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COORDINATION CHEMISTRY REVIEWS

5. Osmium 1994

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CONTENTS

INTRODUCTION

This review covers the coordination chemistry and some of the cluster chemistry of osmium published during the calendar year 1994. I have aimed to make it as comprehensive as possible, whilst restricting coverage to the more prominent journals. The emphasis is mainly on coordination chemistry, though clusters not containing organic fragments are also discussed. Organometallic compounds, and clusters whose primary interest is in the coordinated organic fragments, are not reviewed as they are covered elsewhere.

5.1 OSMIUM(VIII)

An electron diffraction study of $Os(N^tBu)_4$ in the gas phase has shown that the osmium(VIII) centre adopts a distorted tetrahedral arrangement [1]. The effects of spin-orbit

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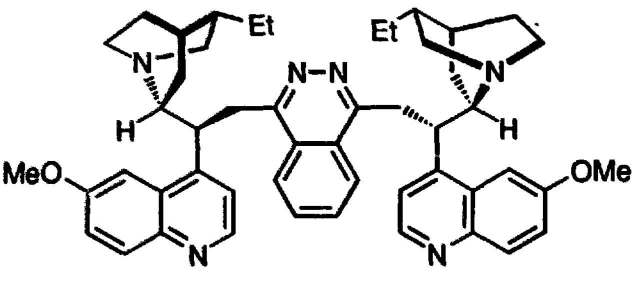
coupling on the valence photoelectron spectrum of OsO_4 have been investigated theoretically using the Discrete Variational X_α method [2]. The coordination complexes resulting from the interaction of OsO_4 with (**1**) or its enantiomer are highly enantioselective catalysts for the asymmetric dihydroxylation of olefins [3]. A kinetic study has been performed comparing (**1**) with a number of related ligands [4]; a comparison by molecular mechanics at a qualitative level has also been carried out [5].

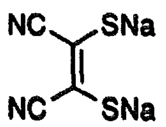


(**1**)

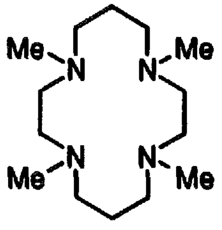
5.2 OSMIUM(VI)

A neutron diffraction study of the solid-state structure of $[OsH_5(PMe_2Ph)_3][BF_4]$ has shown the cation to be approximately dodecahedral. The cation exchanges Os–H with D_2, and reacts with CO to give $[Os^{II}H(CO)_2(PMe_2Ph)_3]^+$, which can catalytically hydrogenate and hydroformylate ethylene [6].

The strongly σ- and π-donating nitride (N^{3-}) ligand labilizes $[OsN(H_2O)(CN)_4]^-$ activating it for displacement of coordinated water by N_3^- in aqueous solution. In contrast, coordinated oxide, O^{2-}, which is isoelectronic with N^{3-}, has a much lower *trans* influence than nitride [7]. Reaction of $[N^nBu_4][OsNCl_4]$ with disodium maleonitrile dithiolate (Na_2**2**) affords $[N^nBu_4][OsN(\mathbf{2})_2]$. The X-ray structure shows the anion to be square-pyramidal, with an osmium–nitrogen distance of 1.639(8) Å, consistent with the proposed Os≡N triple bond. The $^3[(d_{xy})(d_{\pi^*})]$ excited state is emissive at room temperature [8].



(Na_2**2**)



(**3**)

The bis-arylimido complex $[Os(TTP)(4\text{-}NC_6H_4NO_2)_2]$ ($TTPH_2$ = 5,10,15,20-tetrakis(4-methylphenyl)porphyrin) has been prepared and characterized. In the solid state the two axial arylimido groups are compressed towards the osmium-porphyrin plane. The characteristics of the two arylimido N–Os bonds are most consistent with a bond order of two [9]. The reduction potential of $[Os(3)(O)_2]^{2+}$ is highly dependent on the nature of the solvent present; a change of 600 mV was observed on switching from water to hexamethylphosphoramide [10].

An EXAFS study of OsF_6 in anhydrous HF has shown there to be significant ordering of the HF around the OsF_6 centres [11]. Quantum mechanical *ab initio* calculations (performed at the Hartree-Fock and MP2 levels of theory) on $OsOF_4$, $OsOCl_4$, $[OsNF_4]^-$, $[OsNF_5]^{2-}$, $[OsNCl_4]^-$, and $[OsNCl_5]^{2-}$ predicted molecular geometries and vibrational frequencies which were in good agreement with experimentally determined data [12].

5.3 OSMIUM(V)

Exhaustive oxidation of $[Os(terpy)(bpy)(NH_3)]^{2+}$ in the presence of a secondary amine HNR_2 ($HNR_2 = HNEt_2$ or morpholine) affords $[Os^V(terpy)(bpy)(NNR_2)]^{3+}$ [13].

5.4 OSMIUM(IV)

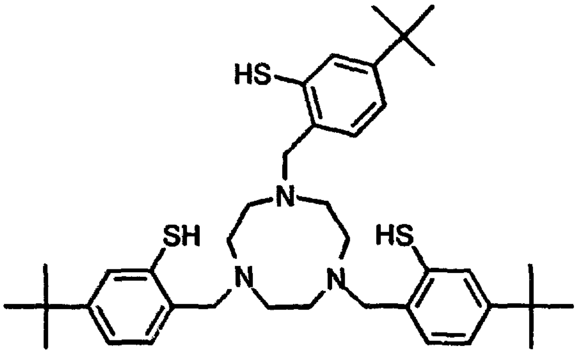
The complex cations $[Os^V(terpy)(bpy)(NNR_2)]^{3+}$ ($HNR_2 = HNEt_2$ or morpholine) can be reversibly reduced to their osmium(IV) analogues. Crystal structures of both of these are consistent with multiple bonding between the bent hydrazido ligand and the distorted octahedral osmium centre [13].

The diamagnetic osmium(IV) thiolate complexes $[Os(SR)_4(PR'_3)]$ ($R = C_6F_5$, C_6F_4H-4, Ph; $PR'_3 = P(C_6F_5)_3$, $P(C_6F_4H\text{-}4)_3$, PMe_2Ph) and $[OsCl(SC_6F_5)_2(SC_6H_4X\text{-}3)(PMe_2Ph)]$ (X = F, CF_3) have been prepared. Crystal structures have shown both $[Os(SC_6F_4H\text{-}4)_4(PPh_3)]$ and $[OsCl(SC_6F_5)_2(SC_6H_4CF_3\text{-}3)(PMe_2Ph)]$ to have trigonal bipyramidal geometries, with the PPh_3 in the former, and the Cl and PMe_2Ph ligands in the latter, occupying the apical coordination sites [14].

The complex [(4)NaOsNa(4)] has been prepared and characterized. The crystal structure of the ruthenium(IV) analogue has been determined. The complex has an octahedral $M^{IV}S_6$ core surrounded by two trigonal bipyramidal N_3NaS_3 centres. Thus, each sulfur bridges the ruthenium and one sodium [15].

The compound $[Os(TTP)Cl_2]$ can be prepared by the reaction of $[Os(TTP)(O)_2]$ with either tin(II) chloride [16] or thionyl chloride [17]. The octaethylporphyrin analogue $[Os(OEP)Cl_2]$ was also prepared by the thionyl chloride route [17]. Both $[Os(porphyrin)Cl_2]$ species are paramagnetic with $\mu_{eff} \approx 2.7\ \mu_B$, and have temperature-independent ^1H NMR spectra. Both also react with excess alkyl and aryl lithium reagents to give air-stable $[Os(porphyrin)R_2]$ species (R = Ph, Me_3SiCH_2), and the crystal structure of $[Os(TTP)(CH_2SiMe_3)_2]$ is reported. $[Os(TTP)Ph_2]$ can be oxidized with cerium(IV) or with $Ag[BF_4]$ to give $[Os(TTP)Ph_2]^+$, which has $\mu_{eff} \approx 1.7\ \mu_B$ [17].

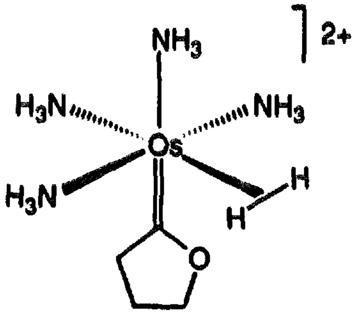
Five coordinate $[OsX(dcpe)_2]^+$ (X = H, Cl) reacts with oxygen to give the stable peroxo complex $[OsX(O_2)(dcpe)_2]^+$. The crystal structure of $[OsX(O_2)(dcpe)_2][BPh_4]$ shows that the η^2-O_2 ligand is bound symmetrically to the osmium, and that the O–O distance is 1.45(1)Å, consistent with the proposed peroxo formulation. This is believed to be the first reported crystal structure of a dioxygen complex of osmium [18].



(H_34)

The complex $[OsH_3(\eta^2\text{-}H_2BH_2)(P^iPr_3)_2]$ has been prepared; infrared and ^1H and ^{31}P NMR spectroscopies were used to determine the mode of coordination of the $[BH_4]^-$ ligand. *Ab initio* MP2 calculations predict a pentagonal bipyramidal structure with *trans*-axial P^iPr_3 ligands [19]. $[OsH_2Cl_2(P^iPr_3)_2]$ reacts with potassium acetate in methanol to give the analogous complex $[OsH_3(\eta^2\text{-}O_2CCH_3)(P^iPr_3)_2]$ [20]. Under the same experimental conditions, however, $K[S_2COEt]$ and $K[SOCCH_3]$ react with $[OsH_2Cl_2(P^iPr_3)_2]$ to give the formally osmium(II) dihydrogen complexes $[Os(\eta^2\text{-}S_2COEt)(\eta^1\text{-}SC(S)OEt)(\eta^2\text{-}H_2)(P^iPr_3)_2]$ and $[Os(\eta^2\text{-}OSCCH_3)(\eta^1\text{-}SC(O)CH_3)(\eta^2\text{-}H_2)(P^iPr_3)_2]$, respectively [20].

When reduced, $[Os(NH_3)_4(CF_3SO_3)_2][CF_3SO_3]$ reacts with thf to form the dihydrogen complex cation (5), which contains a coordinated carbene derived from the cyclic ether [21].



(5)

5.5 OSMIUM(III)

The crystal structure of $Rb_3[Br_3Os(\mu\text{-}Br)_3OsBr_3]$ suggests that there is a net σ-bonding interaction between the two osmium centres; each osmium centre has an octahedral arrangement of bromine atoms around it. The electronic spectrum has been assigned by computational methods [22].

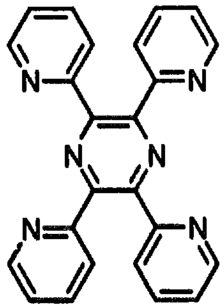
Studies of the oxidation of *L*-ascorbic acid by $[Os(CN)_6]^{3-}$ at 25°C under elevated pressure in aqueous acidic media have lead to the conclusion that the reaction may proceed *via* a bicyclic intermediate [23]. [Os(OEP)Me] can be synthesized by methylation of $[Os^{I}(OEP)]^{-}$ with a variety of reagents, or by treatment of the dimeric dication $[Os(OEP)]_2$ with MeMgBr [24].

The oxidation of *cis*-$[Os^{II}(NH_3)_4(N_2)_2]Cl_2$ in CF_3SO_3H affords the useful precursor *cis*-$[Os(NH_3)_4(CF_3SO_3)_2][CF_3SO_3]$ [25]. A study of the rate of substitution of $[Os(NH_3)_5(H_2O)]^{3+}$ by $M^{n}(CN)_6^{(6-n)-}$ giving $[(NH_3)_5Os(\mu\text{-}NC)M(CN)_5]^{(3-n)-}$ ($M^{n} = Fe^{II}, Fe^{III}, Ru^{II}, Co^{III}$) shows that in most cases the reaction proceeds *via* ion-pair formation. An alternative mechanism is proposed for the iron(III) case, in which the iron(III) oxidizes the osmium(III) giving $[(NH_3)_5Os^{IV}(\mu\text{-}NC)Fe^{II}(CN)_5]$ [26]. The heterodinuclear mixed valence complexes $Li[(NH_3)_5Os((\mu\text{-}NC)M^{IV}(CN)_7].H_2O$ (M = Mo, W) both have moderately intense inter-valence charge transfer processes in the visible region and exhibit Robin and Day Class II behaviour [27]. The homo- and hetero-dinuclear complexes $[(NH_3)_5Os^{III}(\mu\text{-}NC)Os^{II}(\eta^5\text{-}C_5H_5)(PPh_3)_2][CF_3SO_3]_3$ and $[(NH_3)_5Os^{III}(\mu\text{-}NC)Ru^{II}(\eta^5\text{-}C_5H_5)(PPh_3)_2][CF_3SO_3]_3$ also exhibit Class II behaviour [28].

5.6 OSMIUM(II)

5.6.1 Complexes with oligopyridine-based ligands

The six mononuclear complexes incorporating the potentially dinucleating ligand tetra-(2-pyridyl)pyrazine (**6**), $[(\mathbf{6})Os(terpy)]^{2+}$, $[Os(\mathbf{6})_2]^{2+}$, $[(\mathbf{6})Os(dppe)X]^{n+}$ and $[(\mathbf{6})Os(PPh_3)_2X]^{n+}$ (X = Cl^{-}, CH_3CN) have been prepared and characterized. All have long-lived excited states in fluid solution at room temperature [29].



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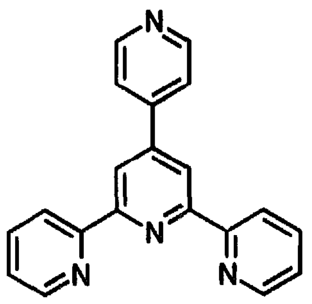

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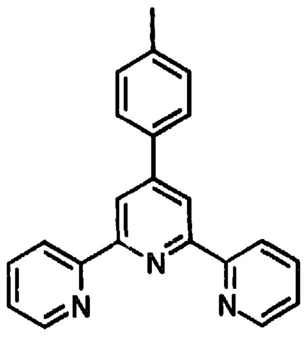

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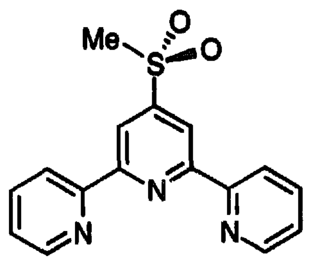
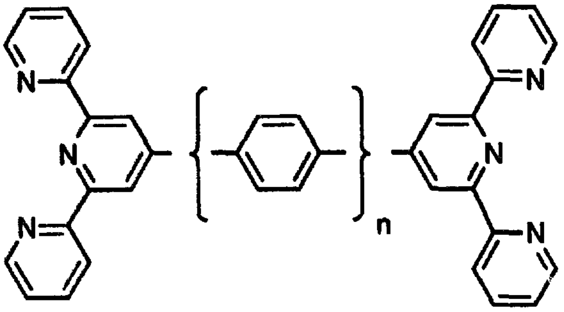


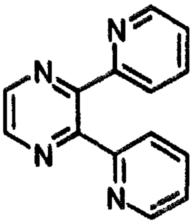
(9)

The two 4'-(4-pyridyl)-2,2':6',2''-terpyridine ligands in $[Os(7)_2][PF_6]_2$ both coordinate to the osmium in a terdentate bonding mode. Each coordinated (7) therefore has one remote non-coordinated pyridyl moiety which can be protonated or methylated to give $[Os(7\text{–}H)_2]^{4+}$, $[Os(7)(7\text{–}Me)]^{3+}$ or $[Os(7\text{–}Me)_2]^{4+}$, respectively [30]. Six heterodimetallic complexes of the form $[(Xterpy)Ru(L)Os(Yterpy)]^{4+}$ (Xterpy = **8** or **9**; L = **10**, **11**, **12**; Yterpy = terpy or **8**) were prepared. In all cases, the luminescence of the ruthenium(II) center is quenched efficiently by the connected osmium(II) component regardless of the number of interposed phenylene spacers [31].



(10) n = 0; **(11)** n = 1; **(12)** n = 2

The potentially dinucleating bis-bipyridine-type ligands (**13**) and (**14**) have been used to assemble a variety of homo- and hetero-metallic multinuclear complexes (Fig. 1). All exhibit an osmium-based emission in the near-infrared spectral region in rigid matrix form at 90 K. This luminescence originates from the lowest energy osmium centres, with efficient energy transfer occurring from the other, higher energy, metal centres. These molecules can therefore be thought of as potential *antenna* supramolecules for the harvesting of light energy [32]. The tetranuclear complexes $[Os\{(\mu\text{-}13)Rh(PPy)_2\}_3]^{5+}$ and $[Os\{(\mu\text{-}13)Ir(PPy)_2\}_3]^{5+}$, containing peripheral bis-cyclometallated rhodium(III) and iridium(III) moieties have been compared to their non-cyclometallated ruthenium(II) and osmium(II) counterparts [33].



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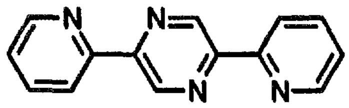

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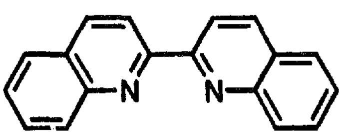


(15)

The spectroscopic properties of the cyclometallated complexes $[(8)Os(16)]^{+}$ and dinuclear $[(8)Os(17)M(8)]^{2+}$ (M = Ru or Os) have been compared with those of $[Os(8)_2]^{2+}$. In the case of heterodinuclear $[(8)Os(17)Ru(8)]^{2+}$, efficient ruthenium to osmium energy transfer occurs, and at room temperature, luminescence is observed to occur from the osmium centre only [34].

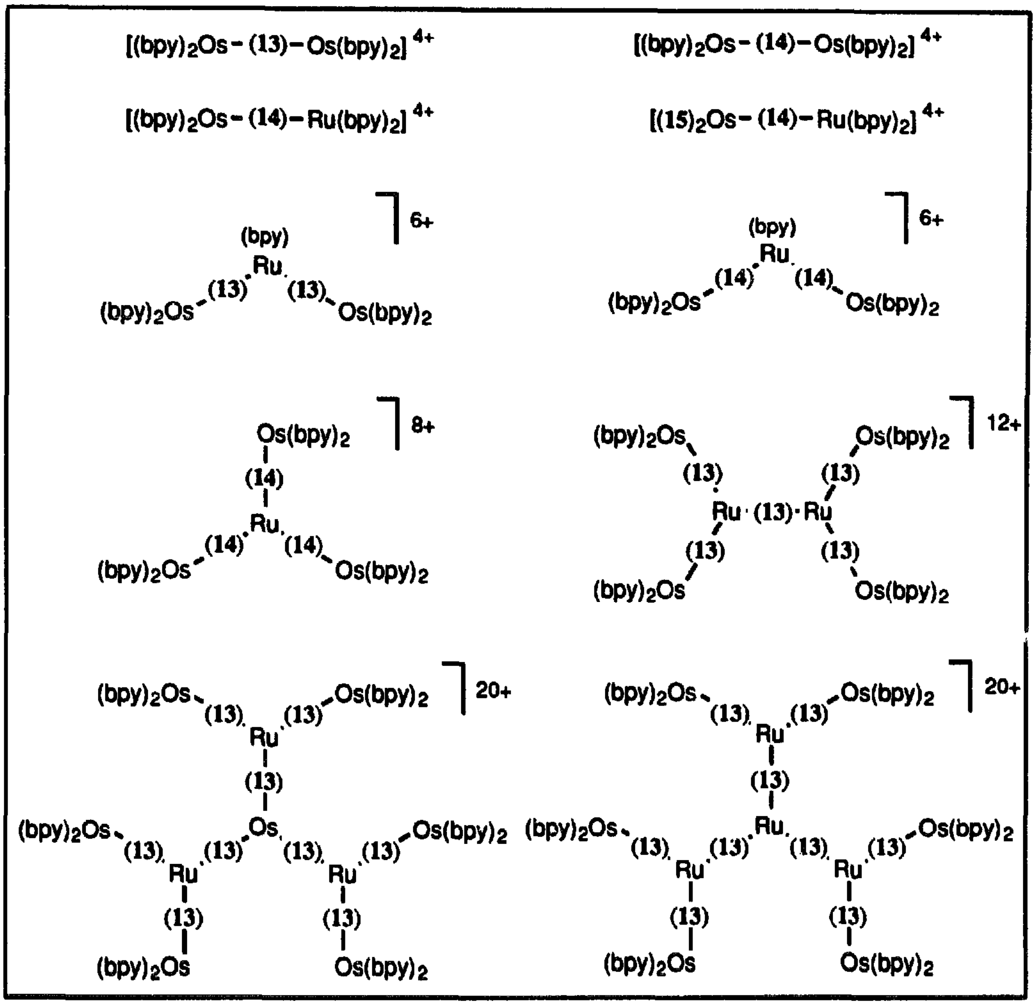
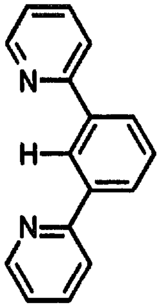
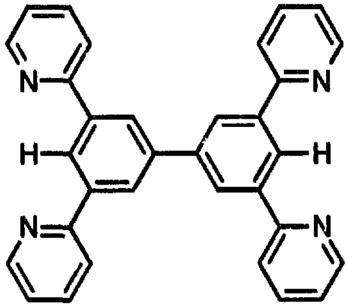


Figure 1: *Homo- and hetero-polynuclear complexes containing bis-bipyridine-type ligands.*

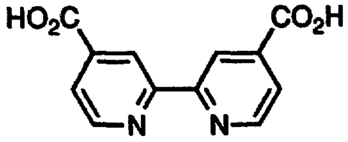


(H16)



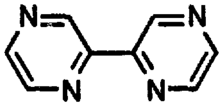
($H_2$17)

Photoactive $[Ru(bpy)_2(\mathbf{18})][PF_6]_2$ and $[Os(bpy)_2(\mathbf{18})][PF_6]_2$ complexes can be bound together (as well as independently) to glass surfaces by formation of an ester linkage through the coordinated 4,4'-dicarboxy-2,2'-bipyridine ligands (**18**). When both are bound, the ruthenium emitters are efficiently quenched by the co-attached osmium centres [35].

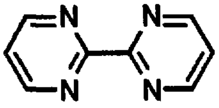


(**18**)

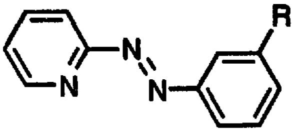
The mononuclear $[Os(L)_2(\mathbf{19})][ClO_4]_2.H_2O$ and $[Os(L)_2(\mathbf{20})][ClO_4]_2.H_2O$ complexes of the didentate 2-(arylazo)pyridine ligands L = (**21**), (**22**) have been reported [36].



(**19**)

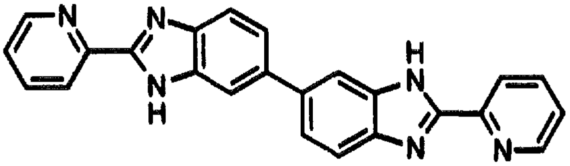


(**20**)



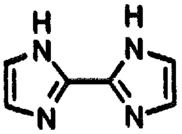
(**21**) R = H; (**22**) R = Me

The σ- and π-donor ability of the potentially dinucleating ligand ($H_2\mathbf{23}$) in mononuclear $[Os(bpy)_2(H_2\mathbf{23})][ClO_4]_2$, and homo- and hetero-dinuclear $[(bpy)_2Os(H_2\mathbf{23})Os(bpy)_2][ClO_4]_4$ and $[(bpy)_2Os(H_2\mathbf{23})Ru(bpy)_2][ClO_4]_4$ can be altered by changes in pH with significant effects on their absorption spectra and redox potentials [37].



($H_2\mathbf{23}$)

The complex $[OsH_2Cl_2(P^iPr_3)_2]$ reacts with ($H_2\mathbf{24}$) to give $[OsCl(\eta^2\text{-}H_2)(H_2\mathbf{24})(P^iPr_3)_2]Cl$, which has been characterized crystallographically. Partial deprotonation of the coordinated diimidazole ligand affords the neutral complex $[OsCl(\eta^2\text{-}H_2)(H\mathbf{24})(P^iPr_3)_2]$. $[OsH_2Cl_2(P^iPr_3)_2]$ also reacts with pyrazole (Hpz) to give the *trans*-dichloro complex $[OsCl_2(\eta^2\text{-}H_2)(Hpz)(P^iPr_3)_2]$, which isomerizes at 60°C in hexane to give the *cis* form [38].



($H_2\mathbf{24}$)

The complex cation $[(bpy)OsCl(\eta^6\text{-}Ar)]^+$ ($Ar = C_6Me_6$, $4\text{-}MeC_6H_4{}^iPr$) undergoes a two electron chemical or electrochemical reduction to afford the coordinatively unsaturated formally osmium(0) complex $[(bpy)Os(\eta^6\text{-}Ar)]$. Spectroscopic evidence, however, suggests that the ligand is partially reduced. These osmium(0) systems are proposed as potential systems for hydride transfer; the stable hydride intermediates $[(bpy)OsH(\eta^6\text{-}Ar)]^+$ were prepared and could be reversibly reduced to stable, neutral, radical complexes [39].

A transient resonance Raman spectroscopic study of the chromophore-quencher complex *cis*-$[(bpy)Os(CO)(MQ^+)]^{3+}$ ($MQ^+ = N$-methyl-4,4'-bipyridine) following MLCT excitation indicates that $bpy^{\bullet -} \rightarrow MQ^+$ intramolecular electron transfer occurs with $\tau < 7$ ns [40].

A study correlating the ligand-based reduction potential of 14 complexes containing $\{Os^{II}(bpy)\}$ fragments and of three containing $\{Os^{II}(NO)\}$ fragments has been performed in an attempt to allow the prediction of the potentials of similar processes in other complexes containing these fragments [41]. A study reviewing recent work on interchromophore electronic interactions in symmetrical ligand-bridged homo-polynuclear complexes compares a number of osmium(II) complexes [42].

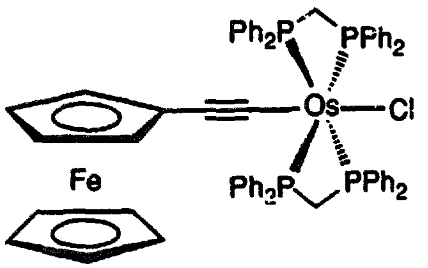
5.6.2 *Other coordination complexes*

The complex $[(\eta^5\text{-}Cp)(PPh_3)_2Os^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5][CF_3SO_3]_2$ exhibits a moderately intense, broad, inter-valence charge transfer transition, as do its $Ru^{II}Os^{III}$ and $Os^{II}Os^{III}$ analogues (see 5.5 above) [28]. $[(NC)_5Os^{II}(\mu\text{-}CN)Ru^{III}(NH_3)_5]^-$, which also exhibits an IVCT transition, is prepared by the reaction of $[Os(CN)_6]^{4-}$ and $[Ru(NH_3)_5(H_2O)]^{3+}$, and can be isolated as the potassium salt [43]. Photolysis of $K_4[Os(CN_6)]$ with sodium nitrite affords $Na_2[Os(CN)_5(NO)].2H_2O$, which has been characterized by X-ray crystallography. Possible mechanisms for the reaction of $[Os(CN)_5(NO)]^{2-}$ with bases such as HO^-, HS^- and N_2H_4 are discussed [44].

The complex dication $[Os(en)_2(\eta^2\text{-}H_2)(H_2O)]^{2+}$ reacts with $[M^n(CN)_6]^{(6-n)-}$ ($M^n = Fe^{II}$, Ru^{II}, Os^{II}, Co^{III}) and $[Mo(CN)_8]^{4-}$ to give the cyano-bridged dinuclear complexes $[(H_2O)(\eta^2\text{-}H_2)(en)_2Os^{II}(\mu\text{-}NC)M^n(CN)_5]^{(4-n)-}$. In the case of iron(II), the product is readily oxidized (*e.g.* in air) to $[(H_2O)(en)_2HOs^{IV}(\mu\text{-}NC)Fe^{II}(CN)_5]^-$, in which the osmium centre is seven-coordinate. This complex can also be prepared from $[OsH(en)_2(H_2O)_2]^{3+}$ and $[Fe(CN)_6]^{4-}$ [45]. The substitution of $[Os(en)_2(\eta^2\text{-}H_2)(H_2O)]^{2+}$ by a nucleophile proceeds *via* loss of H_2O to give the dihydride intermediate $[Os^{IV}(en)_2H_2]^{2+}$, which was isolated [46]. The solid-state structure of $[Os(en)_2(\eta^2\text{-}H_2)(CH_3COO)][PF_6]$ has been determined both by X-ray and neutron diffraction methods. The H–H distance of 1.34(2) Å determined by neutron diffraction is unusually long [47]. A quantum chemical study has been made of the influence of the *trans* ligand L^n on the geometries and properties of $[Os(NH_3)_4(\eta^2\text{-}H_2)L^n]^{(2+n)+}$ ($L^n = H_2O$, CH_3COCH_3, CH_3COO^-, Cl^-, H^-, py, MeCN) [48]. Reduction of $[Os^{III}(NH_3)_4(CF_3SO_3)_2][CF_3SO_3]$ in the presence of L = MeCN or L_2 = bpy affords the complex *cis*-$[Os(NH_3)_4L_2]^{2+}$ [25].

The Mo–Os bond in the mixed-triad heterometallic multiply bonded porphyrin dimer $[(OEP)Mo^{II}Os^{II}(OEP)]$ has some ionic character owing to the difference in electronegativities of the two metals. A molecular orbital scheme for the bonding is proposed [49]. The lowest excited states of a series of osmium(II) porphyrin complexes [Os(por)(CO)L] and [Os(por)L_2] (L = py, dmso, or other σ-donor ligand; por = TTP or OEP) have been found to be metal-to-porphyrin $^3[(d),(\pi^*)]$ charge transfer in nature, rather than porphyrin centred $^3[(\pi),(\pi^*)]$ CT processes as has previously been proposed for [Os(TTP)(CO)(py)] [50].

The ferrocenylacetylene osmium(II) complex (25), prepared from ferrocenylacetylene (26) and *cis*-[Os(dppm)$_2$Cl$_2$] has been characterized crystallographically. Electrochemical studies suggest that the conjugated bridging ligand facilitates interaction between the metal centres [51].



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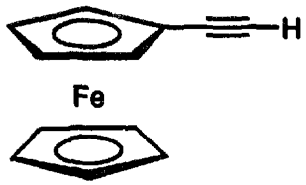
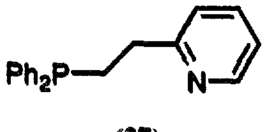


(26)

The potentially didentate ligand (27) can adopt a variety of possible bonding modes. The reaction of (27) with [OsX$_2$(PPh$_3$)$_3$] (X = Cl, Br) in toluene affords mononuclear *trans,cis,cis*-[OsX$_2$(*P*,*N*-27)$_2$], while reaction in ethanol gives the halo-bridged dimer [(*P*,*N*-27)$_2$Os(μ-X)$_2$Os(*P*,*N*-27)$_2$]$^{2+}$. The former, mononuclear, complex reacts with CO to give neutral [OsX$_2$(CO)(*P*-27)(*P*,*N*-27)] or cationic [OsX(CO)(*P*,*N*-27)$_2$]$^+$ depending on the nature of the solvent [52].

The complex [OsH$_2$(CO)(η^2-CH$_2$=CHEt)(P^{i}Pr$_3$)$_2$] (prepared from [OsH(Cl)(CO)(P^{i}Pr$_3$)$_2$] and ^{n}BuLi) reacts with carbon disulphide to give [OsH(CO)(η^2-S$_2$CH)(P^{i}Pr$_3$)$_2$] in which the coordinated η^2-dithioformamate is formed *in situ* by hydride transfer [53]. The chelate complex [OsH(CO)(*N*,*O*-28)(PPh$_3$)$_2$] is formed from [OsH(Cl)(CO)(PPh$_3$)$_3$] and the amino acid *L*-phenylalanine (H28) [54]. Trifluoroacetimidine HN=C(CF$_3$)NH$_2$ undergoes self-condensation, eliminating ammonia, in the presence of a variety of osmium hydride complexes, forming the *N*,*N*'-chelate ligand (H29) *in situ*. For example, [Os(29)H(CO)(PPh$_3$)$_2$] is formed from [OsH$_2$(CO)(PPh$_3$)$_3$], and [Os(29)$_2$(PPh$_3$)$_2$] is formed from [OsH$_4$(PPh$_3$)$_3$] [55].



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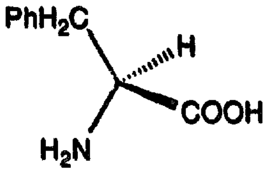

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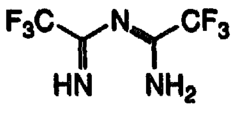


(H29)

Trans,cis-[Os(PPh$_3$)$_2$(CO)$_2$Br(CF$_3$SO$_3$)] reacts with hydroxylamine to give [Os(PPh$_3$)$_2$(CO)$_2$Br(NH$_2$OH)][CF$_3$SO$_3$]. The triflate also reacts with hydrazine to give *trans,cis*-[Os(PPh$_3$)$_2$(CO)$_2$Br(η^1-NH$_2$NH$_2$)][CF$_3$SO$_3$], which in turn reacts with Pb(OAc)$_4$ giving *trans,cis*-[$Os(PPh_3)_2(CO)_2Br(\eta^1$-HN=NH)][$CF_3SO_3$]. These represent the first structurally characterized complexes containing η^1-NH_2NH_2 and η^1-HN=NH, respectively [56]. [$OsCl_2(PR_2H)_4$] (R = Ph, C_6H_{11}) and [$OsCl_2(PPhH_2)_4$] are prepared from [NH_4]$_2$[$OsCl_6$] and excess phosphine. UV-VIS and ^{31}P NMR spectroscopic data are consistent with all of the observed products being *trans*-isomers. The solid-state structure of *trans*-[$OsCl_2(PPh_2H)_4$] has been determined crystallographically [57].

The compound [$OsH(N_2)(PP_3)$][BPh_4] (PP_3 = $P(CH_2CH_2PPh_2)_3$) is a catalyst precursor for the regio- and stereo-selective dimerization of 1-alkynes [58]. Pulsed laser photolysis has been used to investigate the kinetic selectivity of the reaction of [$Os(PP_3)H_2$] with methane and other hydrocarbons [59].

5.7 OSMIUM(0)

Reductive electrocrystallization of millimolar solutions of [$Os(bpy)_3$][PF_6]$_2$ results in the growth of crystals of [$Os(bpy)_3$] at the platinum cathode. The observation that [$Os(bpy)_3$] is EPR silent suggests that the two added electrons are paired in a singly degenerate LUMO. The osmium(0) complex [$Os(bpy)_3$] is re-oxidized to [$Os(bpy)_3$]$^{2+}$ in moist air [60]. Both [$Os(CO)_4(PR_3)$] and [$Os(CO)_3(PR_3)_2$] are formed by the reaction of [$Os(CO)_4(\eta^2$-alkene)] with the phosphine PR_3 (R = OEt, Ph) [61].

5.8 OSMIUM CARBONYL CLUSTERS

5.8.1 Clusters with only carbon-donor and hydride ligands

Coordinatively unsaturated solid [$H_2Os_3(CO)_{10}$] reacts with gaseous carbon monoxide giving the electron-precise adduct [$H_2Os_3(CO)_{11}$] [62]. K[$H_3Os_4(CO)_{12}$] can be prepared in high yield under mild conditions by the reductive carbonylation of either α-[$Os(CO)_3Cl_2$] or $OsCl_3$ adsorbed on a silica support with K_2CO_3 [63].

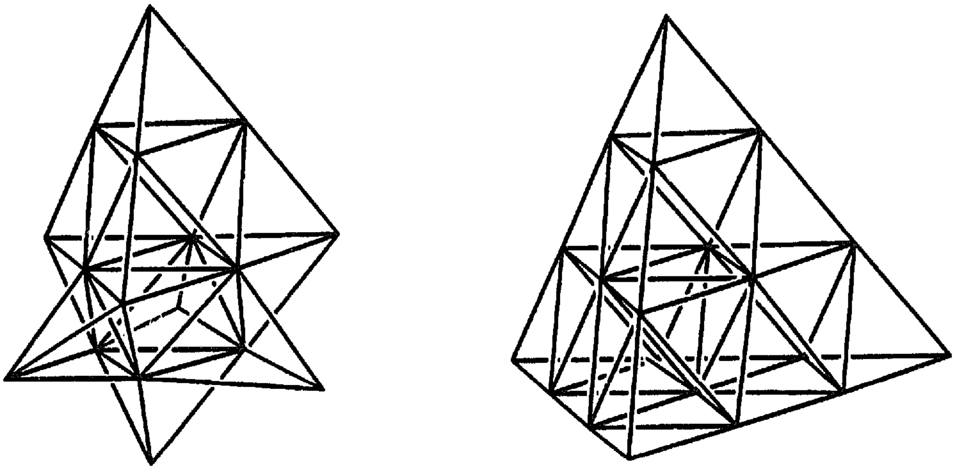
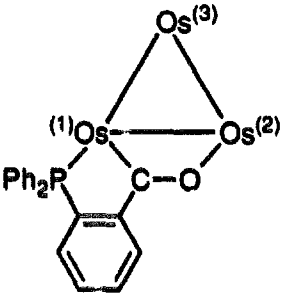


Figure 2: *Core structures of [$Os_{17}(CO)_{36}$]$^{2-}$ and [$Os_{20}(CO)_{40}$]$^{2-}$, respectively; each vertex represents an Os atom.*

Crystalline $[Os_6(CO)_{18}].CHCl_3$ has a bicapped tetrahedral Os_6 core like its unsolvated analogue, but also exhibits weak O····H and O····Cl contacts with the chloroform solvate molecule [64]. Both $[AsPh_4]_2[Os_{17}(CO)_{36}]$ and $[P^nBu_4]_2[Os_{20}(CO)_{40}]$ can be prepared by vacuum pyrolysis of $[Os(CO)_{10}(MeCN)_2]$ and have been characterized by X-ray crystallography. In the former anion, a trigonal bipyramidal core of 14 osmium atoms is capped by 3 extra osmium atoms (Fig. 2). The latter anion consists of a symmetrical, tetrahedral cubic close-packed core of 20 osmium atoms [65].

5.8.2 Clusters with N- and P-donor ligands

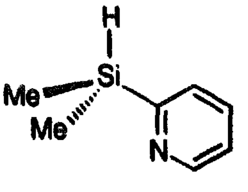
The compound $[H_2Os_3(CO)_{10}(NH_3)]$ is obtained from the reaction of solid $[H_2Os_3(CO)_{10}]$ with ammonia [62]. The three related clusters $[Os_3(CO)_{10}H(\mu_2\text{-}H)(PMe_2H)]$, $[Os_3(CO)_{10}(\mu_2\text{-}H)(\mu_2\text{-}PMe_2)]$ and $[Os_3(CO)_9(\mu_2\text{-}H)_2(\mu_3\text{-}PMe)]$, in which the phosphorus ligands adopt different bonding modes, have been structurally characterized [66]. The X-ray crystal structures of the triosmium clusters $[Os_3(CO)_{11}\{PPh_2(C_6H_4X\text{-}2)\}]$ (X = NH_2, NHC(O)Ph, CHO, $CH{=}NNHC_6H_3(NO_2)_2$-2,4) confirm that in each case the phosphine ligand bonds in a monodentate manner to a single osmium centre. In contrast, the phosphine ligand in $[Os_3(CO)_9(\mu\text{-}H)\{\mu_2\text{-}PPh_2(C_6H_4CO\text{-}2)\}]$ (**30**) adopts a more complex binding mode. The hydride is not actually located by X-ray diffraction, however, it is believed to bridge Os(1) and Os(2) [67].



(**30**)

5.8.3 Clusters with other ligands

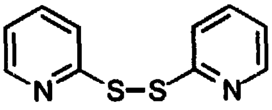
The compound $[(\mu\text{-}H)_2Os_3(CO)_{10}(\mathbf{31})_2]$, prepared from $[(\mu\text{-}H)_2Os_3(CO)_{10}]$ and (**H31**), has been characterized crystallographically; each coordinated $[\mathbf{31}]^-$ ligand bonds to one osmium atom in an η^1-manner *via* a single Si–Os bond. A range of other clusters containing similarly bound ligands of the form $(2\text{-}BrC_6H_4)CH_2Si(CH_3)_{2-n}H_n$ have also been prepared [68].



(**H31**)

The compound $[H_2Os_3(CO)_{10}(H_2S)]$ can be prepared by the reaction of solid $[H_2Os_3(CO)_{10}]$ with gaseous hydrogen sulfide. On dissolution in dichloromethane, the product transforms to the known cluster $[H_2Os_3(CO)_9S]$ [62]. The cluster $[Os_3(CO)_{10}(MeCN)_2]$ reacts with 2,2'-dipyridyldisulfide (**32**) to give a number of mono-, di- and tri-osmium fragments (**33** – **37**) containing pyS moieties adopting a variety of bonding modes [69]. $[Os_3(CO)_{10}(MeCN)_2]$ also reacts with the phenylthioureas (**H38**) and (**H39**) to give the triosmium clusters (**40**) in which the thioureate sulfur bridges two osmium atoms. Photolysis of (**40**) affords (**41**) [70].

Oxidative fluorination of $[Os_3(CO)_{12}]$ by XeF_2 in anhydrous HF gives $[Os(CO)_4F_2]$, as well as minor amounts of $[Os(CO)_5F]^+$, $[(CO)_4FOs(\mu\text{-}F)Os(CO)_3F_2]$ and $[(CO)_4FOs(\mu\text{-}F)Os(CO)_4F]^+$ [71].



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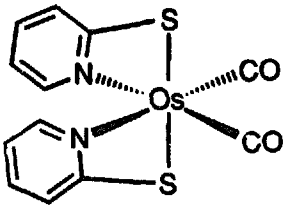

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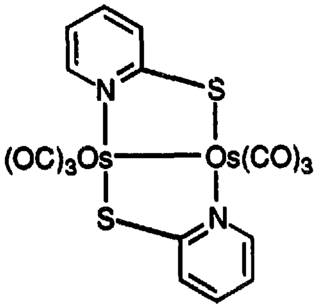

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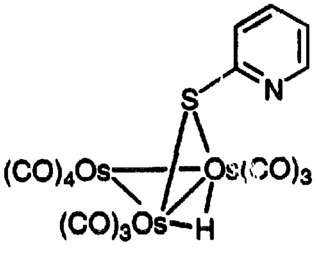

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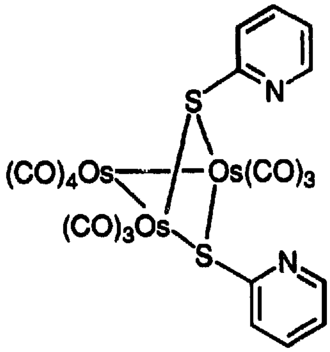

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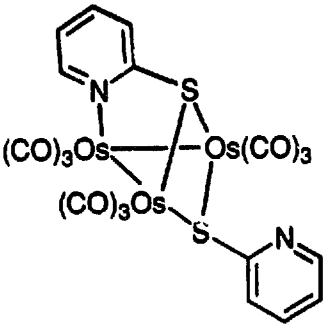

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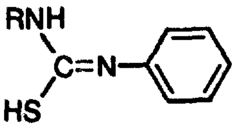
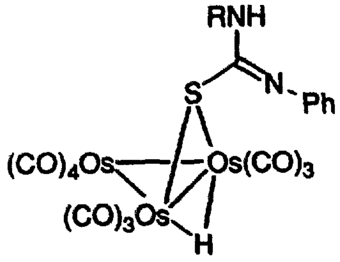
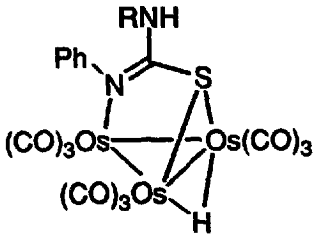


(**H38**) R = H; (**H39**) R = Ph



(**40**)



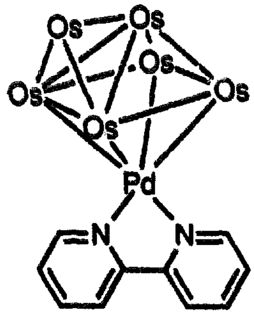
(**41**)

5.8.4 *Clusters containing other transition metals*

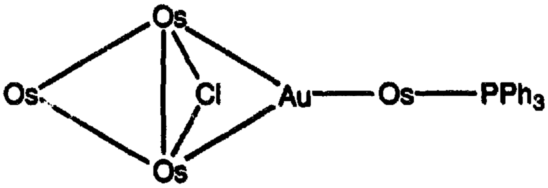
One-electron reduction of the bipyrimidine bridged cluster $[Os_3(CO)_{10}(\mathbf{20})Re(CO)_3Br]$ to give the radical anion $[Os_3(CO)_{10}(\mathbf{20})Re(CO)_3Br]^{\cdot-}$ is fully reversible, and is accompanied by retention of the cluster structure owing to the singly occupied MO being ligand-based. In contrast, the radical anion derived from reduction of $[Os_3(CO)_{10}(\mathbf{20})]$ undergoes irreversible cleavage of an Os–Os(**20**) bond to give an isomeric radical anion [72].

The cluster $[Os_6Pd(CO)_{18}(bpy)]$ (**42**) has been isolated from the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $[Pd(bpy)(O_2CMe)_2]$, and has been characterized by X-ray crystallography. The cluster core is a monocapped octahedron, with the palladium occupying one vertex of the octahedron [73].

$[Os_4(\mu\text{-}Cl)(CO)_{13}]^-$ reacts with $[Au(PPh_3)]^+$ to give $[Os_3\{\mu\text{-}AuOs(CO)_4(PPh_3)\}(\mu\text{-}Cl)(CO)_{10}]$ (**43**), the first known, crystallographically characterized example of an $\{Os(CO)_4\}$-fragment being inserted in a gold-phosphine bond. The previously reported clusters $[Os_3\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Cl)(CO)_{10}]$ and $[H_3Os_4\{\mu\text{-}Au(PPh_3)\}(\mu\text{-}Cl)(CO)_{12}]$ have also been isolated from the reaction mixture [74].

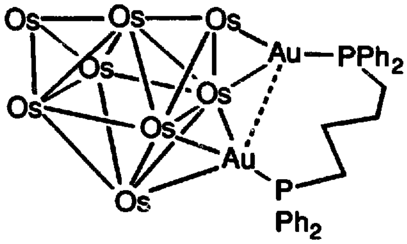


(**42**)



(**43**)

The reaction of $[N(PPh_3)_2]_2[Os_8(CO)_{22}]$ with the dinuclear chelating diphosphine complex $[Cl_2Au_2L]$ (L = dppm, dppe, dppb) in the presence of excess halide acceptor $TlPF_6$ affords the neutral digold cluster $[Os_8(CO)_{22}(Au_2L)]$ almost quantitatively. The cluster has been characterized crystallographically for the case (**44**) where L = dppb. The Os_8 core is a bicapped octahedron, though unlike the previously reported structure of $[Os_8(CO)_{22}(AuPPh_3)_2]$, the two gold atoms are in non-equivalent environments. A second isomer of [$Os_8(CO)_{22}(AuPPh_3)_2$], believed to have an asymmetric structure similar to that of (44), is also reported [75].



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