5. Osmium 1993

Michael D. Ward

CONTENTS

INTRODUCTION

This review covers the coordination chemistry and some cluster chemistry of osmium published in the calendar year 1993. It is not completely comprehensive in that coverage has been restricted to the more well-known journals. The emphasis is on coordination chemistry and development of new cluster frameworks; organometallic compounds, and clusters whose primary interest is in coordinated organic fragments, are not included as they are covered elsewhere.

5.1 OSMIUM(VIII)

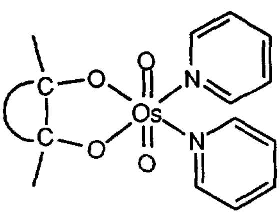
Osmium tetraoxide, OsO_4, exhibits high stereoselectivity in the dihydroxylation of olefins with a cinchona alkaloid co-catalyst [1,2], although the exact mechanism is disputed [3]. The mechanism of asymmetric dihydroxylation by OsO_4 may be stepwise rather than concerted [4]. The kinetics of oxidation of indoles by OsO_4 were examined [5], and the valence photo-electron spectrum of OsO_4 has been analysed [6].

The equilibrium geometries of OsO_4, OsO_3F_2, OsO_2F_4 and OsF_8 in the gas phase were predicted by *ab initio* quantum mechanical calculations, and generally agree well with structural and vibrational spectroscopic experimental data [7]. A new preparation for OsO_3F_2 has been described;

the molecule is thought to be trigonal bipyramidal (D_{3h}) in the gas phase, but the crystal structure shows a polymeric chain of *fac*-OsO_3F_3 units with non-linear Os—F—Os bridges. The crystal structure of OsO_2F_4 consists of a helical chain-like arrangement of discrete molecules in which there is some O/F disorder, but the *cis*-O_2F_4 (C_{2v}) arrangement was established spectroscopically [8]. OsO_2F_4 was also prepared from OsO_4, HF and KrF_2, a method which was originally thought to afford $OsOF_6$. Spectroscopic and theoretical studies confirmed the *cis* (C_{2v}) structure [9].

5.2 OSMIUM(VI)

Osmium tetraoxide adds to fullerenes in the presence of co-ligands such as pyridine to give osmylated products $C_x\{OsO_4(py)_2\}$ with the general structure (**1**). Pendant functional groups on the back of the pyridine ligands which bind to quartz allow formation of C_{60} monolayers (**2**) tethered to quartz and Ge/Si substrates; these monolayers have been investigated by X-ray diffraction [10]. Asymmetric bis-osmylation of C_{60} yields enantiomerically enriched chiral products containing different amounts of the isomers of $C_{60}\{OsO_4(py)_2\}_2$ [11]. Due to the lower symmetry of C_{70} there are four possible sites at which osmylation can occur. However reaction of C_{70} with one or two equivalents of OsO_4/pyridine to give $C_{70}\{OsO_4(py)_2\}_x$ (x = 1, 2) yielded fewer isomers than theoretically possible. The observed regioselectivity agrees with *ab initio* quantum-mechanical calculations on C_{70}, which predict that reaction will preferentially occur across the double bonds at the most curved part of the surface to afford maximum relief from strain [12].



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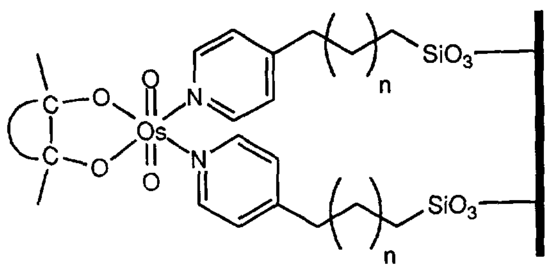
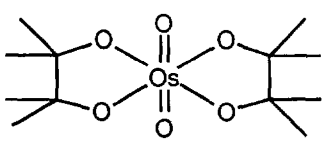


(2)

The IR spectra of oxo-osmium(VI) esters such as (3) and (4) have been re-interpreted with the aid of ^{18}O-substitution [13]. The crystal structures of (5) and (6) have been determined [14].



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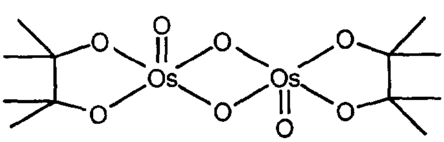

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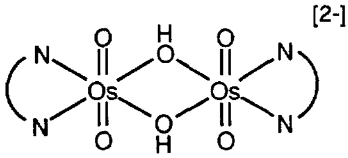

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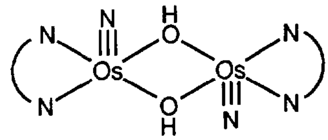

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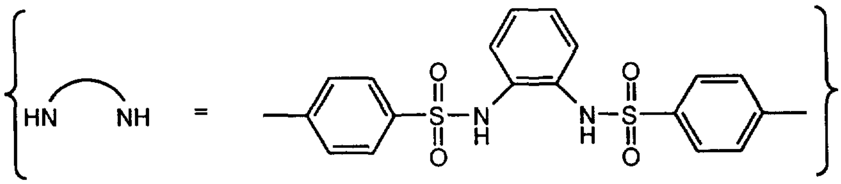


Reaction of $[OsNCl_4]^-$ with 1,1,2,2-tetramethyl-ethane-1,2-diamine (H_2L) affords *trans* $[OsN(H_2L)_2Cl]^{2+}$, which may be converted to $[OsN(H_2L)_2]^{3+}$. This in turn undergoes $3H^+/3e$ reduction of the $Os^{VI}N$ triple bond to give Os^{III}—NH_3. $[OsN(H_2L)_2]^{3+}$ may also be deprotonated to give $[OsN(H_2L)(HL)]^{2+}$ with a coordinated amido nitrogen. The crystal structures and electrochemical properties of the complexes are described [15] (see also ref. 30). *Fac*-$[OsNCl_3(dpae)]$ (dpae = $Ph_2AsCH_2CH_2AsPh_2$) has an octahedral crystal structure and is phosphorescent at 298 K and 77 K [16].

In $[OsL_3]$ (H_2L = 2-amino-4-methylphenol or 2-amino-4-^{t}butylphenol), the dianionic ligands act as *N,O*-chelates [17]. *Ab initio* quantum-mechanical calculations on $[Os(PR_3)_3(H)_5]^+$ suggest that they are best described as Os(VI)-pentahydrides with dodecahedral coordination; over 20 other possible isomers were evaluated [18]; see also ref. [21].

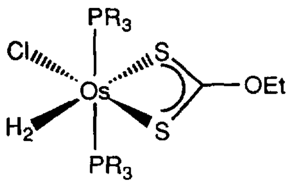
5.3 OSMIUM(V)

A gas-phase electron diffraction study of OsF_5 at 120°C has been carried out and reveals the presence of a mixture of dimeric and trimeric species [19]. The diffuse-reflectance UV-VIS spectrum of OsF_5 has been examined [20].

5.4 OSMIUM(IV)

An *ab initio* quantum mechanical study on the complexes $[Os(PR_3)_3(H)_4]$ indicates that the most stable structure is a pentagonal bipyramid with a PH_4 pentagonal plane and two axial phosphine ligands. The general features of 7-coordination were studied and different descriptions of the complexes were evaluated [21] (see also ref. 18). The heats of protonation of the metal in $[Os^{II}(PR_3)_4(H)_2]$ and $[Os^{IV}(PR_3)_3(H)_4]$ by CF_3SO_3H in 1,2-dichloroethane were measured. This allowed determination of the effects of the phosphine substituents R (alkyl or alkoxy groups) on the basicity of the metal [22]. Reaction of $[Os(NH_3)_5(\eta^2\text{-}H_2)]^{2+}$ with $[Cp_2Fe]^+$ afforded the 7-coordinate Os(IV) complex $[Os(NH_3)_5(H)(solvent)]^{3+}$. Similarly, the 7-coordinate species

$[Os(en)_2(py)_2(H)]^{3+}$ and $[Os(NH_3)_5(H)\{Fe(CN)_6\}]^-$ were prepared. These complexes formally obey the 18-electron rule (d^4 metal ion plus 7 lone-pair donors) [23]. The Os(IV)-dihydride $[Os(H)_2Cl_2(P^iPr_3)_2]$ binds H_2 reversibly to give a species of empirical formula $[Os"H_4"Cl_2(P^iPr_3)_2]$. The ^1H NMR spectrum is consistent with either of the two formulations $[Os(H_2)_2Cl_2(P^iPr_3)_2]$ [i.e. Os(II) with two neutral η^2-H_2 ligands] or $[Os(H_2)(H)_2Cl_2(P^iPr_3)_2]$ [i.e. Os(IV) with two hydrides and one neutral η^2-H_2 ligand], and the crystal structure cannot distinguish between the two possibilities. Traces of $[Os(H_2)(H)_3Cl(P^iPr_3)_2]$ were also detected [24]. Reaction of $[Os(H)_2Cl_2(P^iPr_3)_2]$ with $[EtOCS_2]^-$ and $[MeCOS]^-$ afforded the first Os^{IV}–dihydride complexes with sulfur ligands such as (7) and (8) [25].



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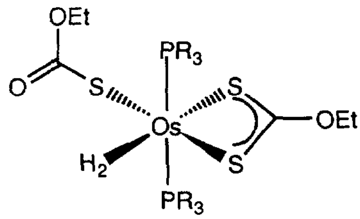

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Reaction of OsO_4 with $[Mo(=NAr)_2(O^tBu)_2]$ results in exchange of oxo and imido groups to give $[Os^{VIII}(=NAr)_2O_2]$ and $[MoO_2(O^tBu)_2]$. This Os(VIII) species may be converted to Os^{IV}-imido complexes by reactions involving loss of the two oxo groups; for example it reacts with phosphines R_3P according to equation (i) [26].

$$[Os^{VIII}(=NAr)_2O_2] + 4\,R_3P \rightarrow [Os^{IV}(=NAr)_2(R_3P)_2] + 2\,R_3P{=}O \qquad \text{(i)}$$

The metal-centred luminescence of *trans*-$[OsO_2(Me_4\text{-cyclam})]$ may be quenched in water by a variety of moderately reducing ions (nitrite, azide, halide) or aqua-complexes [of Fe(II), Co(II) and Ce(III)]. The results were used to estimate the self-exchange rate constants for the Q^+/Q couples (where Q is the quenching species) [27]. Reaction of *trans*-$[Os^{VI}O_2(porph)]$ (porph = dianion of tetraphenylporphyrin or octaethylporphyrin) with arylthiols (RSH) affords the new mercaptide complexes *trans*-$[Os^{IV}(porph)(SR)_2]$. If the porphyrin or the group R is particularly sterically cumbersome, $[Os^{III}(porph)(SR)]$ may be formed instead. Other routes to the same molecules were also developed [28].

5.5 OSMIUM(III)

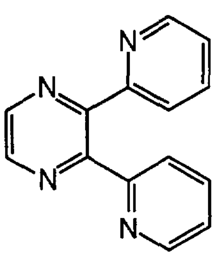
Oxidation of *cis*-$[Os^{II}(Et_2NCS_2)_2(PPh_3)_2]$ with Ce(IV) affords the *trans* Os(III) product $[Os(Et_2NCS_2)_2(PPh_3)_2]^+$; re-reduction with hydrazine results in formation of the metastable *trans* isomer of $[Os^{II}(Et_2NCS_2)_2(PPh_3)_2]$. All complexes were crystallographically characterised. Solution equilibrium data suggest that in the Os(II) state the *cis* S_4P_2 geometry is preferred, whereas in the Os(III) state the *trans* geometry is preferred. The electrochemical properties of all of the complexes, the magnetic properties of the Os(III) complexes, and the isomerisation rates were examined [29]. The cation $[Os(H_2L)_2Cl_2]^+$ (H_2L = 2,3-diamino-2,3-dimethylbutane) undergoes a reversible, pH-dependent Os(III)/Os(IV) couple which involves deprotonation of one coordinated $-NH_2$ group in the Os(IV) state to give a coordinated amide ligand [30]; see also ref. [15]. The compound $[Os(py\text{-}S)_2(PPh_3)_2][PF_6].(H_2O)_n$ (py-SH = pyridine-2-thiol) are the first Os(III) complexes with this ligand. For n = 1, the green complex has *cis-cis-trans*–$OsN_2S_2P_2$ geometry; for n = 0, the red complex has *trans-trans-trans*–$OsN_2S_2P_2$ geometry. The different isomers arise by preservation of different geometries in the Os(II) starting material in solution. Both isomers give rhombic EPR spectra; the ligand-field transitions were also assigned [31]. Variable-temperature magnetic measurements on $[Os_2Cl_2L_4]$ (HL = 2-phenylbenzoic acid) indicate that several different electronic contributions combine to give the observed properties [32]. The $\{Os(NH_3)_5\}^{3+}$ fragment can coordinate to the N7 and C8 positions of purine rings. The structures and spectroscopic properties of the resulting complexes were compared with those of the Ru(III) analogues [33].

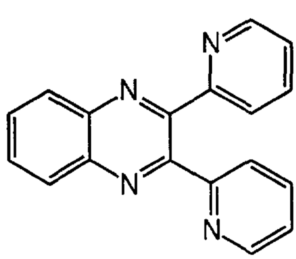
Measurements of the kinetics of reduction of $[Os(CN)_6]^{3-}$ by ascorbic acid and 1,2- and 1,4-dihydroxybenzene afforded a self-exchange rate constant for $[Os(CN)_6]^{3-/4-}$ of 1.7×10^4 dm^3 mol^{-1} sec^{-1}. Inclusion of the dihydroxybenzenes in a β-cyclodextrin host slows down the reaction [34]. The electron-transfer cross-reaction rate-constants for oxidation of $[Fe(4,7\text{-}Me_2phen)_3]^{2+}$ at a poly-$[Os(bpy)_2(vpy)_2]^{3+}$ polymer surface were examined as a function of solvent and electrolyte concentration [35].

5.6 *OSMIUM(II)*

5.6.1 *Complexes with polypyridine-based ligands*

The dinuclear complexes $[\{(bpy)_2Os\}_2(\mu\text{-}L)]^{4+}$ [L = (**9**), (**10**), (**11**)] were thoroughly characterised by electrochemistry, UV-VIS spectroscopy, and a spectro-electrochemical study of all of the possible oxidation states; as well as Os(II)/Os(III) couples there are several ligand-based reductions. The mixed-valence Os(II)/Os(III) species show inter-valence charge transfer bands in the electronic spectra and belong to class II of the Robin and Day classification [36]. The trinuclear complexes $[\{(bpy)_2Ru(\mu\text{-}L)\}_2OsCl_2]^{4+}$ [L = (**9**), (**10**), (**11**)] were also prepared and likewise subjected to a rigorous electrochemical and UV-VIS spectroscopic investigation which permitted correlation of electrochemical and spectroscopic properties [37].


(**9**)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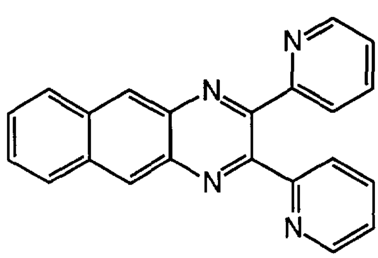
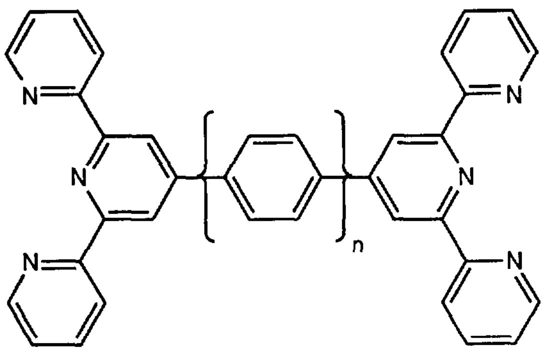
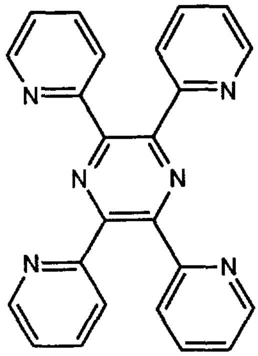

(**11**)

Many mixed-metal dinuclear Os(II)/Ru(II) complexes have been prepared with conjugated bridging ligands containing two binding pockets, in order to evaluate the efficiency of photoinduced Ru(II)→Os(II) intramolecular energy-transfer as a function of metal-metal separation and bridging ligand structure. Such complexes include $[(tterpy)Ru(\mu\text{-}L)Os(tterpy)]^{4+}$ [tterpy = 4'-*p*-tolyl-terpyridine; L = (**12**)–(**14**)] [38] and $[(bpy)_2Ru(\mu\text{-}L)Os(bpy)_2]^{4+}$ [L = (**15**), ref. 39; L = (**16**), ref. 40]. Mono- and dinuclear Os(II) complexes with the same ligands were also examined for their luminescence and electrochemical properties [38–40].



(**12**), n = 0; (**13**), n = 1; (**14**), n = 2



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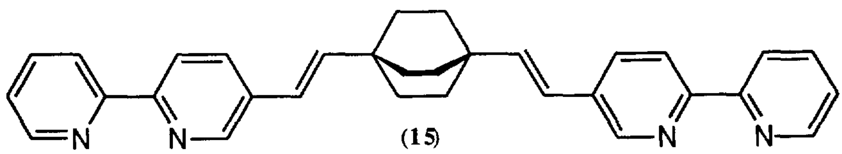

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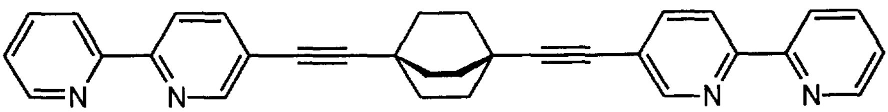
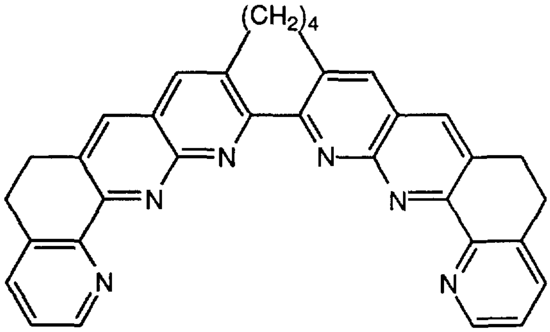


(**16**)

A series of mono-, di- and trinuclear complexes of the potentially bridging ligand (**17**) were prepared; these include $[Os(\mathbf{17})_2]^{2+}$, $[Os(terpy)(\mathbf{17})]^{2+}$, $[(terpy)M(\mu\text{-}\mathbf{17})M'(terpy)]^{4+}$ (M, M' = Ru or Os) and $[(terpy)Ru(\mu\text{-}\mathbf{17})Os(\mu\text{-}\mathbf{17})Ru(terpy)]^{6+}$. Electrochemical studies indicated strong metal-metal interactions across the bridging ligand, and the luminescence properties of the complexes were also examined [41]. A general synthetic route to dinuclear complexes of the type $[(L_t)_2Ru(\mu\text{-}L_b)Os(L_t')_2]^{4+}$ [L_t, L_t' are terminal didentate ligands such as phenanthroline or a substituted bipyridine; the bis-didentate bridging ligand L_b is bipyrimidine or (**9**)] has been developed; the diastereomeric pairs were separated chromatographically and characterised separately [42]. For the complexes $[Os(bpy)_2(\mathbf{18})]^{2+}$ and $[(bpy)_2Ru(\mu\text{-}\mathbf{18})Os(bpy)_2]^{4+}$, ^1H NMR spectroscopy was used to perform a detailed conformational analysis of the flexible bridging ligand; d^8-bpy was used for the terminal ligands to simplify the ^1H NMR spectra. The metal-metal interaction in the dinuclear complex was studied by electrochemical, UV-VIS spectroscopic and luminescence methods [43].



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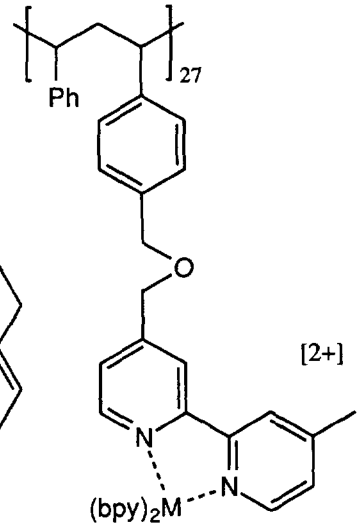
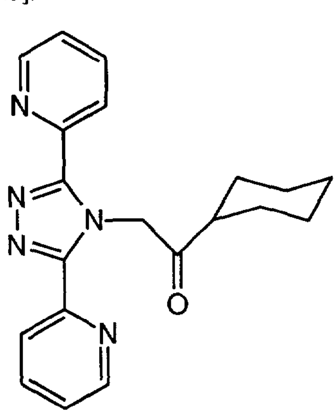


(19)

The polymeric complex (**19**) was prepared with a Ru(II):Os(II) ratio of approximately 22:5. Energy transfer from an excited-state Ru(II) centre could occur to an Os(II) centre only if the two sites were adjacent, although this may be either within a strand or between strands [44]. The electrochemical, spectroscopic and luminescence properties of $[(bpy)_2Os(\mathbf{20})]^{2+}$ and $[(bpy)_2Os(\mu\text{-}\mathbf{21})Os(bpy)_2]^{4+}$ were studied. There is no electrochemical interaction between the metals in the dinuclear complex; the ligand-based luminescence is quenched in each case by coordination to a metal, only the Os-based emission from the ^{3}MLCT excited state being observed [45].



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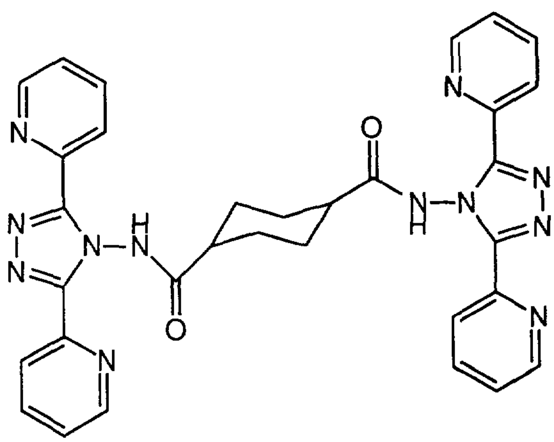
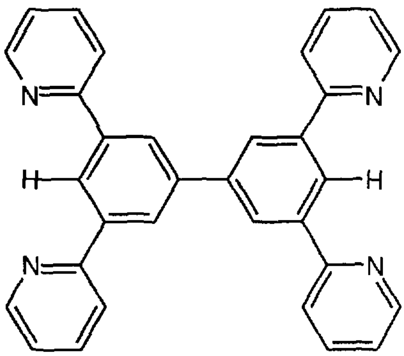
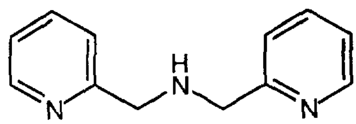


(21)

The unusually large electrochemical interaction across the cyclometallating bridging ligand in $[(\text{tterpy})Os(\mu\text{-}\mathbf{22})Os(\text{tterpy})]^{2+}$ (tterpy = 4'-*p*-tolyl-terpyridine) results in a well-defined mixed-valence state with a strong inter-valence charge transfer transition, even though the metals are 11Å apart [46]. In $[Os(bpy)_2(\mathbf{23})]^{2+}$, ligand (**23**) coordinates *via* pyridyl and amine residues with a pendant pyridyl group: the complex is proposed as a building block for polynuclear luminescent complexes [47].



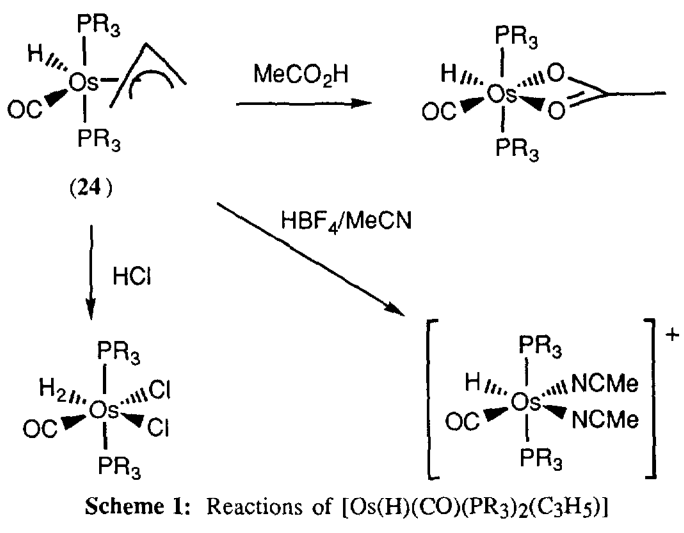
($H_2$22)



(23)

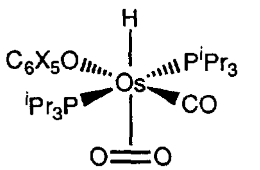
5.6.2 Other coordination complexes

The hydride/hydrogen complex $[Os(PP_3)(H_2)(H)]^+$ [$PP_3 = P(CH_2CH_2PPh_2)_3$] is an efficient catalyst precursor for reduction of α,β-unsaturated ketones by H-atom transfer from secondary alcohols. The catalytic process was studied in detail [48]. Protonation of $[Os(H)(CO)(py\text{-}S)(PPh_3)_2]$ affords $[Os(H_2)(CO)(py\text{-}S)(PPh_3)_2][BF_4]$, which was

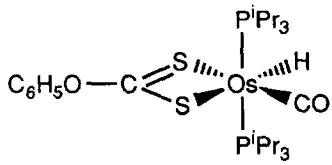


Scheme 1: Reactions of $[Os(H)(CO)(PR_3)_2(C_3H_5)]$

crystallographically characterised and has the phosphine ligands mutually *trans*; despite its acidity (pK_a about −1) it is stable to H_2 loss [49]. Reaction of [Os(H)(Cl)(CO)(PR_3)$_2$] with C_3H_5MgBr affords the rigid allyl complex (**24**), which is a useful starting material for a variety of Os(II) complexes *via* loss of the allyl ligand (Scheme 1) [50]. [Os(H)(EC_6X_5)(CO)(P^iPr_3)$_2$] were prepared in good yield from [Os(H)(Cl)(CO) (P^iPr_3)$_2$] and $NaEC_6X_5$ (E = O, S; X = H, Cl, F). In these the phenolate or thiophenolate derivative is generally monodentate, but pentachlorophenolate can act as an *O,Cl*-didentate chelate. Reaction of these with O_2 affords stable O_2 adducts such as (**25**); reaction with CS_2 results in insertion into the E–Os bond to afford (**26**) [51].

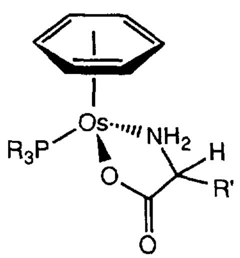


(**25**)



(**26**)

Oxidative addition of the group 14 hydrides HER_3 (E = Si, Ge) to [Os(CO)$_2$(PPh_3)$_3$] affords the Os(II) complexes [Os(ER_3)(H)(CO)$_2$(PPh_3)$_2$], of which two examples [ER_3 = $SiEt_3$ or Ge(*p*-tolyl)$_3$] were crystallographically characterised; further addition of a second equivalent of HER_3 gives Os(IV) dihydrides [52]. [Os{NHC(O)Ph}$_2$(CO)$_2$(PPh_3)$_2$] has a *cis*-carbonyl, *trans*-phosphine geometry in which benzamide acts as an anionic *N*-donor ligand [53]. The *N,N'*-diphenylamidines PhN=C(R)–NHPh were reacted with [Os(H)$_2$(CO)(PPh_3)$_3$], [Os(H)(Cl)(CO)(PPh_3)$_3$] and [Os(CF_3CO_2)$_2$(CO)(PPh_3)$_2$] to prepare an extensive series of complexes in which the deprotonated diphenylamidinates act as didentate chelates analogous to triazenide ligands [54]. The crystal structure of *trans*-[Os(dppe)$_2$Cl$_2$] has been determined [55]. Reaction of α-amino-acids with [(η^6-C_6H_6)Os(PR_3)I_2] to give products such as (**27**) is stereoselective; for example with L-alanine only one diastereoisomer results [56].



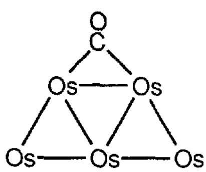
(**27**)

Complexes of the {$(NH_3)_5Os$}$^{2+}$ fragment with π-acidic ligands such as η^2-acetone, MeCN and η^2-dimethyluracil were prepared. The presence of the {$(NH_3)_5Os$}$^{2+}$ fragment in solution may arise from reductive elimination of water from [$Os^{IV}(NH_3)_5(OH)(H)$]$^{2+}$ although this is not certain [57]. Complexation of anilines to the {$(NH_3)_5Os$}$^{2+}$ fragment results in dearomatization of the ligand, yielding 3-aminocyclohexenes [58]. Quantum mechanical calculations on $[Os(NH_3)_4(X)(\eta^2\text{-}H_2)]^+$ (X = acetate or some other monodentate ligand) indicate that the H—H bond should be unusually weak, which is in accord with experimental observations that the bond is rather long [59]. Homo- and hetero-metallic double bonds between metals have been observed in porphyrin dimers such as [(OEP)Os=Ru(OETAP)], $[Os(OETAP)]_2$ and $[Os(OEP)]_2$ ($OETAPH_2$ = octaethyl-tetraazaporphyrin) [60].

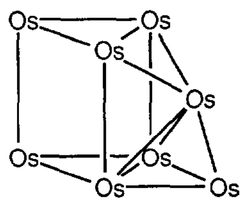
5.7 *OSMIUM CARBONYL CLUSTERS*

5.7.1 *Clusters with only carbon-donor and hydride ligands*

Reaction of the activated cluster $[Os_3(CO)_{10}(MeCN)_2]$ with the dihydrides $[H_2\{Os(CO)_4\}_n]$ (n = 1, 2, 3) allows the controlled assembly of high nuclearity clusters (up to 9 Os atoms) [61]. $[Os_5(CO)_{18}]$ (**28**), which is an intermediate in the conversion of $[Os_5(CO)_{16}]$ (trigonal bipyramid) to $[Os_5(CO)_{19}]$ (bow-tie structure), has an unusual planar raft-like core of Os atoms [62]. Reduction of $[Os_3(CO)_{12}]$ with potassium/benzophenone ketyl affords $[Os_3(CO)_{12}]^{2-}$, which reacts further with $[Os_3(CO)_{12}]$ to give, according to conditions, $[H_2Os_4(CO)_{13}]$, $[H_4Os_4(CO)_{12}]$, $[H_2Os_3(CO)_{10}]$, $[H_2Os_5(CO)_{16}]$ or $[H_2Os_7(CO)_{20}]$. $[H_2Os_4(CO)_{13}]$ was also prepared by reaction of $[Os_3(CO)_{12}]^{2-}$ with $Os(CO)_5$ and has a tetrahedral structure [63]. Facile preparations of the isocyanide complexes $[Os_3(CO)_{12\text{-}n}(CNR)_n]$ (n = 1, 2, 3), by deoxygenation of phosphine imides, were developed [64]. $[Os_8C(CO)_{22}]$ (**29**) was crystallographically characterised; the Os_8 core structure comprises a mono-capped trigonal prism fused with a tetrahedron, with the carbide in the trigonal prismatic cavity [65].



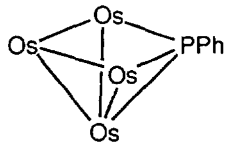
(**28**)



(**29**) Os_8-core only shown

5.7.2 *Clusters with N- and P-donor ligands*

The preparations and structures of $[Os_5(CO)_n(PMe_3)]$ have been reported: for n = 18, the cluster has a bow-tie structure; for n = 17, a planar raft structure; and for n = 15, a trigonal bipyramidal structure with the PMe_3 ligand attached to either axial or equatorial Os atoms [66]. The phosphinidene-stabilised cluster *nido*-$[Os_4(CO)_{10}(\mu_3\text{–}PPh)]$ (**30**), which obeys conventional electron-counting rules for clusters (7 skeletal electron-pairs affording a structure based on an octahedron), is proposed as a model for a catalytically-active Os metal surface [67].

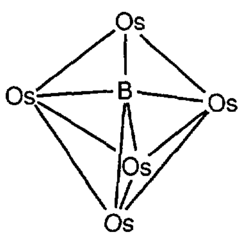


(30)

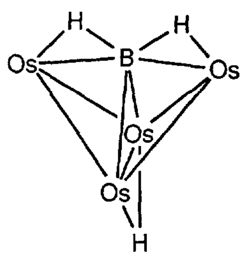
The series of ligands 2-pyridyl-diphenylphosphine, bis-(2-pyridyl)-phenylphosphine and tris-(2-pyridyl)-phosphine have been attached to triosmium cluster cores. In $[Os_3(CO)_{11}L]$ and $[Os_3(CO)_{10}L_2]$ the ligands are all monodentate *P*-donors; in $[Os_3(CO)_{10}(\mu\text{-}L)]$ the ligands act as *N,P*-didentate ligands with a pyridyl residue attached to one metal and the phosphine to another, and undergo a fluxional process in which the *P*-donor is fixed but the *N*-donor rapidly switches between the other two sites [68,69]. In $[Os_3(CO)_{11}L]$ and $[Os_3(\mu\text{-}H)_2(CO)_9L]$, where L is the arsinophosphazene $(CF_3)_2As{-}N{=}PPh_3$, L acts as a monodentate *N*-donor ligand and assumes a high degree of delocalisation over the As–N=P segment on coordination [70]. The triphosphazene ligand $(CF_3)_2P{-}N{=}P(CF_3)_2{-}N{=}PPh_3$ acts as a monodentate *P*-donor ligand in $[Os_3(CO)_{11}L]$ with the PNPNP fragment highly delocalised [71].

5.7.3 *Clusters with other ligands*

The preparations and crystal structures of $[HOs_5(CO)_{16}B]$ (**31**) and $[HOs_4(CO)_{12}BH_2]$ (**32**) have been reported [72]. The compound $[(CO)_4OsSi\{(S\text{-tolyl})(Ru\{Cp^*\}\{PMe_3\}_2)\}]$ (**33**) may exist in three canonical forms (a – c; Scheme 2), of which (c) is the most likely on the basis of structural and IR spectroscopic data [73].

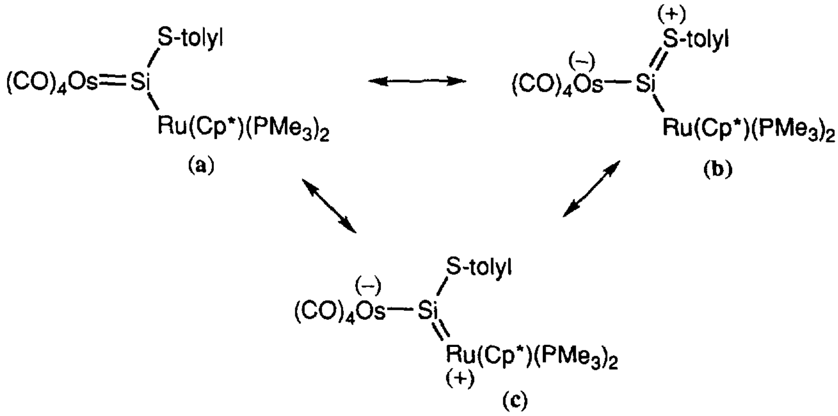


(31)



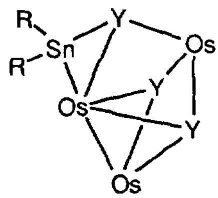
(32)

A variety of new osmium clusters containing both tin and chalcogen (S, Se) atoms, of which (**34**) and (**35**) have been structurally characterised, have been prepared; the R groups are highly sterically hindering 2,4,6-trisubstituted aryl rings [74]. $[Os_5(\mu\text{-}H)(CO)_{15}(\mu_3\text{-}SePh)]$ (**36**) comprises a trigonal bipyramid of Os atoms, with two broken Os—Os edges broken to

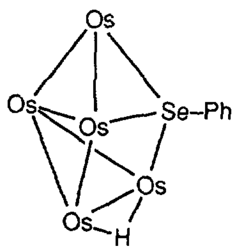


Scheme 2: Canonical forms of (**33**)

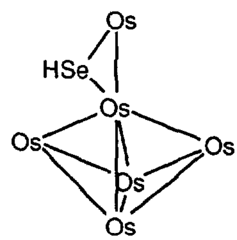
accommodate the Se bridge; $[Os_6(\mu\text{-}H)(CO)_{18}(\mu_2\text{-}SeH)]$ (**37**) comprises a trigonal bipyramid of Os atoms with an equatorial 'spike', and the SeH fragment bridging the 'spike' Os—Os bond [75]. The compound $[Os_3(CO)_{10}(MeCN)_2]$ reacts with 2,4,6-trimercapto-1,3,5-triazene (H_3L) to give $[\{Os_3(CO)_{10}(\mu\text{-}H)\}_3(\mu_3\text{-}L)]$ (**38**) which comprises three linked Os_3 triangles, each with a thiolate and a hydride bridging a common edge [76].



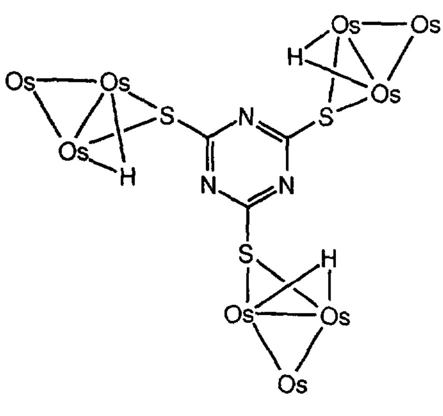
(**34**), Y = S; (**35**), R = Se



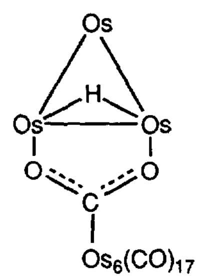
(**36**)



(**37**)



(**38**)

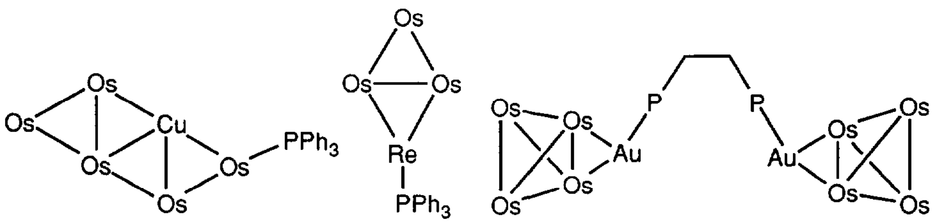


(**39**)

The anion $[Os_3(CO)_{11}(\mu\text{-}H)]^-$ reacts with O_2 and $[Os_6(CO)_{18}]$ in solution to give the unusual cluster $[(\mu\text{-}H)Os_3(CO)_{10}(\mu_2\text{-}O_2C)Os_6(CO)_{17}]^-$ (**39**) with a bridging carboxylate group. The C atom of the carboxylate originates from a CO ligand of $[Os_6(CO)_{18}]$ [77]. The $(CF_3)_2NO$ radical acts as an axial monodentate *O*-donor ligand in $[Os_3(CO)_{10}(\mu\text{-}H)L\{(CF_3)_2NO\}]$ (L = PPh_3, $AsPh_3$, $SbPh_3$). The CF_3 groups are inequivalent at low temperature due to restricted rotation about the N–O bond [78]. A mechanistic study of the reactions of $[Os_3(CO)_{10}(CNPr)(NCMe)]$ with Brønsted acids in CH_2Cl_2 was undertaken, and two crystal structures of products $[Os_3(CO)_{10}(\mu\text{-}H)(CNPr)(\eta^1\text{-}OCOR)]$ determined [79]. The kinetics and mechanisms of ligand substitution reactions of $[Os_3(CO)_{10}LX]^-$ (L = PPh_3, CO; X^- = cyanate, halide) were examined [80].

5.7.4 *Clusters containing other transition metals*

The clusters $[(\mu\text{-}H)Os_5Cu(CO)_{18}(PPh_3)]$ (**40**) [81], $[(Ph_3P)(CO)_3Re(\mu\text{-}H)Os_3(CO)_{11}]$ (**41**) [82] and $[\{H_3Os_4(CO)_{12}\}_2Au_2(dppe)]$ (**42**) [83] have been prepared and crystallographically characterised.



(**40**) (**41**) (**42**)

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