neorg. Khim.* **33,** 665 (1988); *Russ. J. Inorg. Chem. (Engl. Transl.)* **33,** 372 (1988).

483. Schoenen, N., and Schmidtke, H. H., *Mol. Phys.* **57,** 983 (1986).

484. Robinson, P. D., Hinckley, C. C., Matusz, M., and Kibala, P. A., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44,** 619 (1988).

485. Takazawa, H., Ohba, S., Saito, Y., and Sano, M., *Acta Crystallogr. Sect. B: Struct. Sci.* **B46,** 166 (1990).

486. Singh, M. A., and Armstrong, R. L., *J. Magn. Reson.* **84,** 448 (1989).

487. Singh, M. A., and Armstrong, R. L., *J. Magn. Reson.* **78,** 538 (1988).

488. Singh, M. A., and Armstrong, R. L., *J. Phys. C: Solid State Phys.* **19,** L221 (1986).

489. Krupski, M., and Armstrong, R. L., *Can. J. Phys.* **67,** 566 (1989).

490. Bihaye, C., Butler, T. A., and Knapp, F. F., Jr., *J. Radioanal. Nucl. Chem.* **102,** 399 (1986).

491. Peng, Y. B., Vekeman, G., Maenhout-Van der Vorst, W., and Cardon, F., *J. Imaging Sci.* **31,** 55 (1987).

492. Preetz, W., and Irmer, K., *Z. Naturforsch., B: Chem. Sci.* **45,** 283 (1990).

493. Schmidtke, H. H., Grzonka, C., and Schoenherr, T., *Spectrochim. Acta, Part A* **45A,** 129 (1989).

494. Hope, E. G., Levason, W., and Ogden, J. S., *J. Chem. Soc., Dalton Trans.* p. 61 (1988).

495. Chakravarty, A. S., *Indian J. Phys., Sect. A* **63A,** 115 (1989).

496. Kjems, J. K., Vaknin, D., Davidov, D., Selig, H., and Yeshurun, Y., *Synth. Met.* **23,** 113 (1988).

497. Vaknin, D., Davidov, D., Zevin, V., and Selig, H., *Phys. Rev. B: Condens. Matter* [3] **35,** 6423 (1987).

498. Ohana, I., Vaknin, D., Selig, H., Yacoby, Y., and Davidov, D., *Phys. Rev. B: Condens. Matter* [3] **35,** 4522 (1987); Kjems, J. K., Yeshurun, Y., Vaknin, D., Davidov, D., and Selig, H., *ibid.* **36,** 6981 (1987).

499. Gnanasekaran, S., Ranganayaki, S., Gnanasekaran, P., and Krishnan, S. S., *Asian J. Chem.* **1,** 173 (1989).

500. Hope, E. G., Levason, W., and Ogden, J. S., *J. Chem. Soc., Dalton Trans.* p. 997 (1988).

501. Hambley, T. W., and Lay, P. A., *Inorg. Chem.* **25,** 4553 (1986).

502. Fokina, Z. A., Bryukhova, E. V., Pekhn'o, V. I., and Kiznetsov, S. I., *Izv. Akad. Nauk SSSR, Ser. Khim.* p. 1409 (1986).

503. Holloway, J. H., and Rook, J., *J. Chem. Soc., Dalton Trans.* p. 2285 (1987).

504. Robinson, P. D., Hinckley, C. C., Matusz, M., and Kibala, P. A., *Polyhedron* **6,** 1695 (1987).

505. Kritikos, M., Noreus, D., Bogdanovic, B., and Wilczok, U., *J. Less-Common Met.* **161,** 337 (1990).

506. Frost, P. W., Howard, J. A. K., and Spencer, J. L., *J. Chem. Soc., Chem. Commun.* p. 1362 (1984).

507. Collman, J. P., Wagenknecht, P. S., Hembre, R. T., and Lewis, N. S., *J. Am. Chem. Soc.* **112,** 1294 (1990).

508. Bautista, M., Earl, K. A., Morris, R. H., and Sella, A., *J. Am. Chem. Soc.* **109,** 3780 (1987).

509. Bautista, M. T., Earl, K. A., Maltby, P. A., Morris, R. H., Schweitzer, C. T., and Sella, A., *J. Am. Chem. Soc.* **110,** 7031 (1988).

510. Earl, K. A., Morris, R. H., and Sawyer, J. F., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C45,** 1137 (1989).

511. Bautista, M. T., Earl, K. A., and Morris, R. H., *Inorg. Chem.* **27,** 1124 (1988).

512. Antoniutti, S., Albertin, G., Amendola, P., and Bordignon, E., *J. Chem. Soc., Chem. Commun.* p. 279 (1989).

513. Bruno, J. W., Huffman, J. C., and Caulton, K. G., *J. Am. Chem. Soc.* **106,** 1663 (1984).

514. Hamilton, D. G., and Crabtree, R. H., *J. Am. Chem. Soc.* **110,** 4126 (1988).

515. Johnson, T. J., Huffman, J. C., Caulton, K. G., Jackson, S. A., and Eisenstein, O. *Organometallics* **8,** 2073 (1989).

516. Desrosiers, P. J., Cai, L., and Halpern, J., *J. Am. Chem. Soc.* **111,** 8513 (1989).

517. Losada, J., Alvarez, S., Novoa, J. J., Mota, F., Hoffmann, R., and Silvestre, J. *J. Am. Chem. Soc.* **112,** 8998 (1990).

518. Collman, J. P., Prodolliet, J. W., and Leidner, C. R., *J. Am. Chem. Soc.* **108,** 2916 (1986).

519. Tait, C. D., Garner, J. M., Collman, J. P., Sattelberger, A. P., and Woodruff, W. H., *J. Am. Chem. Soc.* **111,** 9072 (1989).

520. Cotton, F. A., and Vidyasagar, K., *Inorg. Chem.* **29,** 3197 (1990).

521. Agaskar, P. A., Cotton, F. A., Dunbar, K. R., Falvello, L. R., Tetrick, S. M., and Walton, R. A., *J. Am. Chem. Soc.* **108,** 4850 (1986).

522. Fanwick, P. E., Tetrick, S. M., and Walton, R. A., *Inorg. Chem.* **25,** 4546 (1986).

523. Fanwick, P. E., King, M. K., Tetrick, S. M., and Walton, R. A., *J. Am. Chem. Soc.* **107,** 5009 (1985).

524. Cotton, F. A., and Vidyasagar, K., *Inorg. Chim. Acta* **166,** 109 (1989).

525. Johnson, T. W., Tetrick, S. M., and Walton, R. A., *Inorg. Chim. Acta* **167,** 133 (1990).

526. Cotton, F. A., and Matusz, M., *Inorg. Chim. Acta* **143,** 45 (1988).
527. Tooze, R. P., Wilkinson, G., Motevalli, M., and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* p. 2711 (1986).
528. Cotton, F. A., and Matusz, M., *Polyhedron* **6,** 1439 (1987).
529. Cotton, F. A., Dunbar, K. R., and Matusz, M., *Polyhedron* **5,** 903 (1986).
530. Clark, R. J., and Hempleman, A. J., *J. Chem. Soc., Dalton Trans.* p. 2601 (1988).
531. Clark, R. J. H., Hempleman, A. J., and Tocher, D. A., *J. Am. Chem. Soc.* **110,** 5968 (1988).
532. Hilts, R. W., Sherlock, S. J., Cowie, M., Singleton, E., and Steyn, M. M. de V., *Inorg. Chem.* **29,** 3161 (1990).
533. Cotton, F. A., and Dunbar, K. R., *J. Am. Chem. Soc.* **109,** 2199 (1987).
534. Lu, K. L., Lin, Y. C., Cheng, M. C., and Wang, Y., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **C44,** 979 (1988).
535. Vogler, A., Osman, A. H., and Kunkely, H., *Inorg. Chem.* **26,** 2337 (1987).
536. Richardson, D. E., Sen. J. P., Buhr, J. D., and Taube, H., *Inorg. Chem.* **21,** 3136 (1982).
537. Lay, P. A., Magnuson, R. H., and Taube, H., *Inorg. Chem.* (to be submitted).
538. Senoff, C. V., *Chem. Can.* **21,** 31 (1969).
539. Elson, C. M., Gulens, J., and Page, J. A., *Can. J. Chem.* **49,** 207 (1971).
540. Emilsson, T., and Srinivasan, V. S., *Inorg. Chem.* **17,** 491 (1978).
541. Hupp, J. T., Neyhart, G. A., and Meyer, T. J., *J. Am. Chem. Soc.* **108,** 5349 (1986).
542. Lay, P. A., and Taube, H., in preparation.
543. Ferguson, J., Krausz, E. R., Lay, P. A., and Maeder, M., unpublished results (1984).
544. Powell, D. W., and Lay, P. A., to be submitted.
545. Schanze, K. S., Neyhart, G. A., and Meyer, T. J., *J. Phys. Chem.* **90,** 2182 (1986).
546. Kalyanasundaram, K., and Nazeeruddin, M. K., *Chem. Phys. Lett.* **158,** 45 (1989).
547. Campagna, S., Denti, G., Sabatino, L., Serroni, S., Ciano, M., and Balzani, V., *J. Chem. Soc., Chem. Commun.* p. 1500 (1989).
548. Hage, R., Haasnoot, J. G., Nieuwenhuis, H. A., Reedijk, J., De Ridder, D. J. A., and Vos, J. G., *J. Am. Chem. Soc.* **112,** 9245 (1990).
548a. Barigelletti, F., De Cola, L., Balzani, V., Hage, R., Haasnoot, J. G., Reedijk, J., and Vos, J. G., *Inorg. Chem.* **30,** 641 (1991).
549. Kaim, W., and Kasack, V., *Inorg. Chem.* **29,** 4696 (1990).
550. Boyde, S., Strouse, G. F., Jones, W. E., Jr., and Meyer, T. J., *J. Am. Chem. Soc.* **112,** 7395 (1990).
551. Furue, M., Kinoshita, S., and Kushida, T., *Chem. Lett.* p. 2355 (1987).
552. Haga, M., Matsumura-Inoue, T., and Yamabe, S., *Inorg. Chem.* **26,** 4148 (1987).
552a. Haga, M., and Bond, A. M., *Inorg. Chem.* **30,** 475 (1991).
553. Hammershøi, A., Lay, P. A., and Taube, H., to be published.
554. Gilbert, J. A., Geselowitz, D., and Meyer, T. J., *J. Am. Chem. Soc.* **108,** 1493 (1986).
555. Cabeza, J. A., Smith, A. J., Adams, H., and Maitlis, P. M., *J. Chem. Soc., Dalton Trans.* p. 1155 (1986).
556. Cabeza, J. A., Mann, B. E., Maitlis, P. M., and Brevard, C., *J. Chem. Soc., Dalton Trans.* p. 629 (1988).
557. Johson, D. W., and Brewer, T. R., *Inorg. Chim. Acta* **154,** 221 (1988).
558. Heath, G. A., and Humphrey, D. G., *J. Chem. Soc., Chem. Commun.* p. 672 (1990).
559. Bruns, M., and Preetz, W., *Z. Anorg. Allg. Chem.* **537,** 88 (1986).
560. Lundquist, E. G., and Caulton, K. G., *Inorg. Synth.* **27,** 26 (1990).
561. Deeming, A. J., Randle, N. P., Bates, P. A., and Hursthouse, M. B., *J. Chem. Soc., Dalton Trans.* p. 2753 (1988).

562. Barron, A. R., and Wilkinson, G., *J. Chem. Soc., Dalton Trans.* p. 287 (1986).
563. Collman, J. P., McCullough, L., and Zisk, M. B., *Gov. Rep. Announce Index (U.S.)* **89,** Abstr. No 905918 (1989).
564. Collman, J. P., McDevitt, J. T., Leidner, C. R., Yee, G. T., Torrance, J. B., and Little, W. A., *J. Am. Chem. Soc.* **109,** 4606 (1987).
565. Collman, J. P., McDevitt, J. T., Yee, G. T., Zisk, M. B., Torrance, J. B., and Little, W. A., *Synth. Met.* **15,** 129 (1986).
566. Jernigan, J. C., and Murray, R. W., *J. Am. Chem. Soc.* **109,** 1738 (1987).
567. Abruña, H. D., and Hurrell, H. C., *Inorg. Chem.* **29,** 736 (1990).
568. Surridge, N. A., Keene, F. R., White, B. A., Facci, J. S., Silver, M., and Murray, R. W., *Inorg. Chem.* **29,** 4950 (1990).
569. Strouse, G. F., Worl, L. A., Younathan, J. N., and Meyer, T. J., *J. Am. Chem. Soc.* **111,** 9101 (1989).
570. Cainelli, G., Contento, M., Manescalchi, F., and Plessi, L., *Synthesis* p. 47 (1989).
571. Cainelli, G., Contento, M., Manescalchi, F., and Plessi, L , *Synthesis* p. 45 (1989).
572. Meites, L., Zuman, P., Rupp, E. B., and Narayanan, A., eds., "CRC Handbook Series in Inorganic Electrochemistry," Vol. 5. CRC Press, Boca Raton, Florida, 1985.
573. Colom, F., *in* "Standard Potential of Ruthenium and Osmium" (A. J. Bard, R. Parsons, and J. Jordan, eds.), pp. 413–427. Dekker, New York, 1985.
574. Lay, P. A., McAlpine, N. S., Hupp, J. T., Weaver, M. J., and Sargeson, A. M., *Inorg. Chem.* **29,** 4322 (1990).
575. Lay, P. A., *J. Phys. Chem.* **90,** 878 (1986).
576. Elson, C. M., Gulens, J., Itzkovitch, I. J., and Page, J. A., *J. Chem. Soc., Chem. Commun.* p. 875 (1970).
577. Yeh, A., Scott, N., and Taube, H., *Inorg. Chem.* **21,** 2542 (1982).
578. Creutz, C., and Taube, H., *J. Am. Chem. Soc.* **95,** 1086 (1973).
579. Lehmann, H., Schenk, K. J., Chapuis, G., and Ludi, A., *J. Am. Chem. Soc.* **101,** 6197 (1979).
580. Kuehn, C. G., and Taube, H., *J. Am. Chem. Soc.* **98,** 689 (1976).
581. Lim, H. S., Barclay, D. J., and Anson, F. C., *Inorg. Chem.* **11,** 1460 (1972).
582. Matsubara, T., and Ford, P. C., *Inorg. Chem.* **15,** 1107 (1976).
583. Richardson, D. E., unpublished results.
584. Sundberg, R. J., Bryan, R. F., Taylor, I. F., Jr., and Taube, H., *J. Am. Chem. Soc.* **96,** 381 (1974).
585. Marchant, J. A., Matsubara, T., and Ford, P. C., *Inorg. Chem.* **16,** 2160 (1977).
586. Bino, A., Lay, P. A., Taube, H., and Wishart, J. F., *Inorg. Chem.* **24,** 3969 (1985).
587. Garcia, E., Kwak, J., and Bard, A. J., *Inorg. Chem.* **27,** 4377 (1988).
588. Tom, G., and Taube, H., *J. Am. Chem. Soc.* **95,** 5310 (1975).
589. Richardson, D. E., and Taube, H., *Inorg. Chem.* **20,** 1278 (1981).
590. Sullivan, B. P., and Meyer, T. J., *Inorg. Chem.* **19,** 752 (1980).
591. Kober, E. M., Goldsby, K. A., Narayana, D. N. S., and Meyer, T. J., *J. Am. Chem. Soc.* **105,** 4303 (1983).
592. Jernigan, J. C., and Murray, R. W., *J. Am. Chem. Soc.* **112,** 1034 (1990).
593. Naegeli, R., Redepenning, J., and Anson, F. C., *J. Phys. Chem.* **90,** 6227 (1986).
594. He, P., and Chen, X., *J. Electroanal. Chem. Interfacial Electrochem.* **256,** 353 (1988).
595. Chen, X., Xia, B., and He, P., *J. Electroanal. Chem. Interfacial Electrochem.* **281,** 185 (1990).
596. Gregg, B. A., and Heller, A., *Anal. Chem.* **62,** 258 (1990).
597. Dubicki, L., Ferguson, J., Finnie, K., Krausz, E. R., Lay, P. A., and Maeder, M., unpublished results.

598. Ferguson, J., Krausz, E. R., and Lay, P. A., unpublished results.
599. Creutz, C., and Chou, M. H., *Inorg. Chem.* **26,** 2995 (1987).
600. Krausz, E., *Comments Inorg. Chem.* **7,** 139 (1988).
601. Krausz, E., and Ferguson, J., *Prog. Inorg. Chem.* **37,** 293 (1989).
602. Juris, A., Barigelletti, F., Campagna, S., Balzani, V., Belzer, P., and von Zelewsky, A., *Coord. Chem. Rev.* **84,** 85 (1988).
603. Krausz, R. A., *Struct. Bonding (Berlin)* **67,** 1 (1987).
604. Kalyanasundaram, K., *Coord. Chem. Rev.* **46,** 159 (1982).
605. Krausz, E., *J. Lumin.* **42,** 283 (1988).
606. Krausz, E., Moran, G., and Riesen, H., *Chem. Phys. Lett.* **165,** 401 (1990).
607. Krausz, E., *Chem. Phys. Lett.* **165,** 407 (1990).
608. Hopkins, M. D., Miskowski, V. M., and Gray, H. B., *J. Am. Chem. Soc.* **108,** 6908 (1986).
609. Dubicki, L., Ferguson, J., and Krausz, E. R., *J. Am. Chem. Soc.* **107,** 179 (1985).
610. Dubicki, L., Ferguson, J., Krausz, E. R., Lay, P. A., Maeder, M., Magnuson, R. H., and Taube, H., *J. Am. Chem. Soc.* **107,** 2167 (1985).
611. Armstrong, R. S., Horsfield, W., and Lay, P. A., work in progress.
612. Gould, S., O'Toole, T. R., and Meyer, T. J., *J. Am. Chem. Soc.* **112,** 9490 (1990).
613. Worl, L. A., Strouse, G. F., Younathan, J. N., Baxter, S. M., and Meyer, T. J., *J. Am. Chem. Soc.* **112,** 7571 (1990).
614. Armor, J. N., and Taube, H., *J. Am. Chem. Soc.* **92,** 6170 (1970).
615. Folkesson, B., *Acta Chem. Scand.* **26,** 4157 (1972).
616. Coleman, G. N., Gesler, J. W., Shirley, F. A., and Kuempel, J. R., *Inorg. Chem.* **12,** 1036 (1973).
617. Broomhead, J. A., Basolo, F., and Pearson, R. G., *Inorg. Chem.* **3,** 826 (1964).
618. Lay, P. A., *Comments Inorg. Chem.* **11,** 235 (1991).
619. Lay, P. A., *Coord. Chem. Rev.* In press.
620. Stebler-Röthlisberger, M., Hummel, W., Pittet, P.-A., Bürgi, H.-B., Ludi, A., and Merbach, A. E., *Inorg. Chem.* **27,** 1358 (1988).
621. Triegaardt, D. M., and Wahl, A. C., *J. Phys. Chem.* **90,** 1957 (1986).
622. Sarala, R., and Stanbury, D. M., *Inorg. Chem.* **29,** 3456 (1990).
623. Creutz, C., Sutin, N., and Brunschwig, B. S., *J. Am. Chem. Soc.* **101,** 1297 (1979).
624. Macartney, D. H., *Inorg. Chem.* **25,** 2222 (1986).
625. Macartney, D. H., and Thompson, D. W., *Inorg. Chem.* **28,** 2195 (1989).
626. Bommarius, A. S., Holzwarth, J. F., Wang, D. I. C., and Hatton, T. A., *J. Phys. Chem.* **94,** 7232 (1990).
627. Baumann, J. A., and Meyer, T. J., *Inorg. Chem.* **19,** 345 (1980).
628. Brothers, P. J., Headford, C. E. L., and Roper, W. R., *J. Organomet. Chem.* **105,** C29 (1980).
629. Moyer, B. A., Sipe, B. K., and Meyer, T. J., *Inorg. Chem.* **20,** 1475 (1981).
630. Groves, J. T., and Ahn, K. H., *Inorg. Chem.* **26,** 3831 (1987).
631. Gilbert, J. A., Eggleston, D. S., Murphy, W. R., Geselowitz, D. A., Gersten, S. W., Hodgson, D. J., and Meyer, T. J., *J. Am. Chem. Soc.* **107,** 3855 (1985).
632. Ware, D. C., and Taube, H., unpublished results.
633. Kirchner, K., Han, L.-F., Dodgen, H. W., Wherland, S., and Hunt, J. P., *Inorg. Chem.* **29,** 4556 (1990).
634. Smith, T. P., Iverson, D. J., Droege, M. W., Kwan, K. S., and Taube, H., *Inorg. Chem.* **26,** 2882 (1987).
635. Lane, B. C., Lester, J. E., and Basolo, F., *J. Chem. Soc., Chem. Commun.* p. 1618 (1971).

636. Ridd, M. J., and Keene, F. R., *J. Am. Chem. Soc.* **103,** 5733 (1981).
637. Lay, P. A., and Taube, H., unpublished results.
638. Fenton, R. R., Honours Thesis, Macquarie University, Sydney, Australia (1985).
639. Anderes, B., and Lavallee, D. K., *Inorg. Chem.* **22,** 3724 (1983).
640. Tom, G., Ph.D. Thesis, Stanford University, Stanford, California, (1975).
641. Guengerich, G. P., and Schug, K., *Inorg. Chem.* **22,** 1401 (1983).
642. Isied, S., and Taube, H., *Inorg. Chem.* **13,** 1545 (1974).
643. Franco, D. W., and Taube, H., *Inorg. Chem.* **17,** 571 (1978).
644. Guengerich, C. P., and Schug, K., *Inorg. Chem.* **22,** 181 (1983).