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COORDINATION CHEMISTRY REVIEWS

Osmium 1995

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Contents

1. Introduction

This review covers the coordination chemistry and some cluster chemistry of osmium published in the calendar year 1995. Coverage is restricted to the more well-known journals. As with earlier reviews in this series, 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. The distinction between 'coordination' and 'organometallic' compounds is sometimes difficult to draw but in general any compounds involving an Os–C bond (apart from carbonyls and cyanides) are excluded.

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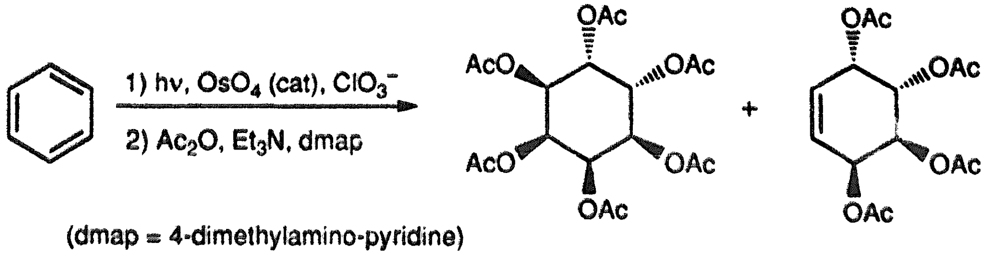
2. Osmium(VIII)

Osmium tetraoxide continues to find widespread use in organic synthesis; routine examples are not given here but two papers are of particular interest. Arenes may be converted *via* osmylation to cyclitol derivatives, following photo-excitation into the charge-transfer band of the initially-formed complex between the arene and OsO_4 (Scheme 1) [1].



Scheme 1.

Use of OsO_4 in conjunction with a specially designed cinchona-alkaloid co-catalyst allows enantioselective dihydroxylation of secondary allylic 4-methoxybenzoate esters. The co-catalyst has a pocket with recognises the 4-methoxy-benzoyl group, and has an open space by the allyl group of the substrate to allow attack of OsO_4 at only one face of the molecule [2,3]. The compound OsO_4(napy) (napy = 1,8-naphthyridine) has been crystallographically characterised and is a trigonal bipyramidal mononuclear species. The napy ligand is monodentate in an axial position; aromatic π-stacking between overlapping, parallel sections of the napy groups dominates the crystal packing. The vibrational and Raman spectra of the compound were recorded [4].

3. Osmium(VI)

3.1. Nitrido and imido complexes

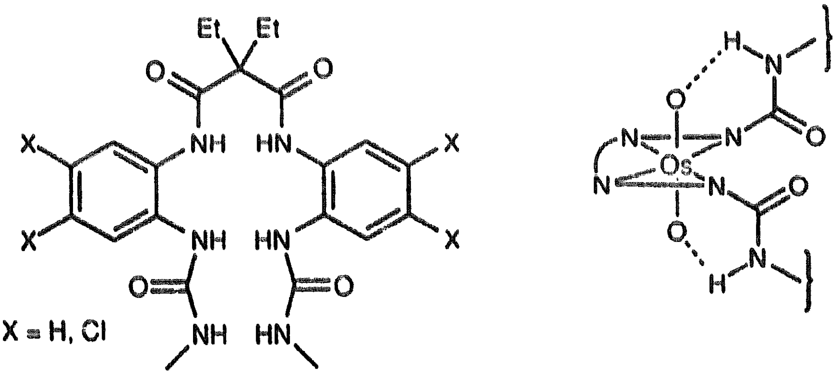
The complex cation $[Os^{VI}(terpy)Cl_2(\equiv N)]^+$ (*cis* or *trans* chlorides) reacts with Me_3NO in MeCN to give $[Os^{II}(terpy)Cl_2(NO)]^+$ (*cis* or *trans*). Although this is formally just addition of one atom of oxygen to the nitrido ligand (a 2-electron oxidation), a substantial reorganisation of internal electron density occurs with the Os^{VI} formally undergoing a four-electron reduction to Os^{II}, and the nitride (N^{3-}) formally undergoing a six-electron oxidation to N^{3+} in the nitrosyl ligand. This cannot be reversed by O-atom transfer to PPh_3. Such multiple electron-transfer reactions to a single ligand are of importance in a wide variety of areas, such as nitrogen fixation [5]. The kinetics and thermodynamic activation parameters for the slow isomerisation of $[Os^{VI}(terpy)Cl_2(\equiv N)]^+$ from the *trans*-Cl form to the *cis*-Cl form have been evaluated. In MeOH, the rearrangement occurs *via* a 7-coordinate solvent adduct [6]. A variety of nitrido-Os(VI) complexes with ancillary ligands such a bpy, terpy and phen have been prepared, such as $\mathrm{[Os(bpy)(\equiv N)Cl_3]}$, $\mathrm{[Os(bpy)(\equiv N)Cl_2(H_2O)]^+}$ and $\mathrm{[Os(terpy)(\equiv N)\ Cl(CF_3SO_3]^+}$. All have long-lived (several μs) luminescent triplet $(d_{xy}^1)(d_{\pi*}^1)$ excited states in fluid solution, with the excited states being powerful photo-oxidants [7].

A theoretical study of methane activation by the trigonal planar species $\mathrm{[Os(=NH)_3]}$ (and other tris-imido metal complexes) has been carried out. The activation energy barriers, and the effects of the nature of the metal, ligand and d-orbital occupancy on the reaction were evaluated [8].

3.2. Oxo complexes

A series of *trans*-dioxo-Os(VI) complexes, including $\mathrm{[Os(N\text{-}N)_2(CN)_2(=O)_2]}$, $\mathrm{[Os(tmeda)\ (CN)_2(=O)_2]}$ and $\mathrm{[Os(N\text{-}N)(Mes)_2(=O)_2]}$ (all with the *cis,cis,trans* geometry; N-N = a diimine ligand such as phen, bpy or a substituted derivative; Mes = mesityl) was prepared, and several were crystallographically characterised. The Os(VI)/Os(V) redox potential may be varied over a wide range depending on the ligand donor set, and the complexes with aromatic didentate diimine (N-N) ligands have long-lived luminescent excited states in fluid solution. These excited states are capable of catalysing the epoxidation of alkenes [9].

'Recognition' of the $\mathrm{\{Os(=O)_2\}^{2+}}$ fragment occurs by multi-mode coordination with tetraamidato ligands. This involves a mixture of conventional coordinative bonding, and strong hydrogen-bonding between the axial oxo groups and amide protons on the ligand (Scheme 2). The electronic and structural properties of the stabilised osmyl cation can be fine-tuned by modifying the ligand [10].



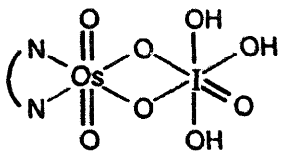
Scheme 2.

The unusual complexes $\mathrm{[(N\text{-}N)Os(=O)_2\{IO_3(OH)_3\}]}$ [(1); N-N = bpy, phen or di(2-pyridyl)amine] have been prepared and structurally characterised [11].

4. Osmium(IV)

4.1. Complexes containing hydride ligands

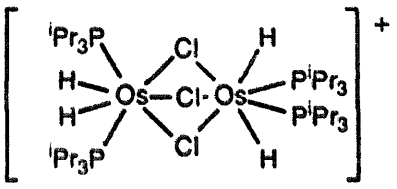
The compound $\mathrm{[Os(H)_2X_2(P^iPr_3)_2]}$ (X = halide), which has an irregular six-coordinate geometry, rapidly interconverts in solution between two isomers with C_2 and



[NN = bpy, phen, di(2-pyridyl)amine]

(1)

C_1 symmetry. Three different rearrangement mechanisms were determined and the thermodynamic activation parameters for each were quantified. The structures were calculated and could be rationalised on the basis of competition between steric interactions between the phosphine and halide groups, and the bonding preferences of the halide ligands [12].



(2)

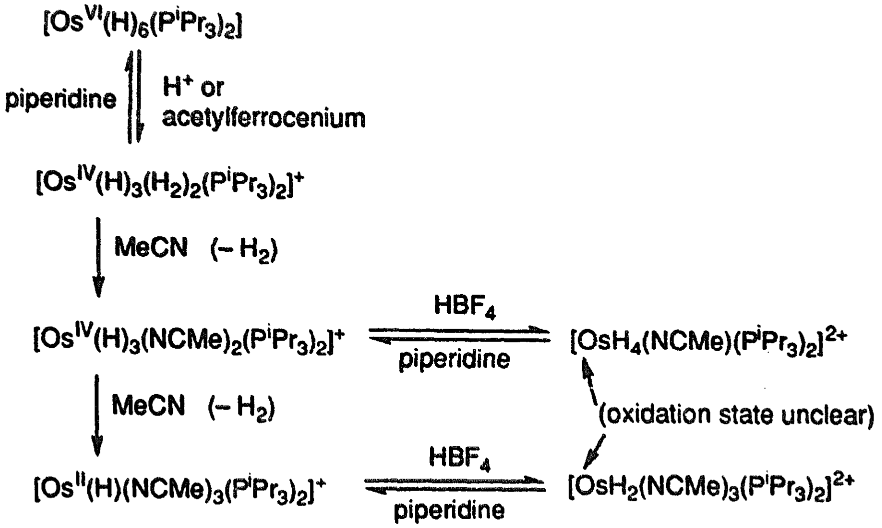
Reaction of $[Os(H)_2(Cl)_2(P^iPr_3)_2]$ with CF_3SO_3H affords $[\{Os(H)_2(P^iPr_3)_2\}_2(\mu\text{-}Cl)_3]^+$ (**2**); one chloride ion has been lost by protonation in preference to any of the hydride ligands [13]. The unusually large and temperature-dependent J_{H-H} NMR couplings in $[Os(H)_3X(PH_3)_2]$ (X = Cl, I) have been rationalised on the basis of the activation-energy barriers for pairwise exchange between the two H atoms in each complex. A theoretical model for calculation of these couplings is presented [14].

The Os(VI)-hexahydride $[Os(H)_6(P^iPr_3)_2]$ reacts with oxidants (H^+ or ferrocinium ions) to give $[(P^iPr_3)_2Os^{IV}(H)_3(H_2)_2]^+$, which contains two η^2-H_2 ligands and three hydrides. Some reactions of this compound are summarised in Scheme 3. In the majority of cases ^1H NMR spectroscopic measurements of T_1 relaxation times and coupling constants allowed unambiguous assignment of the hydrogen ligands as either η^2-H_2 or hydride ligands [15].

The crystal structure of $[Os(H)_2(S\text{–}O)(P^iPr_3)_2]$ (S–O = dianion of *N*-acetylcysteine) is unusual for two reasons. Firstly, the *N*-acetylcysteine coordinates as a doubly deprotonated *S,O*-didentate chelate; secondly, the geometry about the metal is not octahedral but a square antiprism with two sites vacant [16].

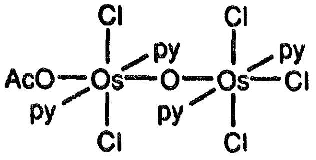
4.2. Other Os(IV) complexes

The complex cation $[Os(=O)(terpy)(bpy)]^{2+}$ is a weaker photo-oxidant of DNA than the Ru(IV) analogue, and cleaves DNA in supercoiled plasmids but not in single-stranded or double-stranded oligomers [17]. The asymmetric $Os_2^{IV}(\mu\text{–}O)$ complex (**3**) can be reduced by one electron to the Os(III)/Os(IV) mono-anion $(\mathbf{3})^-$. The crystal structures of both are similar except that on reduction all bond lengths parallel to the Os–O–Os vector are elongated whereas the equatorial bond lengths



Scheme 3.

are virtually unchanged. The mixed-valence complex is delocalised with a 3.5, 3.5 oxidation-state distribution [18].



(3)

The crystal structures of $[OsF_3Cl_3]^{2-}$ (both *fac* and *mer* isomers) [19] and *trans*-$[OsF_4Cl_2]^{2-}$ [20] have been determined, in every case with the dipyridiniomethane dication. Complex anions like these usually suffer from F/Cl disorder which renders accurate structural determinations difficult. However the irregular structure of the dipyridiniomethane dication results in a low-symmetry lattice in which the complex anions are fully ordered, allowing accurate measurements of Os–F and Os–Cl distances.

Several iodo-complexes of Os(II), Os(III) and Os(IV) have been prepared, such as $[Os^{III}(L\text{-}L)_2I_2]^+$, $[Os^{IV}(L\text{-}L)_2I_2]^{2+}$, $[Os^{IV}L_2I_4]$, $[Os^{II}L_4I_2]$ and $[Os^{III}L_4I_2]^+$ (all *trans*) where L and L-L are monodentate and didentate *P*- or *As*-donor ancillary ligands. The electronic spectra of the complexes are dominated by iodine-to-osmium charge-transfer bands. The crystal structure of *trans*-$[Os^{III}I_2(Me_3As)_4][I_3]$ was also determined [21].

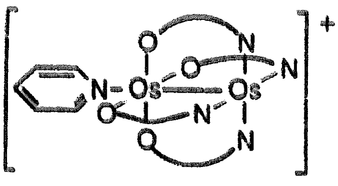
5. Osmium(III)

In the dinuclear complex $[(NH_3)_5Os\text{–}CN\text{–}Os(NH_3)_5]^{5+}$ the metal centres are inequivalent due to the asymmetry of the bridging cyanide ligand. Because of this, the electronic spectrum shows charge transfer bands due to transfer of an electron from the lower-energy Os(III) to the higher-energy site [22]. Reaction of $[Os(NH_3)_6]^{3+}$ with $[Fe(CN)_6]^{3-}$ affords $[(NH_3)_5Os\text{–}NC\text{–}Fe(CN)_5]$, with from loss of one NH_3 ligand. This subsequently disproportionates slowly to give a mixture of Os^{IV}–Fe^{II}, Os^{VI}–Fe^{II} and Os^{III}–Fe^{II} species [23].

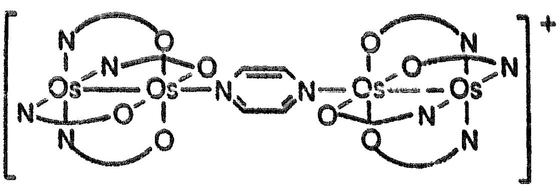
Reaction of $[Os^{IV}Br_6]^{2-}$ with dibenzylsulfoxide (R_2SO, where $R = PhCH_2$) affords the Os(III) species *mer*-$[OsBr_3(R_2S)_3]$ containing three thioether ligands. This is a potentially versatile starting material in osmium-thioether chemistry and a rare example of such a complex [24]. The crystal structure of $[Cp^{\ddagger}OsH]_2[Os_2Br_8]$ shows that the $[Os_2Br_8]^{2-}$ dianion has D_{4h} symmetry with a triple Os–Os bond and the bromine atoms eclipsed. This is in contrast to other structurally characterised salts containing the $[Os_2Br_8]^{2-}$ dianion. The Os–Os vector is threefold-disordered within an ordered cube of bromine atoms [25].

The redox-related pair $[(OEP)Os^{II}(tch)_2]$ and $[(OEP)Os^{III}(tch)_2]^+$ (H_2OEP = octaethylporphyrin; tch = thiacyclohexane) has been structurally characterised. In both cases the metal atom is in the porphyrin plane; in the Os(III) complex the Os–N bonds are slightly shorter, and the Os–S bonds significantly longer, than in the Os(II) complex [26]. Five-coordinate $[Os(SR)_3(PMe_2Ph)_2]$ ($R = C_6F_5$, $4\text{-}HC_6F_4$) reacts with thiocarboxylic acids R′C(O)SH (R′ = Me, Ph) to give $[Os^{III}(SR)_2(\eta^2\text{-}SOC\text{-}R')(PMe_2Ph)_2]$ (*trans* thiolates, *cis* phosphines, chelating thioacetate). The Os(II)/Os(III) redox potential varies as a function of the groups R and R′ [27].

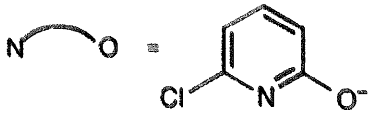
The complexes $[Os^{II}Os^{III}(chp)_4(py)][BF_4]$ (**4a**) and $[\{Os^{II}Os^{III}(chp)_4\}_2(\mu\text{-}pyrazine)][BF_4]_2$ (**4b**) (chp = anion of 6-chloro-2-hydroxypyridine, which acts as an *N*,*O*-donor bridging ligand) have been prepared and characterised both structurally and by magnetic susceptibility measurements. All $\{Os_2(chp)_4\}^+$ units have the chp ligand oriented the same way such that one Os has four *O*-donors and the other has four *N*-donors [28].



(**4a**)



(**4b**)

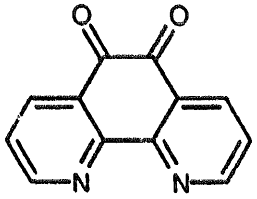


6. Osmium(II)

6.1. *Complexes with polypyridyl ligands*

The electronic absorption spectra of $[Os(bpy)_3]^{2+}$ doped into various crystalline hosts have been compared [29]. Redox-active Os(II)-polypyridyl complexes can be adsorbed into montmorillonite clays [30]. The electrochemical and electronic spectral properties of $[Os(bpy)(CN)_4]^{2-}$ are strongly solvent-dependent, due to different interactions of the various solvents with the polar peripheries of the cyanide groups. The complex is weakly luminescent [31]. Coordination of phenanthroline-5,6-dione (**5**) to Os(II) modifies the mechanism of its $2H^+/2e^-$ reduction, by inducing addition of H_2O to the quinone carbonyl groups [32]. Intercalation of the extended aromatic phenazine derivative of complex (**6**) into DNA results in quenching of the Os-based luminescence, so the complex acts as a 'light-switch' for which the on/off trigger is the presence or absence of DNA [33].

Osmium(II) complexes of 4- and 6-vinyl-terpyridine can be electropolymerised onto glassy carbon electrodes. The resultant redox-active films show electrocatalytic activity towards CO_2 reduction, which is suppressed in the presence of coordinating anions [34]. A resonance-Raman study of complex (**7**) [and its Ru(II) analogue], which contain the *N*-methyl-4,4′-bipyridinium radical ($M\dot{Q}$), has been carried out. Various $M\dot{Q}$-based transitions have been identified, and the complexes undergo a $M^{II}(\pi)\rightarrow M\dot{Q}(\pi^*)$ MLCT transition [35].



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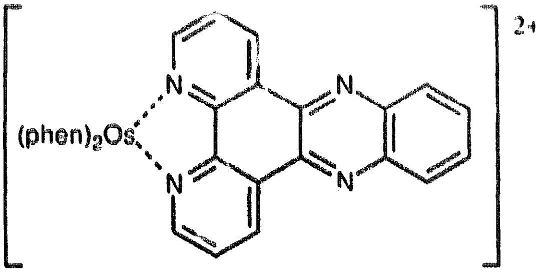

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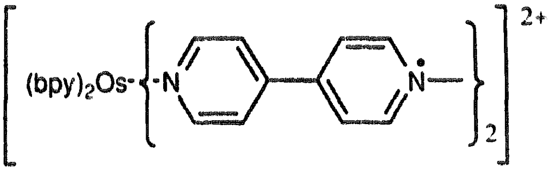
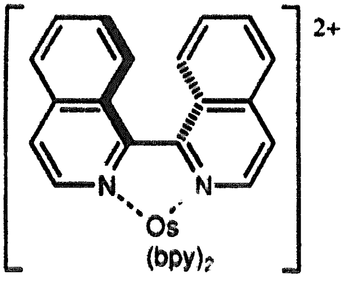


(7)

The complex cation $[Os(bpy)_2(biq)]^{2+}$ ((**8**); biq = 1,1′-biiso-quinoline) and its Ru(II) analogue have two diastereomeric forms due to the chirality of the tris-chelate metal core and the chirality of the biq ligand, which is non-planar due to the steric interaction between H^8 and $H^{8'}$. The two *N*-donor ligands of biq are therefore 'misdirected' and these M–N (M = Ru, Os) bonds are weak. The two diastereomers interconvert *via* atropisomerisation of the biq ligand *via* a planar, C_2-symmetric transition state in which the *N*-donor atoms are properly directed for coordination and therefore these M–N bonds are transiently strengthened. This leads to the unusual situation that the complex with the more thermodynamically stable bonds (Os) has a higher driving force to attain the transition state, and is therefore more kinetically labile than the Ru complex [36]. Electrospray mass spectrometry has been found to offer significant advantages over fast ion bombardment mass spectrometry for characterisation of polynuclear complexes such as $[(bpy)_2Os^{II}\text{–}NC\text{–}Ru^{III}(NH_3)_5]^{4+}$ [37].



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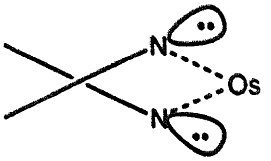
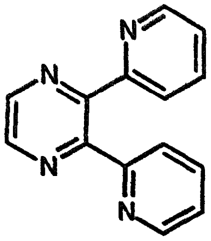


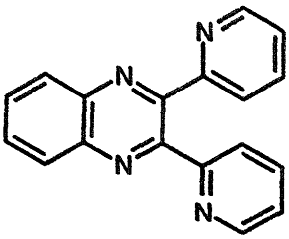
Lone pairs not in correct orientation for coordination; 'misdirected' bonds

Many dinuclear complexes containing Os(II)-polypyridyl fragments have been prepared, based on bridging ligands with two didentate or terdentate binding pockets. The interest in these is related to electrochemical and/or photophysical interactions between the metal centres across the bridging ligand. Thus, $[\{Os^{II}(bpy)_2\}_2(\mu\text{-}L)]^{4+}$ (L = (**9**), (**10**), (**11**)) and the analogous Ru^{II}/Ru^{II} and mixed-metal Ru^{II}/Os^{II} and Ru^{II}/Os^{III} complexes with the same ligands have been spectroscopically characterised. The electronic spectra of the mixed-metal complexes are assignable in terms of the sum of the spectroscopic properties of the component mononuclear fragments, albeit with some perturbations [38]. In $[\{Os^{II}(bpy)_2\}_2(\mu\text{-}\mathbf{12})]^{4+}$ the excited electron of the MLCT excited state is substantially delocalised over the bridging ligand (**12**), which results in very long excited state lifetimes [39]. $[\{Os^{II}(bpy)_2\}_2(\mu\text{-}\mathbf{13})]^{4+}$ shows a strong electrochemical interaction across the bridging ligand, with a separation of 0.36 V between the Os(II)/Os(III) couples and inter-valence transitions apparent in the electronic spectrum of the mixed-valence state. There are also multiple ligand-based reductions, and the dinuclear complex and its mononuclear counterpart have low-energy MLCT excited states [40].

Mono- and di-nuclear complexes of (**14**), with $\{Ru(bpy)_2\}^{2+}$ and/or $\{Os(bpy)_2\}^{2+}$ fragments in each binding site, have been prepared. With this ligand the two binding sites are inequivalent and the electrochemical and spectroscopic properties of a metal fragment are therefore site-dependent. The mixed-metal Ru(II)/Os(II) complexes show efficient intramolecular energy-transfer, such that excitation of the Ru(II) centre results in emission from the lower-energy Os-based MLCT excited state [41]. Similarly, complex (**15**) shows Ru(II)→Os(II) energy-transfer with a rate constant of $8 \times 10^6\ s^{-1}$ [42].



(9)



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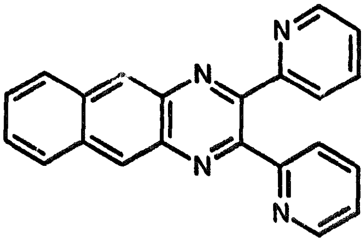

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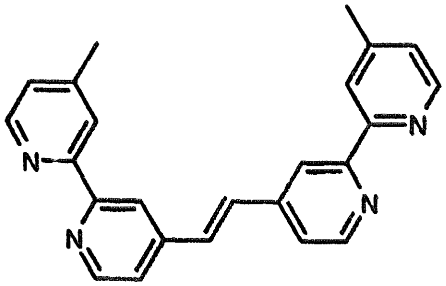

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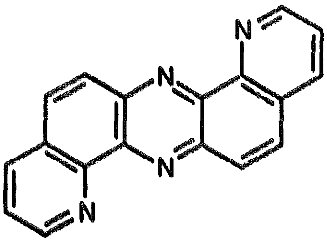

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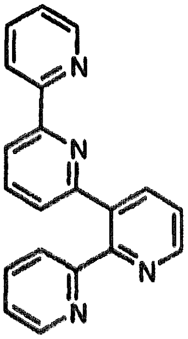

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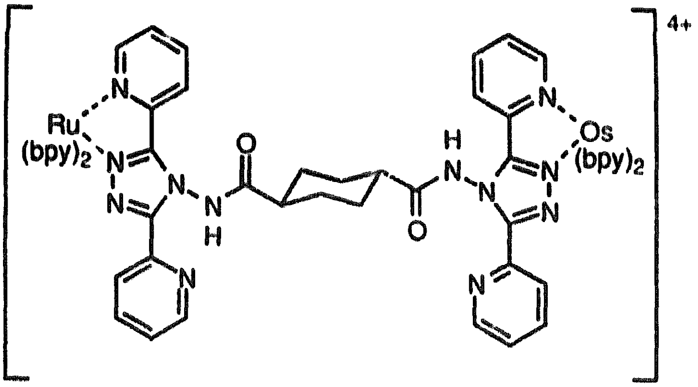
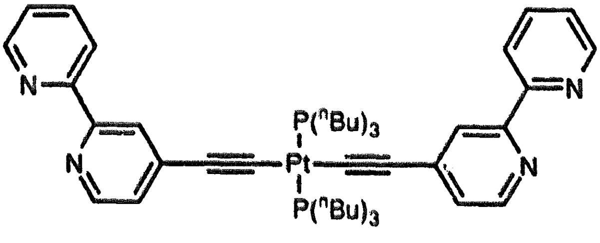
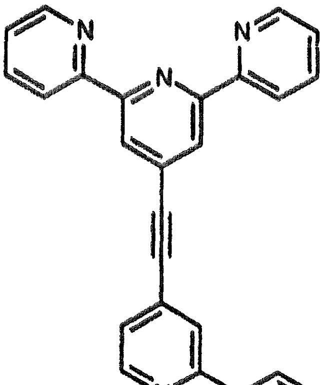


(15)

Dinucleating ligands with bpy or terpy binding sites and alkynyl spacers have been prepared, such as (**16**) (which contains a metallic spacer group), and (**17**)–(**19**) (which are directly linked). These have been used to synthesise a variety of high-nuclearity, polychromophoric complexes. Attachment of $\{Os(bpy)_2\}^{2+}$ fragments to the termini of (**16**), for example, affords a trinuclear Os–Pt–Os complex [43]. In contrast attachment of an $\{Os(bpy)_2\}^{2+}$ fragment to one bipyridyl terminus of (**16**) or (**17**) allows the resulting 'complex ligands', which have free binding sites, to be used as the building blocks of even larger species by assembling several of them around a single metal centre *via* their free binding sites [44]. In $[(terpy)Ru–L–Os(terpy)]^{4+}$ (L=(**18**), (**19**)) the rate of intramolecular Ru(II)→Os(II) energy-transfer decreases by about one third when the second alkynyl spacer is inserted between the chromophores; this allows an estimate of 0.17 $Å^{-1}$ for the attenuation factor for energy-transfer through carbon-carbon triple bonds [45].

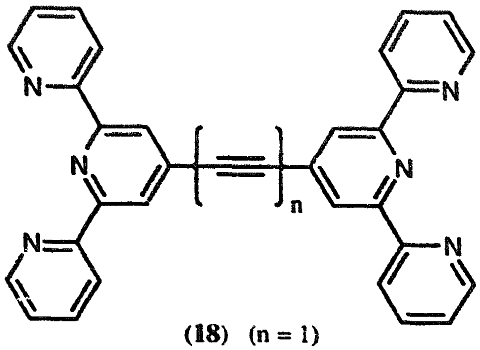


(**16**)

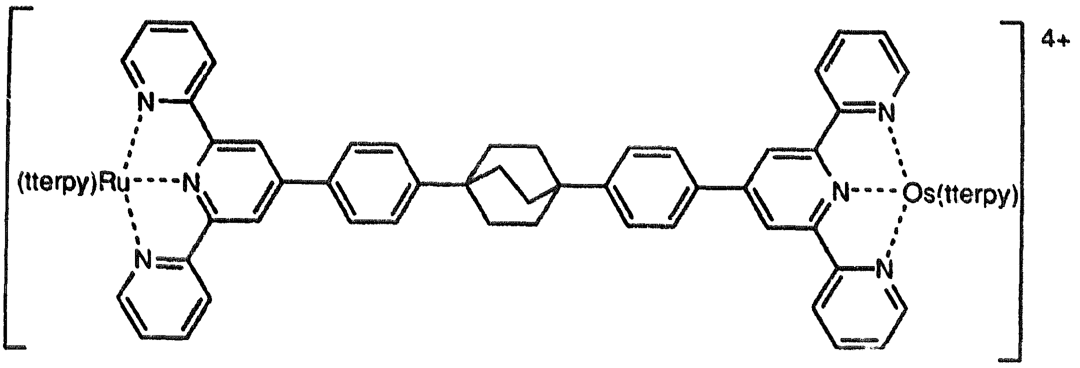


(**17**)

Complex (**20**) has a 24 Å separation between the Ru(II) and Os(II) centres. At 77 K in a rigid glass it displays Ru(II)→Os(II) energy-transfer with a rate constant of $4.4 \times 10^6 \, s^{-1}$. The oxidised Ru(II)/Os(III) complex does not undergo electron-transfer quenching [to Os(III)] on irradiation under these conditions since the necessary solvent repolarisation is prevented by the rigid matrix [46]. Dinuclear complexes (**21**)–(**24**) have lower quantum yields and shorter excited-state lifetimes than a mononuclear Os(II) complex with the same ligand, due to electron-transfer quenching. The electron-transfer rates correlate with the thermodynamic driving force for the process [47].



(18) (n = 1)
(19) (n = 2)



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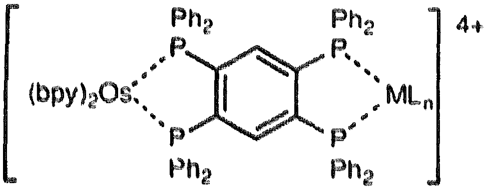


(21) ML_n = Ni(dppb)
(22) ML_n = Pd(dppb)
(23) ML_n = Pt(dppb)
(24) ML_n = $Os(bpy)_2$
[dppb = $Ph_2P(CH_2)_4PPh_2$]

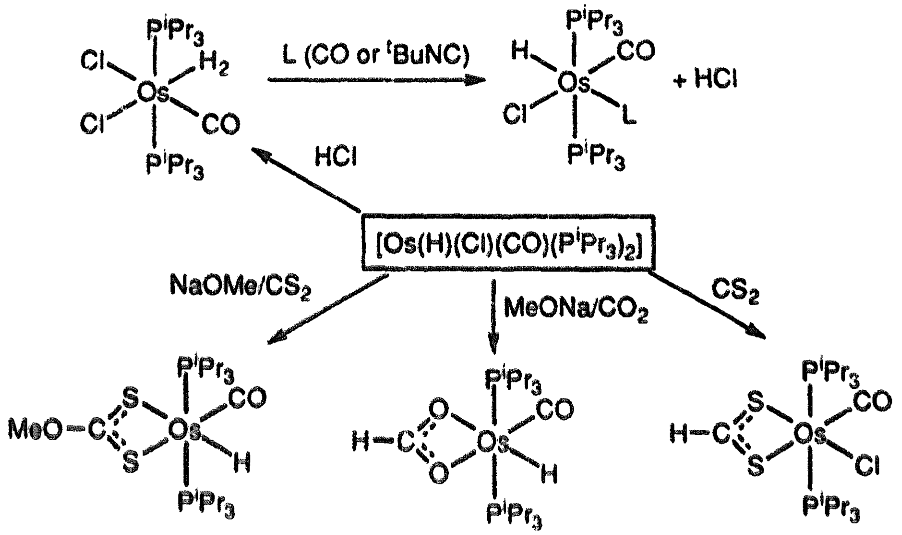
Very large high-nuclearity (up to 10 metals) complexes of Ru(II) and Os(II) based on bridging ligands such as (**9**) undergo aggregation in solution even at concentrations as low as 10^{-6} M, despite their high charge (up to +20) to give particles as large as 100 nm across. This is thought to be due to attractive interactions between the aromatic, hydrophobic exteriors [48].

6.2. *Complexes containing hydrogen or hydride ligands*

A theoretical study using quasi-relativistic density functional methods has been carried out on the various isomers of $[M(PH_3)_3H_4]$ (M = Fe, Ru, Os). Whereas the Fe and Ru complexes are most stable in oxidation state 0 with two H_2 ligands, the osmium complex is predicted to be more stable as the dihydride $[Os^{II}(PH_3)_3(\eta^2\text{-}H_2)(H)_2]$, due to a relativistic destabilisation of the Os 5d orbitals which makes the metal more basic. This agrees with experimental data [49].

The compound $[Os(H)(Cl)(CO)(PPh_3)_3]$ reacts with $CH_2{=}CH(SnR_3)$ (R = Me,

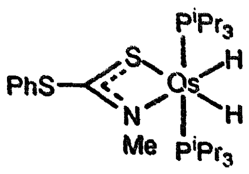
^{n}Bu) to give the five-coordinate product [Os(Cl)(CO)(PPh$_3$)$_2$(SnR$_3$)]. The vinyl group of the tin reagent, and the hydride on the osmium starting complex, are eliminated together β as ethene. This is a good route to coordinatively unsaturated Os(II) complexes, which undergo facile addition of ligands such as isonitriles and CO [50]. Five-coordinate [Os(H)(X)(CO)(P^{i}Pr$_3$)$_2$] (X=Cl, I) inserts a variety of reagents into the Os–H bond (Scheme 4). Reaction of [Os(H)(SPh)(CO)(P^{i}Pr$_3$)$_2$] with MeNCS results in insertion into the Ph–S bond to give (**25**), whereas reaction with MeSCN simply results in coordination of the MeSCN at the vacant coordination site [51].



Scheme 4.

The hydrido complex [Os(H)(Cl)(CO)(P^{i}Pr$_3$)$_2$] adds HCl to give [Os(CO)(H$_2$)(Cl)$_2$(P^{i}Pr$_3$)$_2$], which loses HCl again on addition of other ligands L (Scheme 4). Some reactions of [Os(CO)(H$_2$)(Cl)$_2$(P^{i}Pr$_3$)$_2$] with acetylenes were also examined [52]. In [Os(H)(CO)(PPh$_3$)$_3$(1,2-S-C$_6$H$_4$SiPh$_3$)] the deprotonated 2-(triphenylsilyl)benzenethiol ligand is a monodentate *S*-donor [53]. Complex (**26**) contains an unusual example of a monodentate *N*-coordinated amide ligand; in ruthenium complexes, the same ligand bridges two metal centres *via* the N and O atoms [54]. A number of complexes such as (**27**) have been prepared by insertion of the B-H bond of boranes (BRR′H, such as 9-borobicyclononane or thexylborane) into the Os–C bond of the metallated trimethylphosphine precursor. ^{1}H and ^{31}P NMR spectroscopic studies allow determination of the activation energies for exchange of Os–H and Os–H–B fragments [55].

Protonation of [Os(H)(CO)(PPh$_3$)$_2$(quS)] (quSH = quinoline-8-thiol) gives a mixture of tautomers in which the proton combines either with the anionic quS ligand or with the hydride (Scheme 5). The position of the equilibrium is temperature-dependent [56]. *Trans*-[Os(N$_2$)(H)(PR$_3$)$_4$]$^+$ (where PR$_3$ is one of a variety of phosphites) is a versatile starting material for a variety of other species, as the N$_2$ ligand is easily replaced by a wide variety of other monodentate ligands including H$_2$, CO and isonitriles [57].



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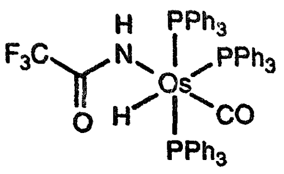

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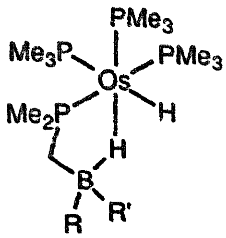

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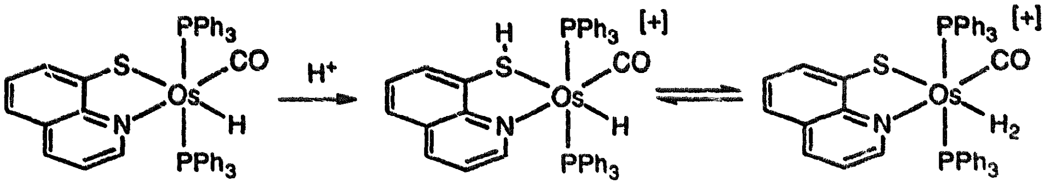


(+ isomer with H/CO interchanged)

Scheme 5.

6.3. Other Os(II) complexes

The complex *trans,mer*-[Os(Cl)$_2$(MeCN)(PMe$_2$Ph$_3$)] was crystallographically characterised and has a linear Os–NCMe linkage [58]. The new carbonyl dication [Os(CO)$_6$]$^{2+}$ has been prepared, as its [Sb$_2$F$_{11}$]$^-$ salt, by reductive carbonylation of Os(SO$_3$F$_3$)$_3$ in liquid SbF$_5$ [59]. [Os(MeCN)$_6$]$^{2+}$, [Os(MeCN)$_5$Cl]$^+$ and *cis*-[Os(MeCN)$_4$(Cl)$_2$] have been prepared in good yields by photolysis in MeCN of various Os(II) precursors containing η^6-benzene ligands. These complexes show reversible Os(II)/Os(III) couples at potentials about 0.5 V lower than those of their Ru(II) analogues [60]. The electronic spectral and photochemical properties of [Os(SnCl$_3$)$_6$]$^{4-}$, [Os(SnCl$_3$)$_5$Cl]$^{4-}$ and [Os(SnCl$_3$)$_5$(MeCN)]$^{3-}$ were examined. The lowest-energy transition is a ligand-to-ligand charge-transfer process. Photolysis of these complexes in MeCN generates [Os(SnCl$_3$)$_4$(MeCN)$_2$]$^{2-}$ [61].

The complex anion [Os(NO)(CN)$_5$]$^{2-}$ has two metastable electronically excited states which may be accessed by UV irradiation at low temperature, and are similar to those found in nitroprusside salts. The IR spectra of the excited-state complexes show that both excited states involve metal d(π) to nitrosyl charge transfer. The excited states decay on warming, but at different rates [62]. [Os(CO)$_4$Me$_2$] reacts with HF to give *cis*-[Os(CO)$_4$(F)$_2$] and [{F(CO)$_4$Os}$_2$(μ-F)]$^+$, and with HOTeF$_5$ to give *cis*-[Os(CO)$_4$Me(OTeF$_5$)]. Elimination of methane gas is a strong entropic driving force for these reactions [63]. [Os(CO)$_3$(PPh$_3$)$_3$] is oxidised by XeF$_2$ to give [Os(CO)$_2$(F)$_2$(PPh$_3$)$_2$]. This reaction occurs *via* oxidation of the metal by [XeF]$^+$, followed by nucleophilic attack of fluoride ion on a carbonyl ligand to give a fluoroacyl intermediate [i.e. containing an Os–C(O)F fragment], followed by loss of CO. This represents the first evidence for formation of a fluoroacyl complex of Os(II) [64].

7. Osmium(0)

Two calculations of the first M–C bond dissociation energy of $Os(CO)_5$ have predicted values of 34.7 kcal mol^{-1} [65] and 42.4 kcal mol^{-1} [66] (c.f. the experimentally determined value of 31 kcal mol^{-1}). The equilibrium geometry of $Os(CO)_5$ was also calculated [66]. High-resolution, variable-energy photoelectron spectra of $Os(CO)_5$ using synchrotron radiation have been used to study the valence, inner and core electron shells [67].

The 16-electron, square-planar Os(0) complexes $[Os(Cl)(NO)(PR_3)_2]$ react with CO to give the five-coordinate adducts $[Os(Cl)(NO)(CO)(PR_3)_2]$ and with H_2 to give *trans,trans*-$[Os^{II}(H)_2(PR_3)_2(NO)(Cl)]$ by oxidative addition [68].

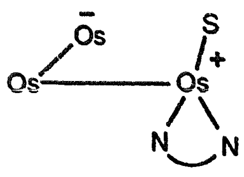
8. Osmium clusters

8.1. Clusters with only carbonyl and hydride ligands

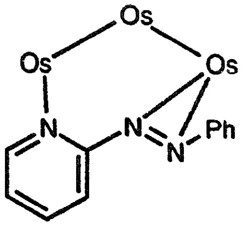
A historical review of osmium and ruthenium cluster chemistry, with the emphasis on synthetic routes to higher nuclearity clusters, has been published [69]. ^1H Magic-angle spinning NMR spectroscopy has been shown to be a valuable structural tool for examining osmium carbonyl hydride clusters such as $[H_2Os_3(CO)_{10}]$ [70]. Variable-temperature crystallography on $[Fe_2Os(CO)_{12}]$ shows evidence for dynamic disorder arising from reorientation of the metal triangle inside the ligand polyhedron [71].

8.2. Clusters with N- or P-donor ligands

Solid/gas reactions between solid $[Os_3(CO)_{11}(MeCN)]$ and gaseous substrates such as NH_3, CO or H_2 have been examined. At about 80°C reaction occurs with displacement of MeCN by the new ligand, and the site selectivities for these reactions were examined. The reaction with NH_3 occurs *via* the intermediate $[Os_3(CO)_{11}]$ in which the vacant site exchanges rapidly between axial and equatorial positions [72]. ^{13}C NMR spectroscopy was used to examine the solution structures and dynamic behaviour of $[Os_3(CO)_{12-x}(MeCN)_x]$ ($x = 1,2$). In the ground state the MeCN ligands are in axial positions and all carbonyl ligands are terminal; fluxional behaviour in solution involves carbonyl exchange by a 'merry-go-round' mechanism [73]. $[Os_3(CO)_{10}L]$ (L = an α,α′-diimine such as 2,2′-bipyridine, 2,2′-bipyrimidine, (**9**) or (**10**)) all undergo Os→L MLCT electronic transitions which were studied by resonance Raman spectroscopy. In toluene the MLCT excited state collapses to the ground state, but in coordinating solvents a zwitterionic species (**28**) is transiently formed by cleavage of one Os–Os bond and solvent coordination to the positively charged metal centre. In 2-methyl-tetrahydrofuran this zwitterionic species could be isolated at 113 K [74]. $[Os_3(CO)_{10}(MeCN)_2]$ reacts with phenylazopyridine to give (**29**), in which the ligand coordinates in a $\mu^2:\eta^3$ mode, and (**30**), in which the ligand has been oxidised [75]. (Note that in the structural diagrams of clusters, carbonyl and hydride ligands are omitted for the sake of clarity).



(28) (S = solvent)



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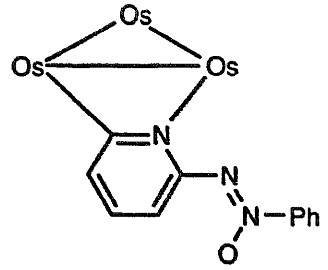
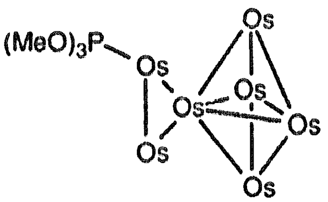


(30)

A detailed study on the kinetics of addition of *P*-donor (and other) nucleophiles to [$H_2Os_3(CO)_{10}$] as a function of pressure and temperature has been carried out [76,77]. [$Os_7H_2(CO)_{21}$\{P(OMe)$_3$\}] (31) has been structurally characterised and is based on a trigonal bipyramidal core; the hydrides could not be located [78]. [$Os_4(CO)_{15}$], [$Os_4(CO)_{13}(PMe_3)$ \{P(OMe)$_3$\}] and [$Os_4(CO)_{14}$(CN^{t}Bu)] all have a planar diamond-shaped metal skeleton. All three complexes are fluxional in solution, undergoing CO exchange by an equatorial 'merry-go-round' mechanism, but [$Os_4(CO)_{13}(PMe_3)$\{P(OMe)$_3$\}] requires considerably higher temperatures than the other two to observed the fluxional behaviour by ^{13}C NMR spectroscopy [79]. Reaction of [$Os_3(CO)_{11}$(MeCN)] with ^{t}Bu$_2$PF gives the expected adduct [$Os_3(CO)_{11}$(^{t}Bu$_2$PF)]; however, reaction of [$Os_3(CO)_{10}$(MeCN)$_2$] with ^{t}Bu$_2$PF gives not only the expected product [$Os_3(CO)_{10}$(^{t}Bu$_2$PF)$_2$] (in which the phosphine ligands are attached to different metals) but also [$Os_3(CO)_{10}$(^{t}Bu$_2$PF)(^{t}BuPF$_2$)] in which the substituents on one of the phosphine ligands have become scrambled [80]. [$Os_3(CO)_{10}$(μ-dppp')] [dppp' = 1,5-bis(diphenylphosphino)pentane, $Ph_2P(CH_2)_5PPh_2$] reacts with another equivalent of dppp' to give [$Os_3(CO)_9$(μ-dppp')(η^1-dppp')]. In contrast reaction of [$Os_3(CO)_{10}$(μ-dppm)] with a second equivalent of dppm gives [$Os_3(CO)_8$(μ-dppm)$_2$] in which the dppm ligands bridge different edges of the triangular cluster. This illustrates the effect of chain length on the chelating behaviour of polydentate ligands on osmium clusters [81]. [$Os_3(CO)_{10}$(MeCN)$_2$] reacts with pentaphenylcyclopentaphosphine to give (32) as a mixture of two isomers which differ in the orientations of the phenyl rings. In [$Os_3(CO)_{11}(P_5Ph_5)$] the pentaphenylcyclopentaphosphine is a monodentate *P*-donor, and in [\{$Os_3(CO)_{11}$\}$_2$(μ-P_5Ph_5)] it acts as a monodentate donor to each of the two \{$Os_3(CO)_{11}$\} fragments [82].



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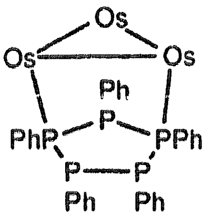
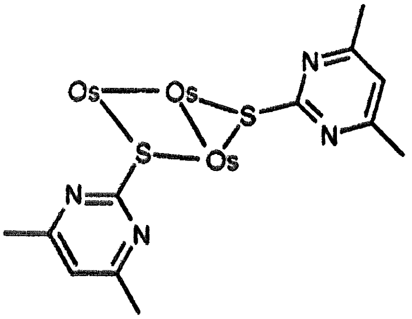


(32)

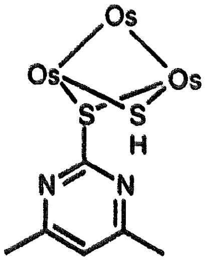
8.3. Clusters with O- or S-donor ligands

The crystal structure of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ has been determined; the two bridging groups are on the same edge of the triangular core [83]. Reaction of $[Os_3(CO)_{11}(\mu\text{-H})]^-$ with $[Cu(PPh_3)_2(BH_4)]$ affords a mixture of $[Os_3(CO)_{10}(\mu\text{-H})(\mu\text{-OH})]$ and two isomers of $[Os_3(CO)_8(\mu\text{-H})(\mu\text{-OH})(PPh_3)_2]$ in which the phosphine substituents are in different positions [84].

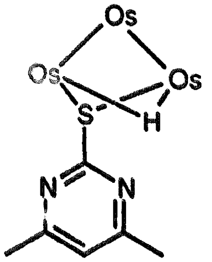
The ligand 4,6-dimethylpyrimidine-2-thione reacts with $[Os_3(CO)_{10}(MeCN)_2]$ to give a variety of products such as (**33**)–(**35**) in which the new ligand is only *S*-bonded. Thermolysis leads to more products such as (**36**) and (**37**) in which the ligand can coordinate through a nitrogen atom as well. Most of these products have been crystallographically characterised [85,86].



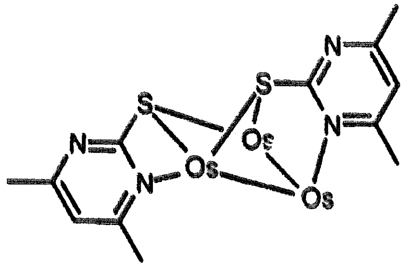
(**33**) (one non-bonded Os–Os edge)



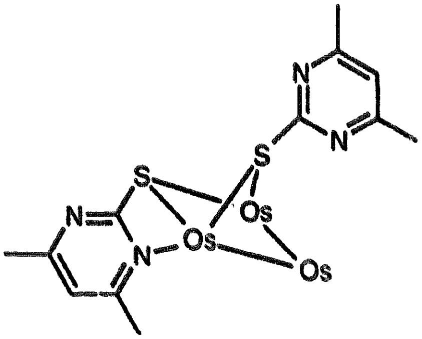
(**34**)



(**35**)

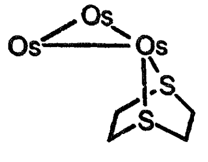


(**36**)

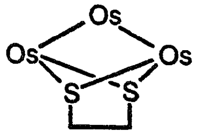


(**37**)

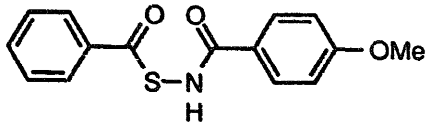
Reaction of 1,4-dithiacyclohexane with Os_3 clusters affords a variety of products such as (**38**) and (**39**) in which the 1,4-dithiacyclohexane can chelate to one metal (**38**) or bridge two metals (**39**). Many other products with Os–C bonds were also characterised [87]. Thietane (thiacyclobutane, tcb) reacts with $[H_4Os_4(CO)_{11}(MeCN)]$ to give $[H_4Os_4(CO)_{11}(tcb)]$ in which the tcb acts as a monodentate *S*-donor ligand. The coordinated ligand can then undergo catalytic cyclo-oligomerisation to give 12-ane-S_3 and 24-ane-S_6 fragments which are coordinated as monodentate *S*-donor ligands to the Os_4 core. A mechanism for this has been proposed [88]. On reacting with $[Os_3(CO)_{10}(MeCN)_2]$, ligand (**40**) undergoes desulfurisation to give $[Os_3(CO)_{10}(\mu_3\text{-}S)]$, $[Os_6(CO)_{20}(\mu_4\text{-}S)(MeCN)]$ (**41**) {which decarbonylates to give square-pyramidal $[Os_5(CO)_{15}(\mu_4\text{-}S)]$} and $[Os_6(CO)_{19}(\mu_3\text{-}S)]$ (**42**) [89].



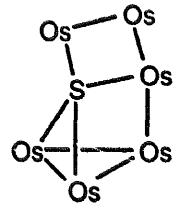
(**38**)



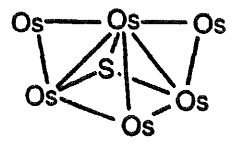
(**39**)



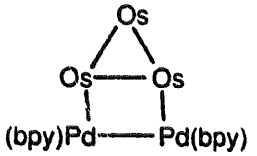
(**40**)



(**41**)



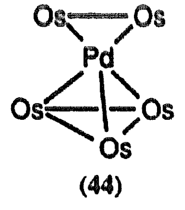
(**42**)



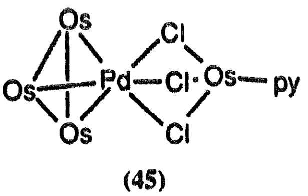
(**43**)

8.4. *Clusters containing other metals*

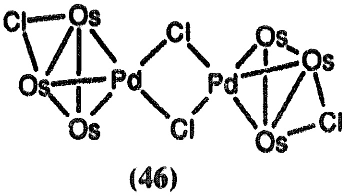
The cluster $[H_2Os_3(CO)_{10}]$ reacts with Ph_3SnCl or $Au(PPh_3)Cl$ to give the pentametallic chains $Ph_3Sn\text{-}\{Os(CO)_4\}_3\text{-}SnPh_3$ and $(Ph_3P)Au\text{-}\{Os(CO)_4\}_3\text{-}Au(PPh_3)$, respectively [90]. $[H_2Os_3(CO)_{10}]$ also reacts with $Pd(bpy)(OAc)_2$ to give $[\{(bpy)Pd\}_2Os_3(CO)_{10}]$ (**43**) [91], and with *trans*-$[Pd(py)_2Cl_2]$ to give a range of mixed Os/Pd clusters including $[Os_5Pd(CO)_{16}(\mu\text{-}H)_6]$ (**44**), $[Os_5Pd(CO)_{16}(\mu\text{-}H)_4H(\mu\text{-}Cl)]$, $[Os_5Pd(CO)_{16}(\mu\text{-}H)_4(\mu\text{-}Cl)_2]$, $[Os_4Pd(CO)_{11}(\mu\text{-}H)_3(\mu\text{-}Cl)_3(py)]$ (**45**) and $[\{Os_3Pd(CO)_9(\mu\text{-}H)_2(\mu\text{-}Cl)\}_2(\mu\text{-}Cl)_2]$ (**46**), all of which have been crystallographically characterised [92].



(**44**)

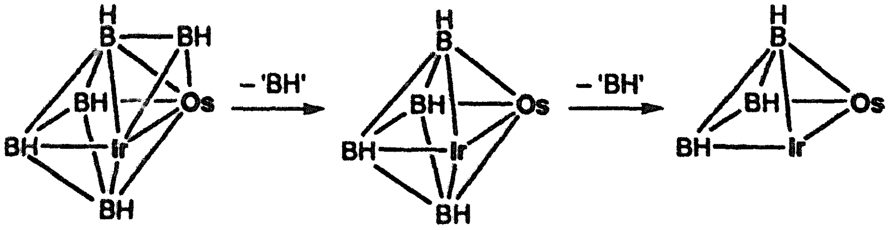


(**45**)



(**46**)

Two series of iridaosmaborane clusters has been prepared and crystallographically characterised (Scheme 6); the members of the series are notionally related by loss of 'BH' fragments (note that in the structural formulae, as with the Os cluster



Scheme 6.

diagrams, bridging hydrides are not shown for the sake of clarity). Both series consist of a *pileo*, *closo*, *nido* sequence in which the same number of polyhedral skeletal electron-pairs gives clusters with 7, 6 or 5 vertices [93,94].

References

[1] W.B. Motherwell, A.S. Williams, Angew. Chem. Int. Ed. Engl. 34 (1995) 2031.
[2] E.J. Corey, M.C. Noe, A. Guzman-Perez, J. Am. Chem. Soc. 117 (1995) 10817.
[3] A.J. Corey, A. Guzman-Perez, M.C. Noe, J. Am. Chem. Soc. 117 (1995) 10805.
[4] W.P. Griffith, T.Y. Koh, A.J.P. White, D.J. Williams, Polyhedron 14 (1995) 2019.
[5] D.S. Williams, T.J. Meyer, P.S. White, J. Am. Chem. Soc. 117 (1995) 823.
[6] D.S. Williams, G.M. Coia, T.J. Meyer, Inorg. Chem. 34 (1995) 586.
[7] K.-F. Chin, K.-K. Cheung, H.-K. Yip, T.C.W. Mak, C.-M. Che, J. Chem. Soc., Dalton Trans., (1995) 657.
[8] M.T. Benson, T.R. Cundari, E.W. Moody, J. Organometal. Chem. 504 (1995) 1.
[9] K.-F. Chin, Y.-K. Cheng, K.-K. Cheung, C.-X. Guo, C.-M. Che, J. Chem. Soc., Dalton Trans., (1995) 2967.
[10] A.S. Borovik, J. Du Bois, K.N. Raymond, Angew. Chem. Int. Ed. Engl. 34 (1995) 1359.
[11] A.J. Bailey, W.P. Griffith, P.D. Savage, J. Chem. Soc., Dalton Trans., (1995) 3537.
[12] D.G. Gusev, R. Kuhlman, J.R. Rambo, H. Berke, O. Eisenstein, K.G. Caulton, J. Am. Chem. Soc. 117 (1995) 281.
[13] R. Kuhlman, W.E. Streib, K.G. Caulton, Inorg. Chem. 34 (1995) 1788.
[14] E. Clot, C. Leforestier, O. Eisenstein, M. Pélissier, J. Am. Chem. Soc. 117 (1995) 1797.
[15] K.T. Smith, M. Tilset, R. Kuhlman, K.G. Caulton, J. Am. Chem. Soc. 117 (1995) 9473.
[16] R. Alencio, M.A. Esteruelas, F.J. Lahoz, L.A. Oro, N. Ruiz, Inorg. Chem. 34 (1995) 1004.
[17] C.-C. Cheng, J.G. Goll, G.A. Neyhart, T.W. Welch, P. Singh, H.H. Thorp, J. Am. Chem. Soc. 117 (1995) 2970.
[18] Y. Imbe, K. Umakoshi, C. Matsunami, Y. Sasaki, Inorg. Chem. 34 (1995) 813.
[19] C. Bruhn, W. Preetz, Acta Crystallogr., Sect. C 51 (1995) 1112.
[20] C. Bruhn, W. Preetz, Acta Crystallogr., Sect. C 51 (1995) 865.
[21] N.R. Champness, C.S. Frampton, W. Levason, S.R. Preece, Inorg. Chim. Acta 233 (1995) 43.
[22] H. Kunkely, V. Pawlowski, A. Vogler, Inorg. Chim. Acta 238 (1995) 1.
[23] V. Poulopoulou, H. Taube, Inorg. Chem. 34 (1995) 1299.
[24] P. Ghosh, K. Pramanik, A. Chakravorty, J. Chem. Soc., Chem. Commun., (1995) 477.
[25] C.L. Gross, S.R. Wilson, G.S. Girolami, Inorg. Chem. 34 (1995) 2582.
[26] W.R. Scheidt, H. Nasri, Inorg. Chem. 34 (1995) 2190.
[27] R. Moreno-Esparza, H. Torrens, M. Arroyo, J.L. Brianso, C. Miravitlles, J. Ruis, Polyhedron 14 (1995) 1601.
[28] F.A. Cotton, Y. Kim, D.L. Shulz, Inorg. Chim. Acta 236 (1995) 43.
[29] E. Krausz, H. Riesen, A.D. Rae, Aust. J. Chem. 48 (1995) 929.
[30] C. Richardson, T. Kade, D. Blauch, J. Chem. Soc., Chem. Commun., (1995) 1821.

[31] M.E. García Posse, N.E. Katz, L.M. Baraldo, D.D. Polonuer, C.G. Colombano, J.A. Olabe, Inorg. Chem. 34 (1995) 1830.

[32] Y. Lei, F.C. Anson, J. Am. Chem. Soc. 117 (1995) 9849.

[33] R.E. Holmlin, J.K. Barton, Inorg. Chem. 34 (1995) 7.

[34] J.A.R. Sade, C.R. Arana, L. Hernandez, K.T. Potts, M. Keshavarz-K, H.D. Abruna, Inorg. Chem. 34 (1995) 3339.

[35] W.D. Bates, P.-Y. Chen, C.A. Bignozzi, J.R. Schoonover, T.J. Meyer, Inorg. Chem. 34 (1995) 6215.

[36] M.T. Ashby, J. Am. Chem. Soc. 117 (1995) 2000.

[37] C.A. Bignozzi, O. Bortolini, O. Curcuruto, M. Haudan, Inorg. Chim. Acta 233 (1995) 113.

[38] M.M. Richter, G.E. Jensen, K.J. Brewer, Inorg. Chim. Acta 230 (1995) 35.

[39] G.E. Strouse, J.R. Schoonover, R. Duesing, S. Boyde, W.E. Jones Jr., T.J. Meyer, Inorg. Chem. 34 (1995) 473.

[40] R.R. Ruminski, D. Serveiss, M. Jacquez, Inorg. Chem. 34 (1995) 3358.

[41] V. Balzani, D.A. Bardwell, F. Barigelletti, R.L. Cleary, M. Guardigli, J.C. Jeffery, T. Sovrani, M.D. Ward, J. Chem. Soc., Dalton Trans., (1995) 3601.

[42] G. Giuffrida, G. Calogero, V. Ricevuto, S. Campagna, Inorg. Chem. 34 (1995) 1957.

[43] M. Hissler, R. Ziessel, J. Chem. Soc., Dalton Trans., (1995) 893.

[44] M. Hissler, R. Ziessel, New J. Chem. 19 (1995) 751.

[45] V. Grosshenny, A. Harriman, R. Ziessel, Angew. Chem., Int. Ed. Engl 34 (1995) 1100.

[46] F. Barigelletti, L. Flamigni, J.-P. Collin, J.-P. Sauvage, A. Sour, New J. Chem. 19 (1995) 793.

[47] P.-W. Wang, M.A. Fox, Inorg. Chem. 34 (1995) 36.

[48] S. Campagna, A. Giannetto, S. Serroni, G. Denti, S. Trusso, F. Mallamace, N. Micali, J. Am. Chem. Soc. 117 (1995) 1754.

[49] J. Li, R.M. Dickson, T. Ziegler, J. Am. Chem. Soc. 117 (1995) 11482.

[50] P.R. Craig, K.R. Flower, W.R. Roper, L.J. Wright, Inorg. Chim. Acta 240 (1995) 385.

[51] H. Werner, M.A. Tena, N. Mahr, K. Peters, H.-G. von Schnering, Chem. Ber. 128 (1995) 41.

[52] M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, C. Valero, B. Zeier, J. Am. Chem. Soc. 117 (1995) 7935.

[53] M.T. Ahmet, C. Lu, J.R. Dilworth, J.R. Miller, Y. Zheng, D.E. Hibbs, M.B. Hursthouse, K.M.A. Malik, J. Chem. Soc., Dalton Trans., (1995) 3143.

[54] S.D. Robinson, A. Sahajpal, D.A. Tocher, J. Chem. Soc., Dalton Trans., (1995) 3497.

[55] R.T. Baker, J.C. Calabrese, S.A. Westcott, T.B. Marder, J. Am. Chem. Soc. 117 (1995) 8777.

[56] M. Schlaf, R.H. Morris, J. Chem. Soc., Chem. Commun., (1995) 625.

[57] G. Albertin, S. Antoniutti, D. Baldan, E. Bordignon, Inorg. Chem. 34 (1995) 6205.

[58] B.D. Yeomans, G.A. Heath, D.C.R. Hockless, Acta Crystallogr., Sect. C 51 (1995) 1806.

[59] C. Wang, B. Bley, G. Balzer-Jöllenbeck, A.R. Lewis, S.C. Siu, H. Willner, F. Aubke, J. Chem. Soc., Chem. Commun., (1995) 2071.

[60] D.A. Freedman, D.J. Magneson, K.R. Mann, Inorg. Chem. 34 (1995) 2617.

[61] V. Pawlowski, H. Kunkely, A. Vogler, Inorg. Chim. Acta 234 (1995) 55.

[62] J.A. Guida, O.E. Piro, P.J. Aymonino, Inorg. Chem. 34 (1995) 4113.

[63] S.A. Brewer, L.A. Buggey, J.H. Holloway, E.G. Hope, J. Chem. Soc., Dalton Trans., (1995) 2941.

[64] S.A. Brewer, K.S. Coleman, J. Fawcett, J.H. Holloway, E.G. Hope, D.R. Russell, P.G. Watson, J. Chem. Soc., Dalton Trans., (1995) 1073.

[65] J. Li, G. Schreckenbach, T. Ziegler, J. Am. Chem. Soc. 117 (1995) 486.

[66] A.W. Ehlers, G. Frenking, Organometallics 14 (1995) 423.

[67] Y.F. Hu, G.M. Bancroft, Z.F. Liu, K.H. Tan, Inorg. Chem. 34 (1995) 3716.

[68] H. Werner, R. Flügel, B. Windmüller, A. Michenfelder, J. Wolf, Organometallics 14 (1995) 612.

[69] J. Lewis, P.R. Raithby, J. Organometal. Chem. 500 (1995) 227.

[70] S. Aime, P.J. Barrie, D.F. Brougham, R. Gobetto, G.E. Hawkes, Inorg. Chem. 34 (1995) 3557.

[71] D. Braga, L.J. Farrugia, F. Grepioni, A. Senior, J. Chem. Soc., Chem. Commun., (1995) 1219.

[72] S. Aime, W. Dastrù, R. Gobetto, J. Krause, E. Sappa, Organometallics 14 (1995) 3224.

[73] S. Aime, W. Dastrù, R. Gobetto, J. Krause, L. Violano, Inorg. Chim. Acta 235 (1995) 357.

[74] J.W.M. van Outersterp, M.T.G. Oostenbrink, H.A. Nieuwenhuis, D.J. Stufkens, F. Hartl, Inorg. Chem. 34 (1995) 6312.

[75] Y.-K. Au, K.-K. Cheung, W.-T. Wong, Inorg. Chim. Acta 238 (1995) 193.
[76] A. Neubrand, A.J. Poë, R. van Eldik, Organometallics 14 (1995) 3249.
[77] R.E. Hudson, A.J. Poë, Organometallics 14 (1995) 3238.
[78] G.L. Powell, T.F. Tekut, Inorg. Chim. Acta 229 (1995) 483.
[79] F.W.B. Einstein, V.J. Johnston, A.K. Ma, R.K. Pomeroy, Can. J. Chem. 73 (1995) 1223.
[80] L. Heuer, D. Schomburg, J. Organometal. Chem. 495 (1995) 53.
[81] S.E. Kabir, A. Miah, L. Nesa, K. Uddin, K.I. Hardcastle, E. Rosenberg, A.J. Deeming, J. Organometal. Chem. 492 (1995) 41.
[82] H.-G. Ang, S.-G. Ang, W.-L. Kwik, Q. Zhang, J. Organometal. Chem. 485 (1995) C10.
[83] D.W. Knoeppel, J.-H. Chung, S.G. Shore, Acta Crystallogr., Sect. C 51 (1995) 42.
[84] W.G.-Y. Ho, W.-T. Wong, Polyhedron 14 (1995) 2849.
[85] Y.-K. Au, K.-K. Cheung, W.-T. Wong, Inorg. Chim. Acta 228 (1995) 267.
[86] Y.-K. Au, K.-K. Cheung, W.-T. Wong, J. Chem. Soc., Dalton Trans., (1995) 1047.
[87] R.D. Adams, L. Chen, J.H. Yamamoto, Inorg. Chim. Acta 229 (1995) 47.
[88] R.D. Adams, S.B. Fallon, Organometallics 14 (1995) 4549.
[89] S.-M. Lee, K.-K. Cheung, W.-T. Wong, J. Organometal. Chem. 503 (1995) C19.
[90] J. Lewis, J.R. Moss, Can. J. Chem. 73 (1995) 1236.
[91] S. Chan, W.-T. Wong, J. Organometal. Chem. 489 (1995) C78.
[92] S. Chan, W.-T. Wong, J. Chem. Soc., Dalton Trans., (1995) 3987.
[93] J. Bould, N.P. Rath, L. Barton, J. Chem. Soc., Chem. Commun., (1995) 1285.
[94] J. Bould, M. Pasieka, J. Braddock-Wilking, N.P. Rath, L. Barton, C. Gloeckner, Organometallics 14 (1995) 5138.