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1. Osmium

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CONTENTS

INTRODUCTION

This review covers the coordination, organometallic and cluster chemistry of osmium published in the calendar year 1991, and is the first since the 1981 review published in volume 67 of Coordination Chemistry Reviews. It is not completely comprehensive in that coverage has been restricted to the more well-known journals. In keeping with earlier reviews of osmium chemistry, the emphasis is on coordination chemistry and development of new cluster frameworks. Whilst

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organometallic chemistry is also covered the depth is less; in particular, papers which describe numerous transformations of organic fragments attached to cluster cores are not described in detail. For the purposes of this review, binuclear metal-metal bonded species are discussed under clusters.

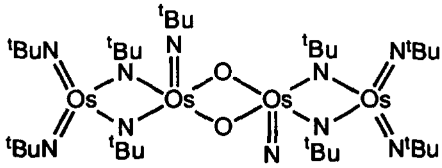
1.1 OSMIUM(VIII)

OsO_4 catalyses the oxidation of $[N_2H_5]^+$ to N_2 by the chlorate ion. Mechanistic investigations revealed that OsO_4 acts as a two-electron oxidant in two separate steps, giving Os^{VI} and Os^{IV} intermediates:

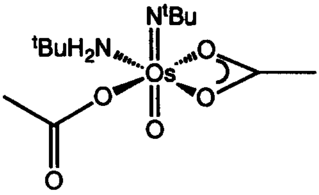
$$[N_2H_5]^+ + OsO_4 + 5\,H^+ \rightarrow Os^{VI} + N_2H_2 + 4\,H_2O$$
$$N_2H_2 + Os^{VI} + 2\,H_2O \rightarrow OsO_2 + N_2 + 6\,H^+$$

The OsO_2 is then oxidised back to OsO_4 by the chlorate ion. The $[ClO]^-$ which is produced in this last step is also involved in oxidising the substrate [1]. Os^{VIII} also catalyses oxidation of the hypophosphite ion $[H_2PO_2]^-$ by *N*-chlorotoluene-*p*-sulphonamide (chloramine T); the kinetics and mechanism of this were investigated [2].

Reaction of OsO_4 with $HN^tBu(SiMe_3)$ yielded the homoleptic tetra-imide $Os(=N^tBu)_4$, together with the tetranuclear Os^{VI} complex (**1**) in which the outer Os centres are tetrahedral and the inner are square pyramidal. $Os(=N^tBu)_4$ may be reduced to the Os^{VI} dimer $[Os(=N^tBu)_2(\mu\text{-}N^tBu)]_2$, and reacts with $[Me_3O][BF_4]$ to give the analogous Os^{VII} dimer $[Os(=N^tBu)_2(\mu\text{-}N^tBu)]_2[BF_4]_2$ [3]. The reactions of the tetra-imide $Os(=N^tBu)_4$ with carboxylic acids and halogens were also investigated. Reaction with acetic acid and pivalic acid gave the mononuclear Os^{VI} complexes (**2**) and (**3**) respectively; whereas (**2**) contains one monodentate and one bidentate acetate, both pivalate ligands are monondentate in (**3**). Reaction of $Os(=N^tBu)_4$ with I_2 produced (**4**) and (**5**). In (**4**) one Os^{VI} centre is tetrahedral and the other trigonal bipyramidal, whereas (**5**) is a mixed-valence Os^{VI}/Os^{VII} compound. An analogue of (**4**) containing Cl in place of I was prepared by reaction of $Os(=N^tBu)_4$ with Cl_2 [4].



(**1**)



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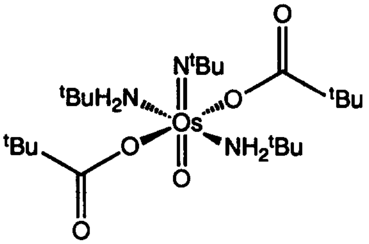

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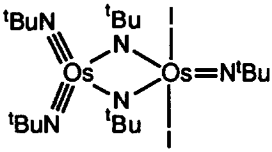

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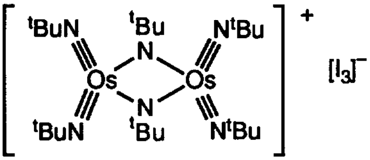

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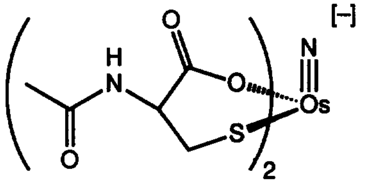
1.2 OSMIUM(VI)

1.2.1 Nitrido amd imido complexes

Reaction of $[Os(\equiv N)(terpy)Cl_2]^+$ with one equivalent of PPh_3 in acetonitrile results in N-atom transfer to the phosphine to give the Os^{VI}-phosphoranimato complex *trans*-$[Os(terpy)(NPPh_3)Cl_2]^+$. Similar results were obtained with a variety of other phosphines. Depending on the nature of the phosphine used, the resulting phosphoranimato complexes can undergo up to two one-electron reductions and one one-electron oxidation [5]. Several $Os^{VI}(\equiv N)$ complexes with heterocyclic ligands have been prepared. $[Os(\equiv N)(\eta^2\text{-terpy})Cl_3]$, in which the terpy ligand adopts a very unusual bidentate binding mode, undergoes chelate ring closure to give $[Os(\equiv N)(terpy)Cl_2]^+$. Numerous other complexes such as mononuclear $[Os(\equiv N)Cl_3(LL)]$ (where LL is two equivalents of a monodentate ligand such as pyridine or pyrazine, or one bidentate ligand such as 4,4'-dimethylbipyridine) and binuclear $[\{Os(\equiv N)Cl_4\}_2(\mu\text{-}L)]^{2-}$ (where L = dioxan, pyrazine) were prepared; the crystal structure of $[Bu_4N]_2[\{Os(\equiv N)Cl_4\}_2(\mu\text{-pyrazine})]$ was determined. The nitrido ligands may be reduced to ammines in protic media [6]. Addition of pyridines to $[Os(\equiv N)Cl_5]^{2-}$ results in liberation of N_2 *via* an N-N coupling reaction and concomitant reduction of the osmium centre. The reaction is triggered by attachment of a pyridine ligand *trans* to the nitride. Thus, heating $[Os(\equiv N)Cl_3(py)_2]$ to 100°C in pyridine yields *mer*-$[OsCl_3(py)_3]$ and N_2, and heating *trans*-$[Os(\equiv N)Cl_3(pic)_2]$ (pic = picoline) in acetonitrile gives *mer*-$[OsCl_3(pic)_2(MeCN)]$ and N_2. For $[Os(\equiv N)Cl_2(terpy)]^+$ the coupling is so facile that the complex is rather unstable. The coupling is thought to occur *via* a (μ–N_2) bridged binuclear intermediate; evidence for this comes from detection of $[\{(pic)_2Cl_3Os^{III}\}N{\equiv}N\{Os^{II}Cl(pic)_4\}]^+$ during a reaction [7].

Anionic complexes $[Os^{VI}(\equiv N)L_2]^-$, where L is *N*-acetyl-L-cysteinate, 3-sulphidopropionate (both S,O-bidentate ligands) or 3-sulphidopropionamidate (an S,N-bidentate ligand) (**6** - **8** respectively) were prepared as models for the iron centre of isopenicillin-*N*-synthetase. All have square pyramidal geometries [8].



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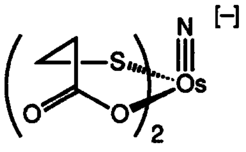

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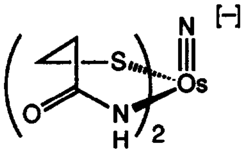

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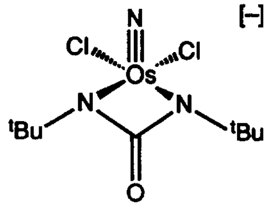
Complex (**9**), prepared from $[Os^{VI}(=O)_2Cl_4]^{2-}$ and ^tBuNCO in acetonitrile, is the first structurally characterised example of an N,N-bidentate ureato ligand. The apical nitride is thought to arise from C-N bond cleavage of an intermediate containing an $Os(=N^tBu)$ linkage [9]. By contrast, reaction of OsO_4 with 2,6-diisopropyl-phenylisocyanate gives the trigonal Os^{VI} complex $[Os(=NAr)_3]$ (Ar = 2,6-diisopropylphenyl; c.f. the Os^{VIII} tetraamides of refs. 3 and 4), which reacts with Me_3NO to give $[Os(=NAr)_3(=O)]$. This Os^{VIII} species reacts with olefins (RCH=CHR) to give tetrahedral metallaimidazolidine complexes such as (**10**).



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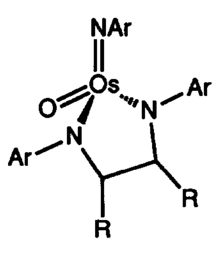

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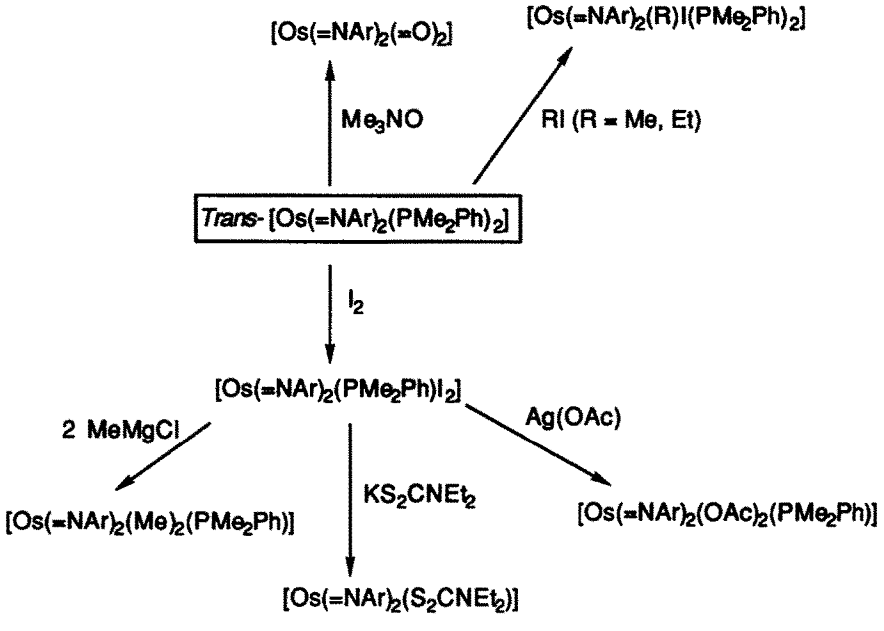
$[Os(=NAr)_3]$ also reacts with small phosphines and phosphites (L) to give planar Os^{IV} species $[Os(=NAr)_2L_2]$, whose further reactions are summarised in scheme 1 [10]. $[Os(\equiv N)Cl_2(CH_2SiMe_3)_3]$ reacts with NaCp or NaCp* to give $[(Cp)Os(\equiv N)(CH_2SiMe_3)_2]$ and $[(Cp^*)Os(\equiv N)(CH_2SiMe_3)_2]$ respectively, the first examples of cyclopentadienyl-nitrido transition-metal complexes. The N atom in these is a 'soft' Lewis base, forming a 1:1 adduct with BF_3 and a 2:1 adduct with Ag^+; $[\{(Cp)Os(CH_2SiMe_3)_2(\equiv N)\}_2Ag][BF_4]$ has been crystallographically characterised. The N atom may also be alkylated [11].

1.2.2 *Oxo complexes*

$[Me_4Os(=O)]$ could be prepared either from OsO_4 and Me_2Zn in 19% yield, or from OsO_4 and $[Ti(O^iPr)_3Me]$ in 50% yield, or by methylation of the glycolate complex $[Os(=O)(OCH_2CH_2O)_2]$ in 60% yield. It undergoes an irreversible oxidation at +2.2 V and a reversible reduction at -1.58 V.



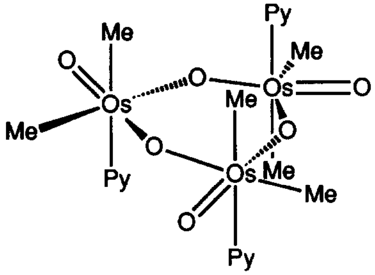
Scheme 1: Reactions of *trans*-$[Os(=NAr)_2(PMe_2Ph)_2]$

The gas-phase structure, determined by electron diffraction, has C_4 symmetry with Os–C = 2.096(3) Å and Os=O = 1.681(4) Å. $Et_4Os(=O)$ was also prepared, and is an orange, air-stable crystalline solid [12]. The first perfluorophenyl complex of osmium, $[(\eta^1\text{-}C_6F_5)_2Os(=O)_2(py)_2]$, was prepared from the glycolate complex $[Os(=O)_2(OCH_2CH_2O)(py)_2]$ by reaction with $[(C_6F_5)_2Zn(py)_2]$. The crystal structure has been determined; the oxo ligands are mutually *trans*, the two pyridyl groups mutually *cis* and the two perfluorophenyl ligands also mutually *cis*. It sublimes at 230°C without decomposition, its high stability being due to the electron-withdrawing, σ-bound C_6F_5 ligands [13]. Glycolate-Os^{VI} complexes were also used as starting materials for the alkyl complexes [$R_2Os(=O)_2L$] and [$R_2Os(=O)_2L_2$], where L is a neutral, monodentate ligand. For L = pyridine, the equilibrium

$$R_2Os(=O)_2(py)_2 \rightleftharpoons R_2Os(=O)_2(py) + py$$

may be driven to the right *in vacuo* and to the left by excess pyridine. Although $Me_2Os(=O)_2(py)$ is monomeric in solution, it exists as a trimer in the solid state (**11**); in contrast, [$(Me_3SiCH_2)_2Os(=O)_2(py)$] has a trigonal bipyramidal monomeric crystal structure [14].

The series of complexes [$Os(=O)_2(py)_2L$], [$Os(=O)_2(3\text{-pic})_2L$], where L is an O,O-bidentate ligand (lactate, atrolactate, citrate, oxalate, quinate, oxo-isobutyrate, tartrate etc.) were prepared as models for the complexation of sugars to metal ions; all were characterised by XPS and mass spectrometry, and contain *trans*-OsO_2 groups. Some binuclear complexes with tartrate as bridging ligand were also prepared [15]. The crystal structure of [$\{Os(=O)_2(py)_2\}_2(C_{10}H_{12}O_9)$], a binuclear osmate ester containing two $Os(=O)_2(py)_2O_2$ centres prepared from reaction of OsO_4 with 3,4-diethyl-furandicarboxylate and pyridine, has been determined [16].



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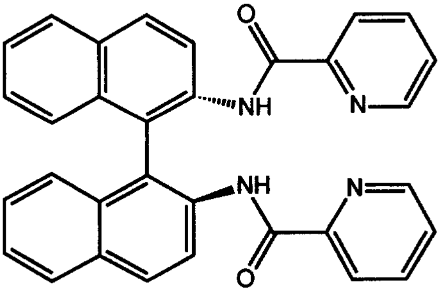
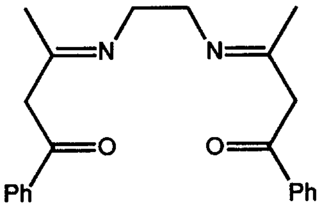


(H_2**12**)



(H_2**13**)

The *trans*-dioxoosmium(VI) complex of the chiral tetradentate binaphthyl-based ligand (H_2**12**) has been prepared. Since high-oxidation state osmium complexes are potential catalysts for oxidation reactions, this chiral complex ofers a possible route to chiral catalysis [17]. *Trans*-dioxoosmium(VI) complexes of dibasic tetradentate Schiff bases such as (H_2**13**), prepared from β-diketones and 1,2-diaminoethane, have been studied. Reduction with thiols leads to complexes such as *trans*-[$Os^{IV}(SCH_2Ph)_2$(**13**)], which was crystallographically characterised. The Os^{IV}/Os^{III} reduction potentials of these complexes vary with the delocalisation ability of the axial thiolates [18].

The 4-fluorophenylimido-oxoosmium(VI) porphyrin complexes [$Os(=O)(=NC_6H_4F)$(**P**)] (where P is the dianion of *meso*-tetraphenylporphyrin or *meso*-tetrakis(3,4,5-trimethoxyphenyl)-porphyrin) were prepared and characterised by ^1H NMR and UV/VIS spectroscopy; the UV/VIS spectra are similar to those of *trans*-dioxoosmium(VI) porphyrin complexes [19]. Detailed ^2D and ^{13}C NMR and mass spectra of $C_{60}(OsO_4)(4\text{-}^tBu\text{-pyridine})_2$ have been performed [20,21]. The presence of an $O_2Os(=O)_2$ unit added across one double bond of the C_{60} reduces the symmetry and allows spectroscopic studies to be performed which are not feasible on free C_{60}.

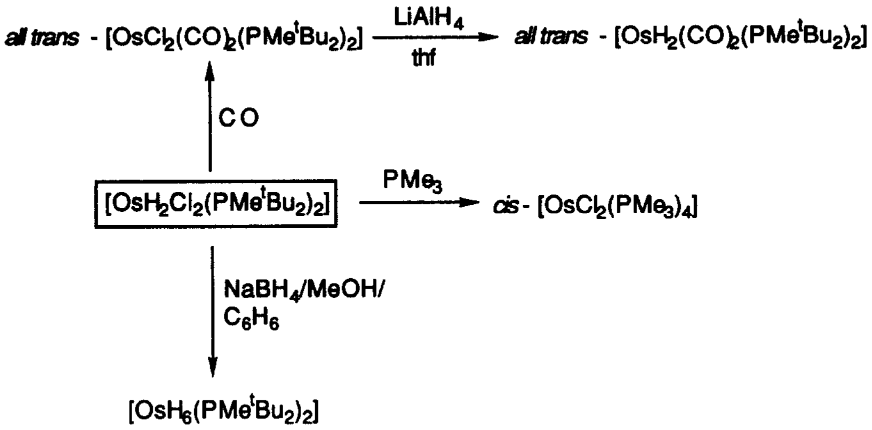
1.3 OSMIUM(V)

The ESR spectrum of $[Os(=O)\{Et_2C(O)CO_2\}_2]^-$ was measured, and the reactivity of the complex compared with analogous $Ru^V(=O)$ complexes with α-hydroxycarboxylate ligands [22]. Normal coordinate analyses for the series of Os^V, Os^{IV} and Os^{III} complexes $[OsX_nY_{6-n}]^{z-}$ ($X \neq Y$ = F, Cl, Br; z = 1,2,3) have been carried out [23].

1.4 OSMIUM(IV)

The kinetics of dissociation of H_2 from $[OsH_4(PTol_3)_3]$ (Tol = $p\text{-}C_6H_4CH_3$) and $[OsH_5(PTol_3)_3]^+$ were measured; the dissociation rate increases with increasing protonation [24]. The hydride spin-lattice relaxation times (T_1) for $[OsH_4(PTol_3)_3]$ and its deuterated isotopomers $[OsH_xD_{4-x}(P\text{-}d\text{Tol}_3)_3]$ (x = 1 - 4; *d*Tol = $p\text{-}C_6H_2D_2CH_3$ with the D atoms ortho to P) were recorded as a function of temperature. For these and 33 other 'classical' hydrides, the relaxation rates correlate well with the expected values. However for $\eta^2\text{-}H_2$ complexes the agreement between theory and observation is less satisfactory [25]. $[Os(NH_3)_4H_2]^{2+}$ undergoes facile substitution of NH_3 by acetonitrile, pyridine, imidazole, halide ion or water. The initial product is *trans*-$[Os(NH_3)_3H_2L]^{2+}$, but NMR spectroscopy shows that this converts to the *cis* isomer, slowly but nearly completely [26].

The preparation of the new diamgnetic complexes $[OsH_2Cl_2(PR_3)_2]$ (PR_3 = P^iPr_3, PMe^tBu_2) has been achieved by reaction of $OsCl_3.xH_2O$ with PR_3 in 2-propanol at reflux; the crystal structure of $[OsH_2Cl_2(P^iPr_3)_2]$ shows a distorted square antiprismatic (formally D_{4d}) geometry with two vacant sites in the alternate positions of one square base. $[OsH_2Cl_2(PMe^tBu_2)_2]$ catalyses hydrogenation of olefins and dienes, and reduction of benzylideneacetone and benzylideneacetophenone to the saturated ketones. Some reactions of $[OsH_2Cl_2(PMe^tBu_2)_2]$ are summarised in Scheme 2 [27].



Scheme 2: Reactions of $[OsH_2Cl_2(PMe^tBu_2)_2]$.

The energy levels of the low-lying d-orbitals of *trans*-$[OsCl_4I_2]^{2-}$ and $[OsCl_3I_3]^{2-}$ (both *fac* and *mer* isomers) were determined, by examination of their UV/VIS spectra (recorded at 10K) and their emission spectra (recorded between 10K and 20K) over the range 4,200 to 12,500 cm^{-1}, a region in which only d-d transitions are expected [28].

1.5 OSMIUM(III)

The electron-transfer cross-reaction rate constant for the thermodynamically unfavourable oxidation of $[Fe(4,7\text{-}Me_2phen)_3]^{2+}$ by *poly*-$[Os(bipy)_2(4\text{-vinyl-bipy})]^{3+}$ was measured at the redox polymer surface in a variety of solvents. A theoretical model incorporating solvent relaxation time, solvent dielectric constant and reaction free energy was developed to explain the solvent dependence of the electron-transfer rate [29]. The kinetics of oxidation of thiosulphate by $[Os(phen)_3]^{3+}$ according to the reaction:

$$2\,[Os(phen)_3]^{3+} + 2\,[S_2O_3]^{2-} \rightarrow 2\,[Os(phen)_3]^{2+} + [S_4O_6]^{2-}$$

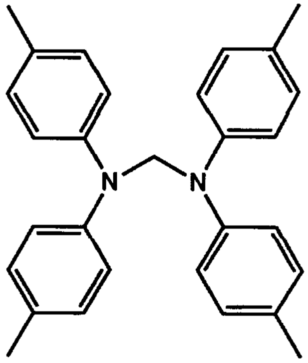
were examined. The redox potential of the osmium centre was varied by using phenanthroline derivatives such as 4,7-dimethylphenanthroline, 5,6-dimethylphenanthroline and 5-chlorophenanthroline. Irrespective of the precise redox potential,the rate law was found to be:

$$-d[Os^{III}]/dt = 2k_1[Os^{III}][S_2O_3^{2-}] + 2k_2[Os^{III}][S_2O_3^{2-}]^2.$$

Both k_1 and k_2 increase as the reduction potential of the Os^{III} increases; both terms describe outer-sphere processes [30]. The kinetics of Os^{II}/Os^{III} self-exchange in $[Os(CN)_6]^{4-/3-}$ in aqueous media were examined by ^{13}C NMR line-broadening techniques. At 25°C the rate constant is $(8.9 \pm 0.5) \times 10^4\ M^{-1}\ sec^{-1}$. It was found that the self-exchange rate decreases with increasing acidity, due to the presence of additional equilibria involving protonated species such as $[(HNC)_2Os(CN)_4]^{2-}$ and $[(HNC)Os(CN)_5]^{3-}$. The rate constants were discussed in terms of inner-sphere and solvent reorganisation barriers, and compared with the values for the analogous Fe and Ru complexes [31].

The electrochemical, UV/VIS and structural properties of the two series of Os^{III} complexes $[OsBr_6]^{3-}$, $[OsBr_5(CO)]^{2-}$, $[OsBr_4(CO)_2]^-$ and *trans*-$[OsX_4(MeCN)_2]^-$, $[OsX_4(MeCN)(CO)]^-$, $[OsX_4(CO)_2]^-$ (X = Cl, Br) were examined to determine the effects of stepwise variation in the number of CO ligands on complex properties. In each case it was found that the Os^{III}/Os^{II} and Os^{III}/Os^{IV} couples shift two to three times further for addition of the first CO than for the second; i.e. a very non-linear accumulation of ligand electronic effects, contrary to recent predictions [32].

The triply-bonded species $[Os_2X_8]^{2-}$ (X = Cl, Br) react with a variety of isonitriles RNC to give the 17-electron complexes $[OsX_4(CNR)_2]^-$ in good yield, and with CO in ethanol to give $[OsX_4(CO)(EtOH)]^-$. The EtOH in this last complex is labile and may be replaced by any of several Lewis bases L (e.g. dmso, thf, pyridine, phosphines, isonitriles) to give $[OsX_4(CO)L]^-$. The spectroscopic and electrochemical properites of the new complexes were examined. Crystal structures of $[Bu_4N][OsCl_4(CN\text{-}xylyl)_2]$ and $[Bu_4N][OsCl_{2.68}Br_{1.32}(CO)(dmso)]$ showed them both to have *trans* geometries [33]. $[Os_2(O_2CCH_3)_4Cl_2]$ reacts with molten di(*p*-tolyl)formamidine (H**14**) to give, after crystallisation, $[Os_2(\mathbf{14})_4Cl_2].C_6H_6$.hexane. The Os–Os bond length is 2.467(1)Å, which is very long for a triple bond between two Os^{III} atoms. The ground-state electronic structure was established by theoretical and magnetic studies, and shows that the long bond is due to the shift of an electron from a δ^* orbital to a more strongly antibonding π^* orbital [34]. Electrochemical studies on $[OsCl_2(PPh_3)_2(sq)]$, where sq is one of a variety of semiquinones, show the presence of an Os^{III}/Os^{IV} oxidation and a semiquinone-catecholate reduction. The complexes catalyse oxidation of primary alcohols by *N*-methylmorpholine-*N*-oxide [35].



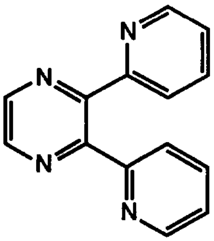
(H14)

Whereas reaction of [Os(SR)$_3$(PMe$_2$Ph)$_2$] (R = C_6F_5, C_6H_4F) with benzoic acid gives the paramagnetic Os^{III} complexes [Os(SR)$_2$(O$_2$CPh)(PMe$_2$Ph)], which are octahedral with mutually *trans* thiolates and mutually *cis* phosphines, reaction with HCl gives the dimagnetic Os^{IV} complexes [OsCl(SR)$_3$(PMe$_2$Ph)] which have trigonal bipyramidal geometries. These may have possible use in further syntheses of new osmium complexes, as they are coordinatively unsaturated and allow access to reactive Os^{III} centres by reduction [36]. In [Os(EtSCS$_2$)$_2$(PPh$_3$)$_2$]$^{0/1+}$ the Os^{II} state has a strong preference for *cis* S_4P_2 geometry whereas the Os^{III} state prefers a *trans* geometry, due to changes in the balance of steric hindrance and $d\pi$-$p\pi$ back-bonding with oxidation state [37]. Similar behaviour is observed with xanthate ligands in the Os^{II} and Os^{III} complexes [Os(ROCS$_2$)$_2$(PPh$_3$)$_2$]$^{0/1+}$ (R = Me, Et, ^{i}Pr, PhCH$_2$). Both *cis* and *trans* forms were isolated for each oxidation state; electrochemical studies confirmed that the Os^{II} state is more stable in a *cis* geometry and the Os^{III} state is more stable in a *trans* geometry. The decrease of back-bonding in the Os^{III} state allows steric effects to predominate, with the bulky phosphines moving as far apart as possible [38].

1.6 OSMIUM(II)

1.6.1 Complexes with N-heterocyclic ligands

The crystal structure of [Os(bipy)$_3$][PF$_6$]$_2$ has been determined; it is isostructural with [Ru(bipy)$_3$][PF$_6$]$_2$ [39]. [Os(bipy)$_3$]$^{2+}$ has been incorporated into Nafion films on electrode surfaces, in order to study the effects of ion association (of electroactive cations and electro-inactive counterions) within the polymer on the dynamics of electron hopping. A very non-linear increase in the apparent diffusion coefficient if incorporated counter-ions with concentration was observed [40]. The quenching of the MLCT excited state of [Os(bipy)$_3$]$^{2+}$ and other Os^{II}-based photoactive complexes by anthracene and 2,3-benzanthracene was shown to occur by energy-transfer in the Marcus-inverted region. This shows that the inverted region can be reached for energy-transfer as well as electron-transfer [41].



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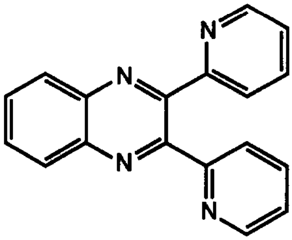

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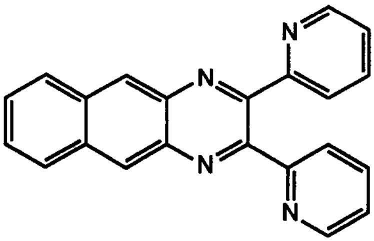

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Copolymeric films of *poly*-$[Ru(4\text{-}Me\text{-}bipy)_2(4\text{-}vinyl\text{-}py)_2]^{2+}$ and $[Os(4\text{-}vinyl\text{-}bipy)_3]^{2+}$ were prepared by reductive electropolymerisation on platinum-disc electrodes. Photolysis in the presence of $[Me_2NCS_2]^-$ leads to ejection of the 4-vinylpyridine fragments and consequent loss of the Ru centres from the polymer. This results in a film of *poly*-$[Os(4\text{-}vinyl\text{-}bipy)_3]^{2+}$ containing specifially-sized voids attached to the electrode surface, capable of 'size-selective' electrochemistry [42]. $[Os(bipy)_2L][PF_6]_2$ (L = **15**, **16**, **17**), in which only one site of the potentially binucleating ligand L is occupied, were prepared and characterised by electrochemistry and UV/VIS spectroscopy. In each case the LUMO is on the ligand L rather than on a bipy ligand [43].

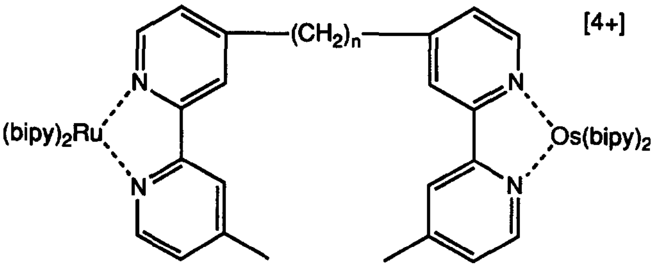
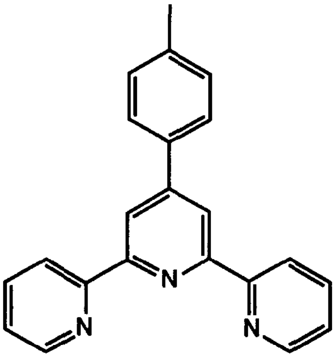


Figure 1. A series of polymethylene-bridged Ru-Os binuclear complexes (n = 2,3,5,7)



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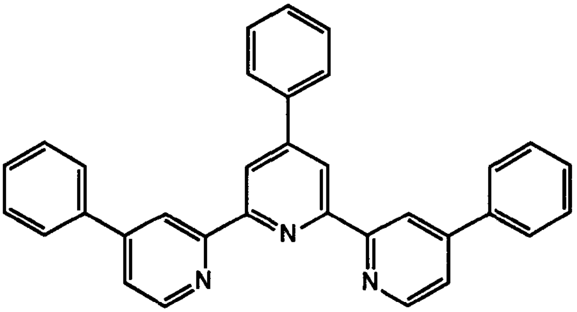
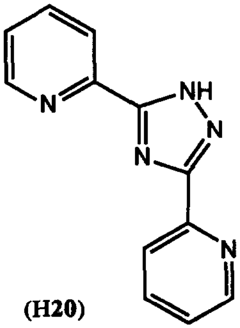


(19)

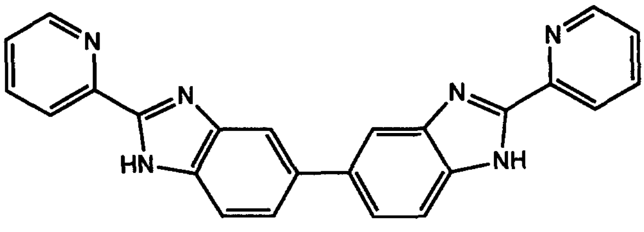
The photophysical properties of the series of complexes in Figure 1, containing polymethylene-linked $[Ru(bipy)_3]^{2+}$ and $[Os(bipy)_3]^{2+}$ chromophores, were examined. The bridging ligands were prepared by deprotonation of a methyl group of 4,4'-dimethylbipyridine with LDA followed by reaction with half an equivalent of $Br(CH_2)_nBr$. Near-complete quenching of the emission from the ruthenium centre was observed, accompanied by an enhancement of the emission from the osmium centre. An energy-transfer mechanism (*via* a Förster-type dipole-dipole interaction) was proposed; the energy transfer rate constant drops from 5.3×10^8 sec^{-1} when n = 2 to 1 x 10^8 sec^{-1} when n = 7, and is proportional to r^{-6} (where r is the Ru-Os separation) [44]. The Os^{II} complexes with terpy, 4'-tolylterpy (**18**) and 4,4',4"-triphenylterpy (**19**) show a continuous variation in redox and spectroscopic proprties according to the degree of ligand substitution. All of the complexes are strongly luminescent in solution at room temperature [45].

Attachment of one or two $Os(bipy)_2{}^{2+}$ units at the N,N-chelating sites of 3,5-bis(2-pyridyl)triazole (H**20**) yielded $[Os(bipy)_2(\mathbf{20})]^+$ and $[\{Os(bipy)_2\}_2(\mu\text{-}\mathbf{20})]^{3+}$, whose electrochemical, UV/VIS spectroscopic and photochemical properties were compared with those of $[Os(bipy)_3]^{2+}$. For both complexes with (**20**), the LUMO is based on a bipyridine ligand, resulting in bipy-based reduction processes and $Os(d\pi) \rightarrow bipy(\pi^*)$ charge-transfer bands in the UV/VIS spectrum. The mononuclear and binuclear complexes have emission lifetimes of 250 ns and 340 ns respectively at 90K [46]. The heterobinuclear complex $[(bipy)_2Ru(\mu\text{-}\mathbf{20})Os(bipy)_2]^{3+}$ exists in two isomeric forms, as the two binding sites of the bridging ligand are inequivalent; their properties are generally similar. In each case, excitation of the Ru^{II} centre is followed by energy transfer with nearly 100% efficiency to the Os^{II} centre (c.f. ref. 44). By contrast the one-electron oxidised form (with an Os^{III} centre) shows no luminescence, due to the presence of a low-lying inter-valence charge transfer (IVCT) state which deactivates the luminescent MLCT levels [47].

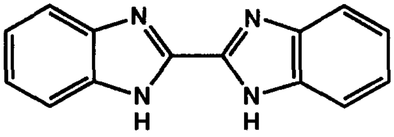
The binuclear complexes $[(N\text{-}N)_2Os(\mu\text{-}H_2\mathbf{21})Os(N\text{-}N)_2]^{4+}$ (N-N is bipy or phen) are dibasic acids due to the imidazole protons of the bridging ligand. Consequently their UV/VIS and electrochemical properties are strongly pH dependent. The IVCT band of the mixed-valence Os^{II}/Os^{III} complex moves to lower energy and becomes 4 to 6 times more intense when the bridging ligand is deprotonated, thereby allowing proton-induced switching of the metal-metal interaction [48]. The homo- and hetero-binuclear complexes $[\{(bipy)_2Os\}_2(\mu\text{-}\mathbf{22})]^{2+}$ and $[(bipy)_2Os(\mu\text{-}\mathbf{22})Ru(bipy)_2]^{2+}$ have an extensive series of redox processes. The bipy ligands may each undergo one-electron reductions, and oxidation state combinations +2/+3, +3/+3 and +3/+4 are accessible for the metal centres [49].



(H**20**)



(H_2**21**)



(H_2**22**)

1.6.2 Complexes containing phosphine ligands

The crystal structures of $[OsCl(CO)(PPh_3)(tacn)]_2[ZnCl_4]$ (where tacn = 1,4,7-triazacyclononane) [50] and of the *cis, cis* and *trans, trans* isomers of $[OsBr_2(CO)(MeCN)(PPh_3)_2]$ [51] have been determined. In the latter case, steric contributions to the structures of the two isomers were discussed [51]. NMR spectroscopy of the five-coordinate complex $[OsHCl(CO)(P^iPr_3)_2]$ in acetone shows that coordinated acetone inserts into the Os–H bond to give a coordinated isopropoxide, which re-converts to coordinated acetone by β-elimination. For such insertion to occur requires side-on η^2-bonding of the C=O bond. The complex catalyses hydrogen atom transfer from 2-propanol to cyclohexanone and acetophenone [52]. $[OsHCl(CO)(P^iPr_3)_2]$ is also an active and selective catalyst for the addition of Et_3SiH to phenylacetylene. Either *cis* or *trans* $PhCH{=}CHSiEt_3$ may be obtained in good yield depending on the reaction conditions; the reaction occurs *via* an $[Os(SiEt_3)(\eta^2\text{-}H_2)Cl(CO)(P^iPr_3)_2]$ intermediate [53]. A labile PPh_3 ligand in $[OsHCl(CO)(PPh_3)_3]$ may be substituted by a variety of other phosphines including PCl_3, PCl_2Ph, $PH_2(C_6H_2Me_3)$ and 3,4-dimethyl-*P*-phenyl-phosphole. In each case the new ligand is *trans* to the hydride and *cis* to the other two PPh_3 ligands; the PCl_3 and PCl_2Ph ligands may in turn be substitued by MeO^-, H^- or toluidine. The hydride ligand may be displaced with $HClO_4$ in MeCN resulting in loss of H_2 to give a cationic acetonitrile adduct, and by Cl_2 to give a mixture of isomeric neutral dichloride complexes [54].

The H_2 ligand in *trans*-$[OsH(dppe)(\eta^2\text{-}H_2)]^+$ [dppe = 1,2-bis(diphenylphosphino)ethane] is rapidly spinning and has a long bond (0.99 Å). Likewise, $[OsH(depe)(\eta^2\text{-}H_2)]^+$ [depe = 1,2-bis(diethylphosphino)ethane] has properties mid-way between a complex containing H^- and $\eta^2\text{-}H_2$, and a trihydride complex. Homolytic cleavage of the H–H bond is a relatively low energy process; NMR spectroscopy of deuterium-substituted isotopomers showed that there is an equilibrium between (spinning H_2 + hydride) and (trihydride) at 180K [55]. The five coordinate structure of $[OsCl(dcpe)_2]^+$ [dcpe = 1,2-bis(dicyclohexylphosphino)ethane] is stabilised by the bulky phosphine ligands. Reaction with H_2 afforded $[OsCl(\eta^2\text{-}H_2)(dcpe)_2]^+$, which could also be prepared by protonation of $[OsHCl(dcpe)_2]$. On the basis of ^1H and $^{31}P\text{-}\{^1H\}$ NMR measurements, $[OsH_3(dcpe)_2]^+$ was proposed to have a seven-coordinate trihydride structure (i.e. formally Os^{IV}). Reaction of $[OsCl_2(dcpe)_2]$ with H_2 gave both *trans*-$[OsHCl(dcpe)_2]$ and *cis*-$[Os(H)_2(dcpe)_2]$ [56].

The *trans* isomers of $[OsL_4X_2]$ (L = PMe_3, PMe_2Ph, $AsMe_3$, $SbPh_3$, py; X = Cl, Br) convert to the *cis* isomers in chlorinated solvents. Oxidation of *trans*-$[OsL_4X_2]$ by O_2 or HNO_3 yielded *trans*-$[Os^{III}L_4X_2]^+$, which have $Os^{II/III}$ and $Os^{III/IV}$ couples whose potentials are dependent on the natures of L and X. The crystal structure of *trans*-$[Os(PMe_3)_4Cl_2][BF_4]$ was determined [57] (c.f. refs. 37 and 38). The charge distribution in neutral osmium-dioxolene complexes was investigated. The structural parameters of $[Os(PPh_3)_2(dbq)Cl_2]$ (dbq = 3,5-$^tBu_2$-1,2-benzoquinone) suggest that the dbq ligand (formally a quinone) is actually intermediate between the semiquinone and catechol oxidation states, resulting in a higher oxidation state than +2 for the osmium centre. Similarly the crystal structure of *cis*-$[Os(PPh_3)_2(dbq)_2]$ suggests that both ligands are in the catecholate oxidation state (i.e. an Os^{IV} complex). These complexes undergo ligand-based interconversions between the redox states, similar to those of the analogous ruthenium complexes [58].

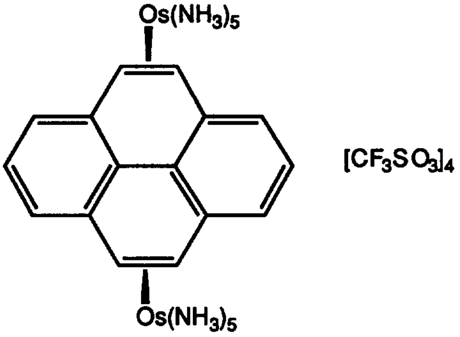
1.6.3 *Other coordination complexes*

The crystal structure of $Na_4[Os(CN)_6].10H_2O$ was determined; it consists of layers of $[Os(CN)_6]^{4-}$ anions intercalated with layers of hydrated Na^+ ions [59]. $[\{Os(CO)_3I\}_2(\mu\text{-}I)_2]$ was prepared by reaction of $[(\mu\text{-}H)Os_3(CO)_{11}]^-$ with CH_2ICl and BCl_3, and the crystal structure determined [60]. Reductive nitrosylation of OsO_4 with $NH_2OH.HCl$ in the presence of oxalate gives the square-pyramidal $[Os(NO)(C_2O_4)]^-$ in which the NO^+ ligand is axial. This reacts with HX (X = halide) to give $[Os(NO)X_5]^{2-}$ as the major product in each case, which all undergo a one-electron oxidation. For X = Cl or I, reaction of $[Os(NO)X_5]^{2-}$ with phen affords $[Os(NO)X_3(phen)]$; for X = Br, the same reaction only results in $[Hphen]_2[Os(NO)Br_5].2H_2O$ which was crystallographically characterised [61]. The crystal structures of $[Os(NO)Br_3(Et_2S)(Et_2SO)]$ and $[Os(NO)Cl_2(Et_2PPh)_2(MeOCH_2CH_2O)]$ were determined; both are octahedral, with the sulphoxide and alkoxide respectively *trans* to the NO^+ [62].

Condensation of [Os(TPP)] (TPP = *meso*-tetrphenylporphyrin) with O_2 gives the peroxo-bridged binuclear complex $[Os(TPP)]_2(\mu\text{-}O_2)$, which has an O–O vibration at 1090 cm^{-1} [63]. [Os(TTP)] [TTP = *meso*-tetra(p-tolyl)porphyrin] reacts with CMe_2–CMe_2–$SiMe_2$ to give the silylene complex $[(TTP)Os{=}SiMe_2.thf]$; similar products are obtained from reaction of $[Os(TTP)]^{2-}$ with R_2SiCl_2 [64].

1.6.4 *Organometallic complexes*

The crystal structure of $[\{Os(NH_3)_5\}_2(\mu\text{-pyrene})][CF_3SO_3]_4.4Me_2CO$ (23) was determined. The metal-centred oxidations are separated by 100 mV, indicative of a weak metal-metal interaction across the bridging pyrene ligand [65]. The η^2-coordination of an $Os(NH_3)_5{}^{2+}$ fragment to anisoles, phenols and anilines results in an enhancement of electrophilic attack at the *para* position of the aromatic rings [66]. Reaction of $[Os(NH_3)_5(diallyl\text{-}ether)]^{2+}$ with triflic acid gives the allyl complex $[Os(NH_3)_5(\eta^3\text{-}C_3H_5)]^{3+}$ in good yield; it shows no redox activity, but undergoes addition of nucleophiles at the terminal allyl carbon atom. Cyclic allyl complexes were also prepared from partial hydrogenation of $Os(NH_3)_5{}^{2+}$ complexes with η^2-bound anisole or 1,4-dimethoxybenzene. The affinity of the $Os(NH_3)_5{}^{2+}$ fragment for the C=C double bond of a conjugated diene is higher than for an isolated alkene [67]. The crystal structure of $[(2,3\text{-}\eta^2\text{-}2,5\text{-dimethylpyrrole})Os(NH_3)_5]^{2+}$ reveals that η^2-2,3-coordination of pyrrole (i.e. as an alkene) transforms the ligand to an enamine, with significant localisation of the π-electron density [68].



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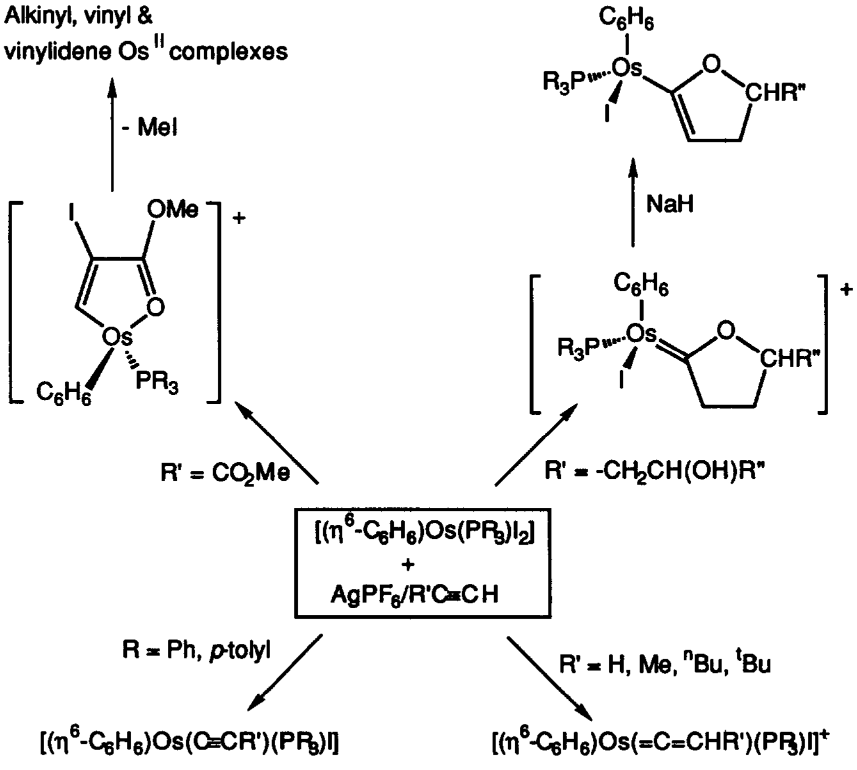
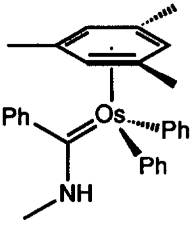


Scheme 3: Reactions of $[(\eta^6\text{-}C_6H_6)Os(PR_3)I_2]$ with terminal alkynes

Reaction of $[(\eta^6\text{-}C_6H_6)Os(PR_3)I_2]$ with terminal alkynes R'C≡CH can proceed along various paths depending on the nature of R' (Scheme 3). If R' is an alkyl or aryl group, the product is either a neutral alkinyl [69, 70] or a cationic vinylidene [70] species; if R' = CO_2Me, the product is a vinyl complex containing a five-membered ring in which an O atom also coordinates to the Os [70]; if R' = $CH_2CH(OH)R''$ the product is a cyclic oxycarbene, which may be deprotonated to give a vinyl ether [71]. Several other reactions of these products were also described. New routes to the azavinylidene half-sandwich compounds $[(\eta^6\text{-arene})Os(=N=CRR')L]^+$ (R, R' = Et, Ph; L = P^iPr_3, PMe^tBu_2; arene = benzene, mesitylene) have been developed starting from $[(\eta^6\text{-arene})OsLI_2]$ [72].

Numerous reactions of $[(\eta^6\text{-mes})Os(CO)Cl_2]$ and $[(\eta^6\text{-mes})Os(CNR)Cl_2]$ (mes = 1,3,5-trimethylbenzene) with alkyl and aryl Grignard and lithium reagents have been carried out. In general, displacement of a halide occurs to give mononuclear products containing a σ-bound alkyl or aryl group in addition to the π-bound mesitylene [73, 74]. For the reaction of $[(\eta^6\text{-mes})Os(CO)Cl_2]$ with $C_6H_{11}MgCl$, $[(\eta^6\text{-mes})Os(C_6H_{11})_2(CO)]$ is the major product, whereas use of $C_6H_{11}MgBr$ results in $[(\eta^6\text{-mes})Os(C_6H_{10})(CO)]$ where the coordinated cyclohexene has an *endo* configuration [74]. Another unexpected result was the formation of (24) as a by-product in the reaction of $[(\eta^6\text{-mes})Os(CNMe)Cl_2]$ with PhMgBr [73].

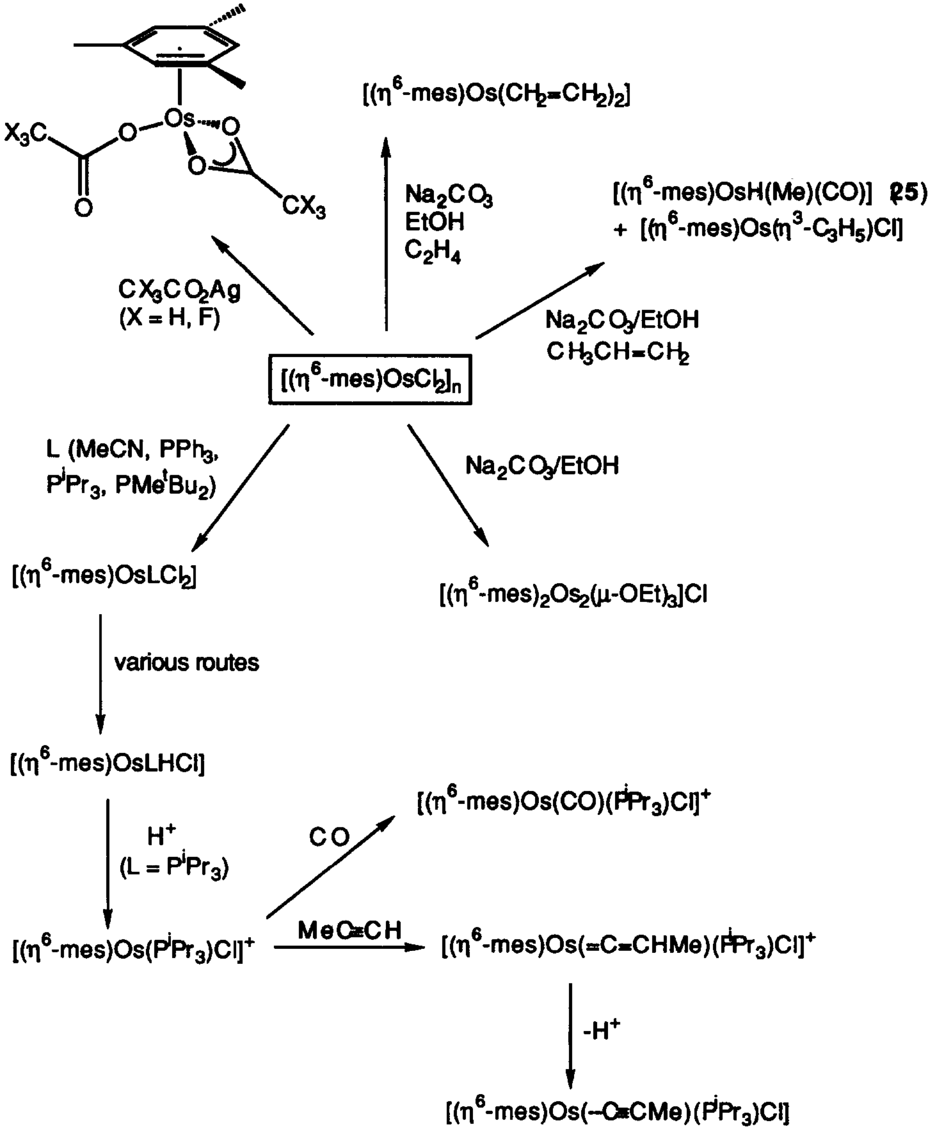
Some reactions of $[(\eta^6\text{-mes})OsCl_2]_n$ are summarised in Scheme 4 [75, 76]. Labelling experiments using C_2D_5OD as solvent showed that in (25), formed by reaction of $[(\eta^6\text{-mes})OsCl_2]_n$ with Na_2CO_3/ethanol/propene, all three new ligands (H, CO and CH_3) have come from the solvent ethanol. The ethanol, therefore, was controllably fragmented to CH_3, CO, H and H_2 (which is trapped by the olefin) [75].



(24)

Protonation of $[(\eta^6\text{-mes})OsH_2(PMe_3)]$ with HBF_4 gives $[(\eta^6\text{-mes})OsH_3(PMe_3)]^+$, which has a classical trihydride structure according to T_1 measurements [76]. $[(\eta^6\text{-}C_6H_6)OsLH_3]^+$ (L = phosphine or phosphite) were readily prepared by protonation of the neutral dihydrides. They are fluxional at room temperature (single hydride resonance in the NMR spectrum) but at low temperature show well-resolved AB_2 or A_2B systems with large, temperature-dependent J_{AB} couplings due to quantum-mechanical exchange coupling between the protons [77]. Reaction of $[(pp_3)OsCl_2]$ with Na/Hg in benzene [$pp_3 = P(C_6H_4\text{-2-}PMe_2)_3$] afforded $[(pp_3)OsH(C_6H_5)]$ [78].

The monomeric arene-nitrido complexes $[(\eta^6\text{-}C_6Me_6)Os(\equiv N^tBu)]$ react with alcohols to give $[(\eta^6\text{-}C_6Me_6)Os(\text{alkoxide})_2]$ and with thiols to give $[(\eta^6\text{-}C_6Me_6)Os(\text{thiolate})_2]$; amine/imido exchange reactions are also possible. These reactions allow new routes into low-valent osmium complexes containing Os–X (X = N, O, S) bonds [79].



Scheme 4: Some reactions of $[(\eta^6\text{-mes})OsCl_2]_n$

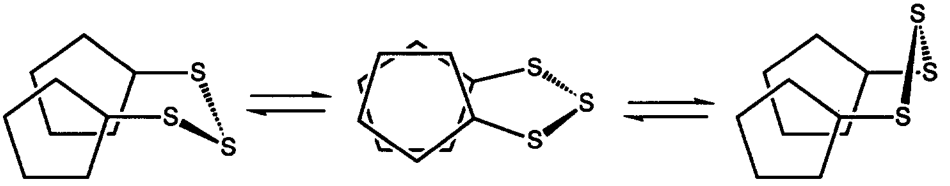
1.7 OSMIUM(I)

Bending potential energy surfaces for twelve isoelectronic states of $[OsH_2]^+$, formed by insertion of Os^+ into H_2 in the gas phase, have been calculated [80].

1.8 OSMIUM(0)

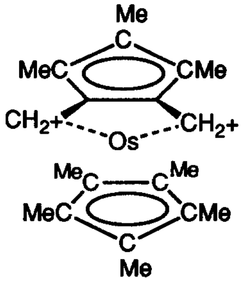
1.8.1 *Sandwich complexes*

The UV/VIS spectra of Cp_2Os and $Cp^*{}_2Os$ in the vapour phase were compared to the solution spectra. Differences arise due to the presence of two sharp bands due to the $5d(a_{1g}) \rightarrow [6p(e_{1u})]^*$ and $5d(a_{1g}) \rightarrow [6p(a_{2u})]^*$ Rydberg excitations in the vapour phase spectra (where * denotes the excited state). Although these transitions also occur in solution, the spectral bands are broadened beyond detection [81]. An osmocene derivative with a trisulphide bridge linking the two rings was shown by NMR spectroscopy to undergo a fluxional bridge-reversal process (Scheme 5) whose activation free energy is related to the strength of the metal-ring bonding and the torsional energies of the S–S bonds [82].

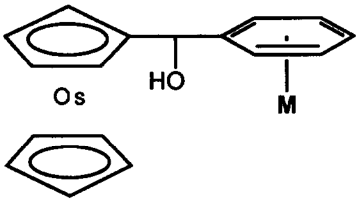


Scheme 5: Fluxional behaviour of trisulphide-bridged osmocene

Decamethylosmocene-1,2-dicarbinol loses two H_2O molecules on protonation, to give $[Cp^*OsC_5Me_3(CH_2)_2]^{2+}$ (**26**) in which the two $-CH_2^+$ groups interact with the metal centre; the 1,1'-isomer $[Os(C_5Me_4CH_2)]^{2+}$ was also prepared. MO calculations suggest that a variety of distortions should occur, including bendong of $-CH_2^+$ groups out of the Cp* ring planes, ring canting, and off-centre ring slipping [83]. α-Osmocenylcarbinols and their Cp* analogues show intramolecular OH···Os hydrogen bonding [84]; the steric influences of substituents on the carbinol group and the Cp rings on this H-bonding were investigated [85]. The pendant phenyl rings of phenyl-substituted α-osmocenyl carbinol could be ligated to other metal complexes to give (**27**) and (**28**) [86].



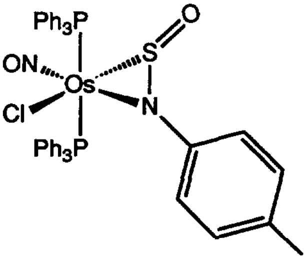
(**26**)

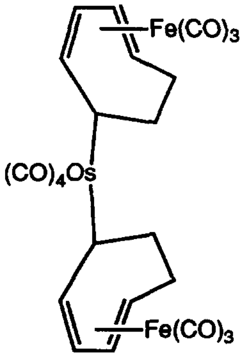


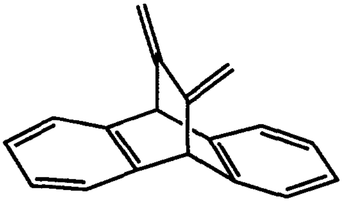
(**27**), M = $Co_4(CO)_9$; (**28**), M = $Cr(CO)_3$

1.8.2 Other Os(0) complexes

$[OsCl(NO)(P^{i}Pr_3)_2]$ is a stable, planar 16-electron complex which undergoes oxidative addition with H_2, HX, MeI, I_2 and MeOH. It reacts with alkynes to give either terminal alkynyl complexes or side-on π-bound alkynes. It adds CO to give a five-coordinate, 18-electron complex [87]. The crystal structure of $[OsCl(NO)(PPh_3)_2(OSNC_6H_4\text{-}4\text{-}Me)]$ (**29**) has been determined; the S^{IV} heterocumulene (formally $O{=}S{=}N\text{-}C_6H_4Me$) adopts a pseudo-olefinic η^2-N,S coordination mode [S-N = 1.61(4) Å] to the Os^0 centre [88]. Addition of the nucleophile $[Os(CO)_4]^{2-}$ to the coordinated, electrophilic hydrocarbon ligands of other complexes affords heterotrimetallic species. Thus reaction of $[Os(CO)_4]^{2-}$ with $[(CO)_3Fe(\text{cycloheptadienyl})]^+$ gives *cis*-$[\{Os(CO)_4\}\{(\mu\text{-}\eta^1{:}\eta^4\text{-}C_7H_9)Fe(CO)_3\}_2]$ (**30**) whose crystal structure has been determined; analogous products were obtained from reaction of $[Os(CO)_4]^{2-}$ with $[Cp(NO)(CO)Mo(\text{allyl})]^+$, $[Cp(CO)_2Mo(\text{butadiene})]^+$, $[(CO)_3Fe(\text{cyclohexadienyl})]^+$ and other electrophiles [89]. Mono-protonation of $[Os(\eta^6\text{-mes})(\mathbf{31})]$ [where the 1,3-diene (**31**) has the molecular formula $C_{18}H_{14}$] gives the fluxional cation $[Os(\eta^6\text{-mes})(C_{18}H_{15})]^+$. Treatment with ^tBuNC causes irreversible hydride transfer to (**31**), giving $[Os(\eta^6\text{-mes})(C_{18}H_{15})(CN^tBu)]^+$ [90].







(29) **(30)** **(31)**

1.9 IONIC SOLIDS

Pr_4I_5Os was prepared from PrI_3, Pr and Os at 875° - 975°C [91].

1.10 OSMIUM CARBONYL CLUSTERS

1.10.1 Clusters with only carbonyl and hydride ligands

A new theoretical analysis accounts very well for the X-ray absorption spectrum of $[Os_3(CO)_{12}]$ [92]. Isotopic labelling experiments suggest that electron transfer reactions between $[Os_3(CO)_{11}]^{2-}$ and $[M_3(CO)_{12}]$ (M = Fe, Ru) to give $[Os_3(CO)_{12}]$ and $[M_3(CO)_{11}]^{2-}$ occur by an outer-sphere mechanism [93]. The crystal structure of $[Ph_4P]_2[Os_{10}(CO)_{26}]$ has been determined. The structure of the core is that of a tricapped octahedron, with an additional $Os(CO)_3$ group on one of the three caps. The cluster is suggested to be at an intermediate stage between the well-known low nuclearity Os clusters and new 'giant' species [94]. A more impressive example of a cluster further along the same route is $[Os_{20}(CO)_{40}]^{2-}$ (Fig. 2), a molecular tetrahedron with four Os atoms along each edge. The Os atoms are arranged in a cubic close-packed array with no interstitial atoms. The arrangement of CO ligands over the surface is similar to that of chemisorbed CO on the (111) surface of close-packed metals. Preliminary experiments show a very rich electrochemical behaviour [95].

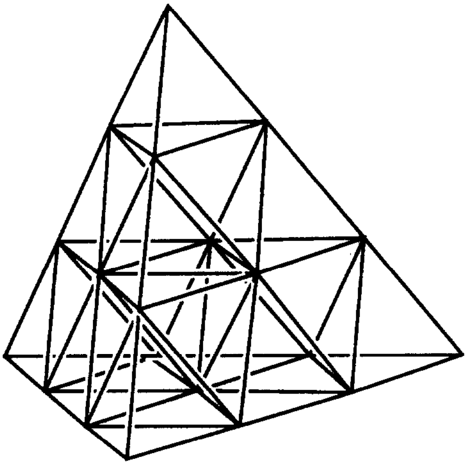


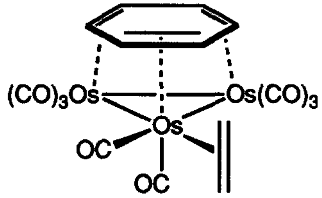
Figure 2: Core structure of $[Os_{20}(CO)_{40}]^{2-}$; each vertex represents an Os atom.

The kinetics of ^{13}CO exchange with ^{12}CO in $[HOs_3(CO)_{11}]^-$ and $[DOs_3(CO)_{11}]^-$ were studied. Two parallel pathways were found, one dissociative and one associative; the rate is cation-dependent due to ion-pairing effects [96]. Examination of the vibrational spectra of the μ_2-H ligands in $[H_4Os_4(CO)_{12}]$ indicates that the molecule has D_{2d} symmetry. The Raman spectral intensities are strongly influenced by the fact that the four hydrides have *pseudo*-D_{4h} symmetry (neglecting the rest of the cluster), and by the spherical symmetry of the hydrogen 1s orbitals [97]. Reaction of $[Os_6(CO)_{18}]$ with R_3NO (R = Me, Et) in a non-coordinating solvent results in formation of $[HOs_6(CO)_{17}]^-$, which was subjected to a variable-temperature NMR spectroscopic study. $[HOs_6(CO)_{17}]^-$ is isoelectronic with $Os_6(CO)_{18}$ and behaves similarly [98]. Pyrolysis of

$[Os_3(CO)_{10}(MeCN)_2]$ *in vacuo* affords $[Os_9H(CO)_{24}]^-$, which was crystallographically characterised. The core structure is the first example of a tri-capped octahedron [99]. A neutron-diffraction study of $[PPN]_2[H_4Os_{10}(CO)_{24}]$ located the hydride ligands directly. All are on the surface; two are triply-bridging and two are doubly bridging. There is an incipient C···H interaction between the CO ligands and the hydrides, which suggests that the cluster is a good model for the chemisorption of 'syngas' (H_2 + CO) on metal surfaces [100].

1.10.2 *Clusters with additional C, Si or Sn ligands*

The stereochemical non-rigidity of $[Os_3(CO)_8(\eta^2\text{-}C_2H_4)(\mu_3\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ (32) was studied by line-shape analysis of its ^{13}C CP/MAS NMR spectrum. Five dynamic processes were identified in solution including a 'jump'-type reorientation of the benzene ring, ethene rotation and 'turnstile'-type rotation of $Os(CO)_3$ vertices [101].



(32)

Activation of $[Os_4(\mu\text{-}H)_4(CO)_{12}]$ with Me_3NO in MeCN gives the reactive intermediate $[Os_4(\mu\text{-}H)_4(CO)_{10}(MeCN)_2]$, which reacts with 1,3-cyclohexadiene to give new clusters with apical C_6H_6 and C_6H_8 ligands. The C_6H_8 ligand converts to $\eta^6\text{-}C_6H_6$ on heating. The crystal structures of $[Os_4(\mu\text{-}H)_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ and $[Os_4(CO)_9(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_8)]$ were determined [102]. Molecular organisation in crystals of $[Os_4H_2(CO)_{10}(\eta^6\text{-arene})]$ was investigated by packing potential-energy calculations; the crystal structures were determined for arene = tolene and *m*-xylene. Crystal packing and ease of reorientational motion of the arene in the solid state were discussed [103]. The benzene ligand in $[Os_4H_2(CO)_{10}(\eta^6\text{-}C_6H_6)]$ is labile and could be displaced by PhC≡CPh in the presence of Me_3NO and MeCN, to give $[Os_4H_2(CO)_9(Ph_2C_2)_2]$. One Ph_2C_2 ligand adopts a typical ($\mu_3\text{-}\eta^2$, $2\sigma + \pi$) face-capping mode, but the other is attached terminally (like an alkene) as a ($\mu_1\text{-}\eta^2$) four-electron donor (Fig. 3). The C–C distance and the Ph–C–C bond angles indicate that the C atoms retain substantial sp character [104]. The crystal structure of $[(\mu\text{-}\eta^1,\eta^2\text{-}C_2H_4)Os_2(CO)_8]$ shows that the ethylene C atoms are almost completely sp^3 hybrids. The C–C bond lengths are similar to those of ethane and ethene chemisorbed on the Pt(111) surface; the complex is therefore a model for chemisorbed ethene [105].

Reaction of $[HOs_3(CO)_{11}]^-$ with PhC≡CPh gave as the unexpected product $[H_2Os_5(CO)_{13}(Ph_2C_2)\{PhCC(H)(C_6H_4)\}]$. The core structure is that of a twisted 'bow-tie', with one Ph_2C_2 adopting a normal μ_3-($2\sigma + \pi$) bonding mode, and the other being ortho-metallated (μ_2-η^2)Ph-CC(H)-C_6H_4 due to intramolecular H-transfer from a phenyl ring to the acetylene carbon atom [106]. By contrast reaction of PhC≡CPh with $[Os_7H_2(CO)_{20}]$ results in C≡C cleavage to give μ_3-carbynes such as $[Os_7(CO)_{18}(\mu_3\text{-CPh})_2]$ and $[Os_7(CO)_{15}(\mu_3\text{-CPh})_4]$; the former has a monocapped octahedral core, whereas the latter is a bi-capped square pyramid [107]. The radical $[H_3Os_3(CO)_9(\mu_3\text{-C}^\bullet)]$ reacts with C_6H_5F to give $[H_3Os_3(CO)_9(\mu_3\text{-C–}C_6H_5)]$ and with C_6F_6 to give $[H_3Os_3(CO)_9(\mu_3\text{-C–}C_6F_5)]$ [108].

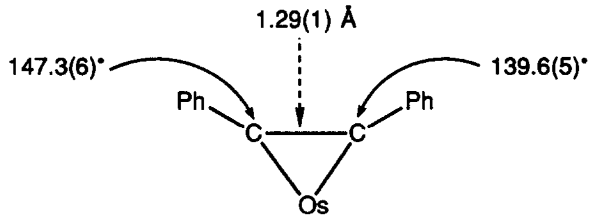
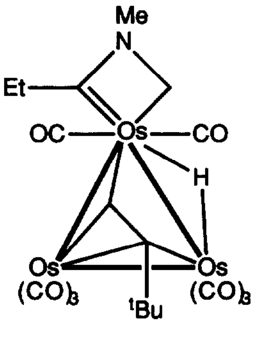
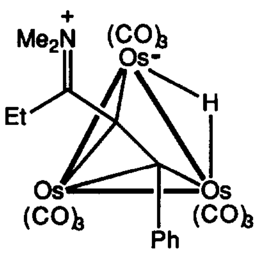


Figure 3: Structural parameters of the (η^2-μ_1)-Ph_2C_2 ligand in $[Os_4H_2(CO)_9(Ph_2C_2)_2]$

The terminal carbene $[Os_3(CO)_{11}\{=C(Et)NMe_2\}]$ reacts with $^tBuC≡CH$ to give a variety of products, *via* new C–C bond forming reactions by transfer of the carbene to the alkyne. Several multicentre transformations of the organic ligands are described, and the crystal structures of the initial adduct $[Os_3(CO)_9\{=C(Et)NMe_3\}\{\mu_3\text{-C(H)C}^t\text{Bu}\}]$ and the products $[Os_3(CO)_8\{=C(Et)\text{-}N(Me)CH_2\text{–}\}\{\mu_3\text{-C(H)C}^t\text{Bu}\}(\mu\text{-H})]$ (**33**) and $[Os_3(CO)_9\{\mu_3\text{-PhC}_2\text{C(Et)(NMe}_2)\}(\mu\text{-H})]$ (**34**) determined [109]. The reactivity of $[Os_3(CO)_8\{\mu_3(=C(Et)N(Me)CH=)\}(\mu\text{-H})_2(MeCN)]$ (**35**), which contains a bridging aminocarbene ligand, to diarylalkynes was examined. New organic ligands attached to the Os_3 core resulted, from insertion of hydride into the alkyne followed by coupling of the resultant alkenyl groups to the bridging carbene [110].



(**33**)



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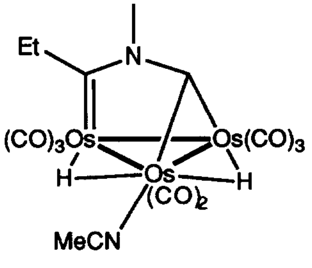
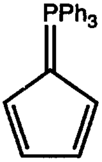
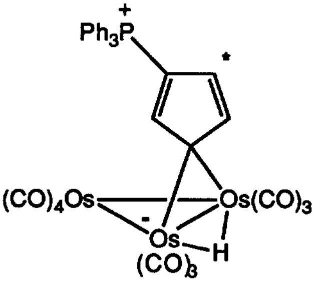


(**35**)

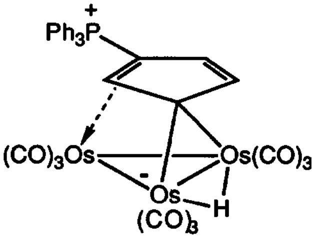
Oxidative addition of cyclopentadienylidene-triphenylphosphorane (**36**) to the activated cluster $[Os_3(CO)_{10}(MeCN)_2]$ affords the zwitterion (**37**), with the C_5 ring coordinated as a μ-alkylidene. In solution it slowly interconverts to the isomer in which the phosphonium group is at the position marked *. Loss of one CO ligand results in $[Os_3(\mu\text{-}H)(\mu_3\text{-}Ph_3PC_5H_3)(CO)_9]$ (**38**), which also exists as a mixture of isomers [111]. *N*-Methylpyrollidine also reacts with $[Os_3(CO)_{10}(MeCN)_2]$, to give a mixture of (**39**) and (**40**) [112].



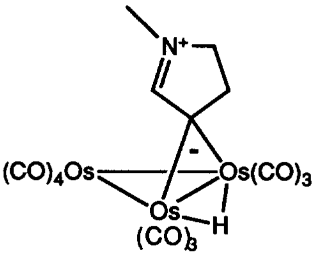
(**36**)



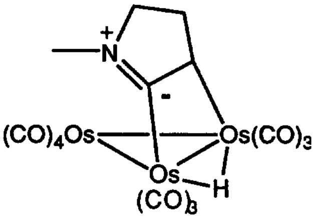
(**37**)



(**38**)



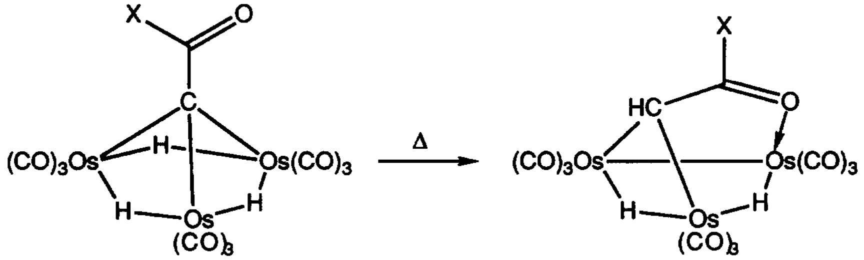
(**39**)



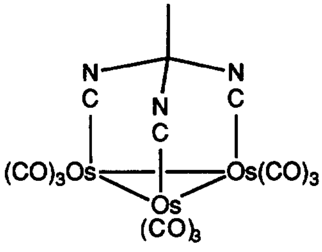
(**40**)

The reactions of various Os_3 clusters with methoxyallene $[CH_2{=}C{=}CH(OMe)]$ and methyl propargyl ether $[HC{\equiv}C{-}CH_2OMe]$ were studied. Methoxyallene behaves simply as a four-electron ligand bridging one edge of the cluster in *syn* and *anti* $[Os_3(CO)_{11}\{\mu\text{-}CH_2CC(H)OMe\}]$, but coupling of the alkyne with itself and with CO gives rise to Os_3 clusters containing coordinated organic fragments such as $MeOCH_2\text{-}C{=}CH\text{-}C(O)\text{-}CH{=}C\text{-}CH_2OMe$, in addition to simple coordination of the starting material in $[Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}\eta^2\text{-}C{\equiv}C{-}CH_2OMe)]$ [113]. The capped clusters $[H_3Os_3(CO)_9(\mu_3\text{-}CY)]$ (Y = CO_2Me, $CONEt_2$, CON(Me)Ph) were prepared by reaction of $[H_3Os_3(CO)_9(\mu_3\text{-}CBr)]$ with $AlCl_3$ and CO in the presence of CH_3OH, Et_2NH and PhNHMe respectively. The same products could be obtained from $[H_3Os_3(CO)_9(\mu_3\text{-}C\text{-}CO)]^+$ with the same reagents. For Y = CO_2Me and $CONEt_2$, pyrolysis converts the alkylidyne to an alkylidene (Scheme 6); the rates and mechanisms of these reactions are discussed [114].

1,1,1-Tris(isocyanomethyl)ethane (tris-NC) acts as a face-capping ligand in [$Os_3(CO)_9$(tris-NC)] (**41**), with one –NC donor to each Os atom. [$Os_3(CO)_6$(tris-NC)$_2$] was also prepared and is thought to have both faces capped in the same manner [115]. Thermolysis of the isonitrile clusters [$Os_3(CO)_{10}X(\mu\text{-}X)(CNR)$] (R = Me, Ph, *p*-tolyl, *o*-tolyl, 2,6-Me_2Ph; X = H, D) can result (apart from loss of CO) in metal-to-isonitrile H transfer. The H atom may transfer to the isonitrile C atom, giving [$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}CH{=}NR)$] or to the N atom, giving [$Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}C{=}NHR)$]. Mechanistic and kinetic studies were performed to probe the dependence of reaction pathway on the nature of the substituent R [116].



Scheme 6: Pyrolysis of [$H_3Os_3(CO)_9(\mu_3\text{-}CX)$] (X = OMe and NEt_2)



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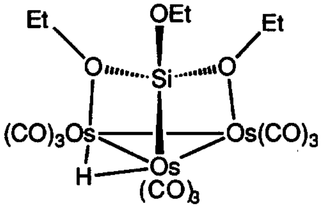
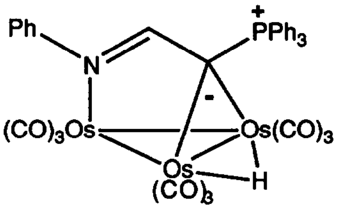


(42)

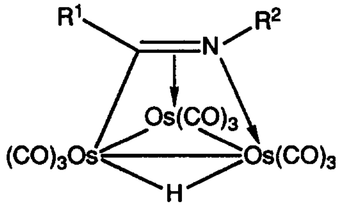
[$Os_3(CO)_9\{\mu_3\text{-}\eta^3\text{-}Si(OEt)_3\}(\mu\text{-}H)$] (**42**) is the first example of a (μ_3-η^3)-siloxy ligand in a trinuclear metal complex. Addition of two equivalents of CO yields [$Os_3(CO)_{11}\{Si(OEt)_3\}(\mu\text{-}H)$], where the -$Si(OEt)_3$ acts just as a terminal ligand. The crystal structures of these two species and of [$Os_3(CO)_{10}(MeCN)\{Si(OEt)_3\}(\mu\text{-}H)$] were determined [117]. In the stannyne complex [$Os_3(CO)_{10}(\mu\text{-}SnR)(\mu\text{-}H)$] [R = pyridyl-2-$C(SiMe_3)_2$, a bidentate C,N-donor to Sn] the SnR group bridges one Os-Os edge. The cluster is therefore a possible precursor to new high-nuclearity Os-Sn species [118].

1.10.3 Clusters with additional N, P, As or Sb ligands

$[Os_3(CO)_{12}]$ reacts with azoethane to give $[HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtN\text{–}N{=}CHMe)]$, which contains a bridging hydrazone ligand; its crystal structure was determined [119]. The reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with some secondary amines were investigated. Whereas reaction with ^nPrNHEt yields two new Os_3 clusters, reaction with MeNHEt yields five; amongst these, the crystal structures of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}MeC{=}NMe)]$, $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^2\text{-}EtNHCH_2)]$ and $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}\eta^1\text{-}CHCHN(Et)CH_2CH_2CH_3]$ were determined [120]. The hetero-cumulene $PhN{=}C{=}C{=}PPh_3$ reacts with $[H_2Os_3(CO)_{10}]$ to give $[HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{-}PhN{=}CH\text{–}C\text{–}PPh_3)]$ (**43**) [121]. The site of addition of trialkylphosphines to the unusually reactive Os_3 clusters (**44**) and (**45**), and the nature of the products formed, varies with the structure of the imide ligand and the steric bulk of the phosphine. In general, addition of PR_3 causes partial displacement of the imidoyl ligand (reducing from a five-electron donor to a three-electron donor); the products undergo thermal rearrangements *via* C–Os and C–N bond cleavage [122]. The factors influencing *exo* vs. *endo* configurations, and η^1 vs. η^2 coordination modes of heterocyclic ligands X in the clusters $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}X)]$ (X = pyrollyl, indolyl, furyl, thienyl) have been examined [123].



(**43**)



(**44**) $R^1 = Et$; $R^2 = {}^nPr$

(**45**) $R^1 + R^2 = -(CH_2)_3-$

The activation volume for terminal/bridging hydride exchange in $[Os_3(CO)_{10}H(\mu\text{-}H)(PPh_3)]$ was determined to be -0.8 (± 0.4) $cm^3\ mol^{-1}$ by analysis of NMR lineshapes at pressures up to 200 MPa. The negative value suggests a transition state in which both hydrides are bridging [124]. New routes to the phosphine-substituted clusters $[Os_3(CO)_{11}(PH_3)]$ and $[HOs_3(CO)_{10}(\mu_2\text{-}PH_2)]$ were developed using PH_4I rather than the more hazardous PH_3. These species are precursors for the preparation of high-nuclearity P-containing clusters [125]. $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}Ar)]$ (Ar = C_6H_4, C_9H_6, C_4H_3N, C_4H_2NMe) may be activated with Me_3NO in MeCN to give the acetonitrile-substitued derivatives $[Os_3(CO)_{9\text{-}n}(\mu\text{-}H)_2(MeCN)_n(\mu_3\text{-}Ar)]$ (n = 1,2) which react in turn with phosphines or phosphites to give $[Os_3(CO)_{9\text{-}n}(\mu\text{-}H)_2(PR_3)_n(\mu_3\text{-}Ar)]$ (n = 1,2; R = Ph, Et, OMe) by displacement of the acetonitrile ligands [126]. $[Os_7(CO)_{20}\{P(OMe)_3\}]$ has a capped octahedral structure, with the capping Os atom bearing the $(MeO)_3P$ ligand [127]. Tris(alkynyl)phosphines $(RC{\equiv}C)_3P$ may be used to prepare functionalised phosphido and phosphinidene clusters; for example, reaction of $[Os_3(CO)_{12}]$ with $P(C{\equiv}C^tBu)_3$ gives $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C{\equiv}C^tBu)\{\mu_2\text{-}P(C{\equiv}C^tBu)_2\}]$ [128].

The diphosphazene ligands are monodentate P-donors in $[Os_3(CO)_{11}\{(CF_3)_2P{=}N{=}PPh_3\}]$ and $[Os_3(CO)_{10}\{(CF_3)_2P{=}N{=}PPh_3\}_2]$. The P–N bonds are of a similar length, suggesting delocalisation of ligand electron density [129, 130]. *P*-Phenylphosphole and 3,4-dimethyl-*P*-phenylphosphole (L) coordinate as monodentate tertiary phosphines in $[Os_3(CO)_{11}L]$ and $[Os_3(CO)_{10}L_2]$. In each case, heating results in oxidative addition of a P–C bond (either to the phenyl group or within the C_4P ring) to an osmium atom with concomitant cleavage of the phosphole ring and the Os_3 ring. For L = 3,4-dimethyl-*P*-phenylphosphole, the crystal structure of the major product $[Os_3(CO)_9(\mu_3\text{-}PhPCHC(Me)C(Me)CH)]$ was determined [131, 132].

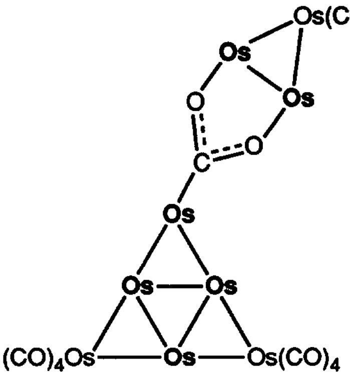
Efficient synthetic routes to the substituted clusters $[Os_6(CO)_{17}L]$ [L = $P(OMe)_3$, PEt_3, PPh_2Me, PPh_3, $AsPh_3$, $SbPh_3$] and $[Os_6(CO)_{16}L'_2]$ (L' = PPh_3, PPh_2Me) are described; they have the same bicapped tetrahedral core structure as $[Os_6(CO)_{18}]$. Decarbonylation of $[Os_6(CO)_{17}L]$ with Me_3NO in CH_2Cl_2 affords the new species $[HOs_6(CO)_{16}L]^-$, which may be protonated with HBF_4 in two separate steps to give $[H_2Os_6(CO)_{16}L]$ and $[H_3Os_6(CO)_{16}L]^+$. The same reaction with Me_3NO/CH_2Cl_2 was used to convert $[Os_6(CO)_{16}L'_2]$ to $[HOs_6(CO)_{16}L'_2]^-$ [133]. $[Os_3(CO)_{10}(\mu\text{-}H)(H)L]$ (L = CO, PPh_3, $AsPh_3$) undergo two-electron, chemically irreversible reductions similar to that of the isoelectronic $[Os_3(CO)_{12}]$. In contrast the 46-electron clusters $[Os_3(CO)_9(\mu\text{-}H)_2L]$ undergo two distinct reductions, the first of which generates $[Os_3H_2(CO)_{10}]^-$ [134]. The new hexaosmium clusters $[\{Os_3(CO)_{11}\}\text{-}As\text{-}\{Os_3(CO)_9H_3\}]$ and $[\{Os_3(CO)_9H_3\}_2(\mu\text{-}As)]$, prepared by reaction of appropriate Os_3 starting materials with AsH_3, each consist of two Os_3 units bridged by the arsenic atom [135].

1.10.4 Clusters with additional O, S, Se or Te ligands

The radical $(CF_3)_2NO$ preferentially attacks the terminal H in $[Os_3(CO)_{11}(H)(\mu\text{-}H)]$, to give $[Os_3(CO)_{11}(\mu\text{-}H)\{(CF_3)_2NO\}]$, the first example of a stable metal carbonyl cluster containing this strongly-oxidising perfluoro radical which coordinates as a monodentate *O*-donor [136]. The ^{13}C MAS NMR of silica-supported $[Os_3(^{12}CO)_{12}]$ revealed the structures and dynamic behaviour of the bound species. It was assigned by comparison with solution spectra of species such as $[Os_3(CO)_{10}(H)(OR)]$ (R = Me, Ph, $SiEt_3$), $[Os_3(CO)_{10}(H)(O_2CH)]$ and $[Os_3(CO)_{10}(OMe)_2]$ which are models for the surface-attached species. The initial product is $[Os_3(CO)_{10}(H)(O\text{-}Si{\equiv}support)]$; physisorbed $[Os_3(CO)_{12}]$ undergoes fast isotropic motion [137].

Reaction of $[HOs_3(CO)_{11}]^-$ with $[Os_3(CO)_{10}(MeCN)_2]$ in acetone under O_2 affords $[HOs_3(CO)_{10}.CO_2.Os_6(CO)_{20}]^-$ (**46**). The role of O_2 in the formation of the CO_2 bridge is not clear [138]. Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with oxalic acid gives $[\{Os_3(CO)_{10}(\mu\text{-}H)\}_2(\mu\text{-}C_2O_4)]$ (**47**) in which two Os_3 groups are linked by the bridging oxalate [139].

The preparation of $[H_2Os_3(CO)_9(O_3SCF_3)_2]$ and some if its reactions are summarised in Scheme 7; (**48**) was crystallographically characterised [140]. The crystal structure of *cis*-$[Os_4(CO)_{12}(\mu_2\text{-}CF_3CO_2)_2]$ (**49**) has been determined [141].



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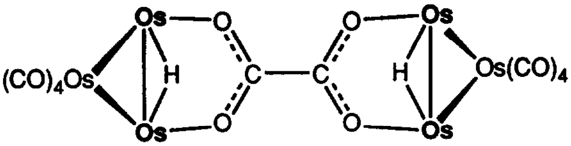
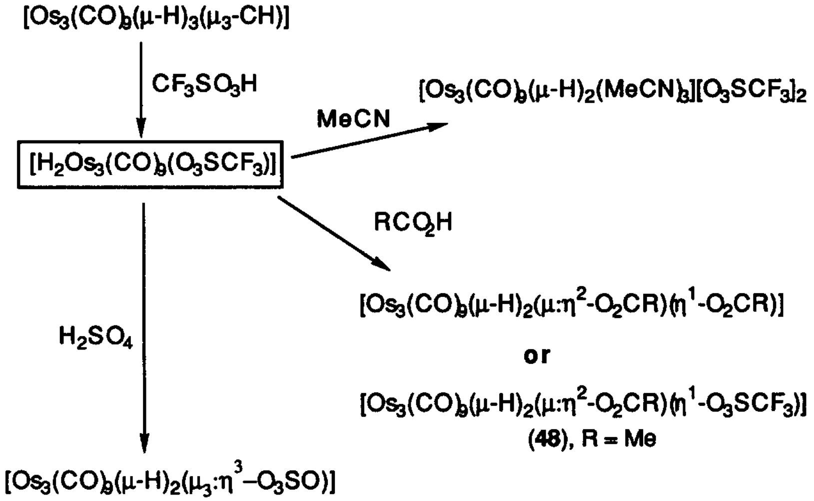


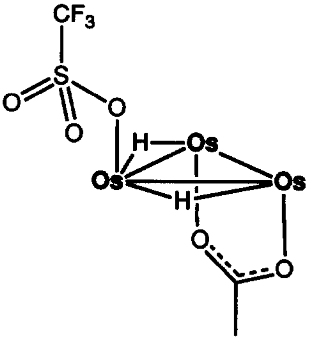
[Os = Os(CO)$_3$]

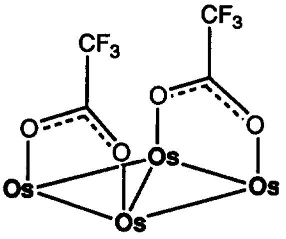
(47)



Scheme 7: Preparation and reactions of [$H_2Os_3(CO)_9(O_3SCF_3)_2$]

Reactions of [$Os_3(CO)_{10}$(μ-dmt)] (**50**; dmt = 3,3-dimethylthietane) have been studied which involve ring-opening of the dmt ligand to give new Os_3 complexes with sulphide ligands. The dmt ring may be opened by oligomerisation with further dmt ligands to give (**51**), nucleophilic attack by chloride to give (**52**), or photochemically to give (**53**). Numerous further reactions of these species involving rearrangement of the ligand fragments have been performed [142, 143].



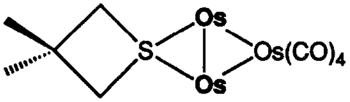


$[\mathrm{Os} = \mathrm{Os(CO)_3}]$

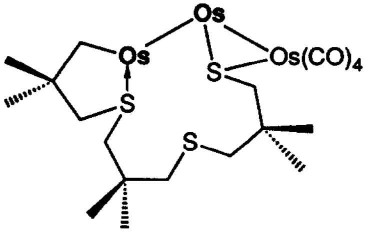
(48)

(49)

Thermolysis of $[Os_3(CO)_{10}(\mu\text{-}SePh)_2]$ (from $[Os_3(CO)_{10}(MeCN)_2]$ and PhSeSePh) gives $[Os_3(CO)_8(\mu\text{-}Ph)(\mu\text{-}PhCO)(\mu_3\text{-}Se)_2]$, in which the original diselenide has been cleaved into four separate ligand fragments, and all three Os atoms have been oxidised to Os^{II} by oxidative addition [144]. Reaction of $[Os_3(CO)_{11}(MeCN)]$ with $Te(CF_3)_2$ in cyclohexane resulted in formation of $[Os_3(CO)_{11}\{Te(C_6H_{11})_2\}]$, where the CF_3 groups originally attached to Te are replaced by cyclohexyl groups. The first C–H activation is thermally induced whereas the second is photochemical; similar results were also obtained with pentane [145].



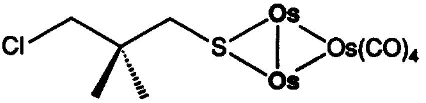
$[\mathrm{Os} = \mathrm{Os(CO)_3}]$



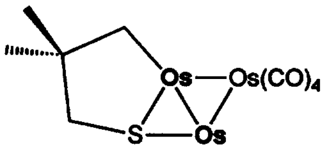
(50)

(51)

[–]



$[\mathrm{Os} = \mathrm{Os(CO)_3}]$



(52)

(53)

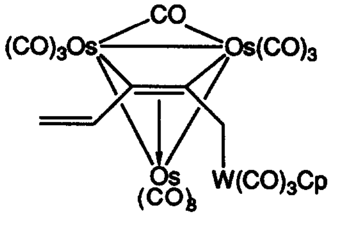
1.10.5 Clusters with additional halogen ligands

Reaction of $[Os_3(CO)_{10}(\mu\text{-}Br)(CH{=}CHPh)]$ with $PhCH_2NC$ and PPh_3 gave $[Os_3(CO)_9(\mu\text{-}Br)(CNCH_2Ph)(CH{=}CHPh)]$ and $[Os_2(CO)_5(PPh_3)(\mu\text{-}Br)(CH{=}CHPh)]$ respectively. NMR spectroscopy showed that whereas the former has a static ethenyl ligand, the latter undergoes π-σ and σ-π rearrangement (vinyl flipping) [146].

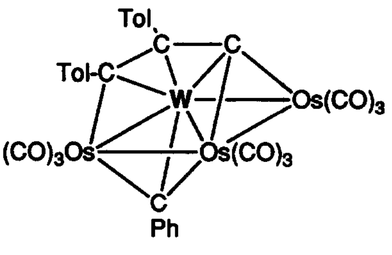
1.11 OSMIUM CLUSTERS CONTAINING OTHER TRANSITION METALS

1.11.1 Groups 6 and 7

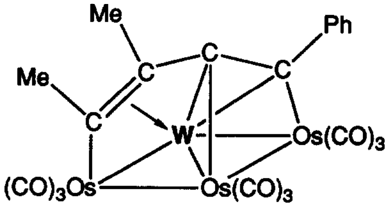
$[(CO)_{5-x}(^tBuNC)_xOs{-}M(CO)_5]$ (M = Cr, Mo, W; x = 1,2) were prepared by reaction of $[Os(CO)_{5-x}(^tBuNC)_x]$ with $[M(CO)_5(thf)]$. The crystal structures were determined for M = Cr and x = 1,2; in both cases the 18-electron $Os(CO)_{5-x}(^tBuNC)_x$ fragment acts as a two-electron donor to Cr *via* an Os–Cr dative bond [147]. $[CpWOs_3(CO)_{13}(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^1{:}\eta^2\text{-}CH_2C{=}CCH{=}CH_2)]$ (54) was prepared by reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $[CpW(CO)_3(CH_2C{\equiv}C{-}CH{=}CH_2)]$; an additional tetranuclear cluster, in which the W atom has migrated to the ligand β-carbon, was also isolated [148]. Both acetylide clusters $[CpLW_2Os_2(CO)_9(C{\equiv}CPh)(\mu\text{-}H)]$ and vinylidene clusters $[CpLW_2Os_2(CO)_9({=}C{=}CHPh)]$ (L = Cp or Cp^*) were isolated from the reaction of $[CpWOs_2(CO)_8(C{\equiv}CPh)]$ with Me_3NO followed by $LW(CO)_3H$. The two products may be reversibly, thermally interconverted [149]. Reaction of $[Os_3(CO)_{10}(RC{\equiv}CR)]$ with $[WL(CO)_3(C{\equiv}CPh)]$ affords the butterfly clusters $[LWOs_3(CO)_9(\mu_3\text{-}CPh)(CCRCR)]$ (R = *p*-tolyl, L = Cp, 55; R = Me, L = Cp^*) *via* scission of the acetylide $C{\equiv}C$ bond and coupling of the acetylide α-carbon atom with the coordinated alkyne. Reaction of these species with ditolylacetylene followed by loss of CO generates new tetranuclear WOs_3 clusters [150]. Thermolysis reactions of the butterfly cluster $[CpWOs_3(CO)_{10}(CMe{=}CMeCCPh)]$ (56) under various conditions lead to core rearrangements *via* loss of CO and activation of the hydrocarbon ligand [151].

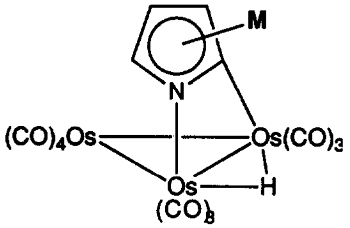


(54)



(55) (W = W-Cp)





(56) [W = WCp(CO)]

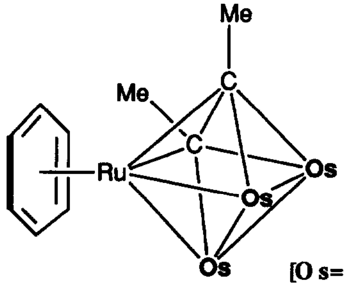
(57): M = Mn(CO)$_3$

(58): M = FeCp

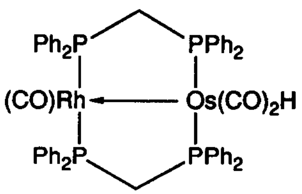
$[Os_3(\mu\text{-}H)(CO)_{10}\{(C_4H_3N)Mn(CO)_3\}]$ **(57)** was structurally characterised; the pyrrole ring acts as an 8-electron donor [152]. Hydrocarbon-bridged polynuclear complexes were prepared by reaction of cationic Re complexes with anionic Os complexes. Thus, addition of $[(CO)_5Re(C_2H_4)]^+$ to $[Os(CO)_4]^-$ gives $[(CO)_5ReCH_2CH_2Os(CO)_4CH_2CH_2Re(CO)_5]$; similarly, reaction of $[(CO)_5Re(C_2H_4)]^+$ with $[Os_3(CO)_{12}]^{2-}$ affords $[(CO)_5ReCH_2CH_2Os(CO)_4Os(CO)_4\text{-}Os(CO)_4CH_2CH_2Re(CO)_5]$ [153].

1.11.2 Groups 8 to 10

The crystal structure of **(58)**, prepared by reaction of azaferrocene with $[Os_3(CO)_{10}(MeCN)_2]$, was determined. The iron centre undergoes a reversible one-electron oxidation [152]. The dianion $[Os_3(CO)_9(R^1C{\equiv}CR^2)]^{2-}$ reacts with $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3]^{2+}$ to give $[(\eta^6\text{-}C_6H_6)Ru(R^1C{\equiv}CR^2)Os_3(CO)_9]$, whose crystal structure was determined for $R^1 = R^2 =$ Me **(59)** [154].



[Os = Os(CO)$_3$]



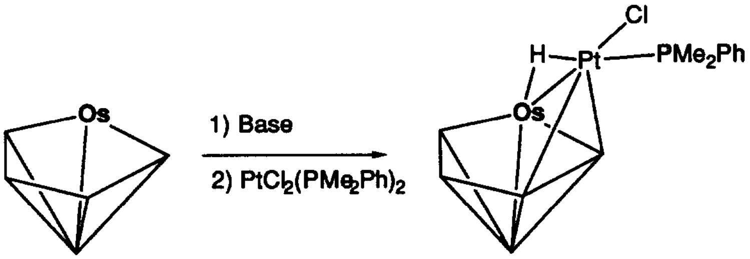
(59)

(60)

An extensive series of dppm-bridged Os-Rh complexes has been prepared starting from **(60)**, which contains a coordinatively unsaturated rhodium centre. Examples include reaction with

CCl_4 to give $[RhOsCl(CO)_3(\mu\text{-dppm})_2]$ and with HBF_4 to give $[RhOs(CO)_3(\mu\text{-H})_2(\mu\text{-dppm})_2]^+$ [155]. $[HOs(CO)_4]^-$ reacts with $[IrCl(\eta^2\text{-dppm})_2]$ to give $[IrOs(H)_2(CO)_3\{\mu_2\text{-}\eta^3\text{-}(o\text{-}C_6H_4)PhPCH_2PPh_2\}(\mu\text{-dppm})]$, in which one phenyl group is ortho-metallated at the iridium atom. Addition of a proton or $[Au(PPh_3)]^+$ reverses the metallation, giving $[IrOs(CO)_3(\mu\text{-H})(\mu\text{-X})(\mu\text{-dppm})_2]^+$ [X = H, $Au(PPh_3)$] which have core structures similar to **(60)** with an osmium-to-iridium dative bond. Other transformations af the core are described, and the crystal structure of $[IrOs(CO)_5(\mu\text{-dppm})_2][BF_4]$ reported [156]. Carbonyl fluxionality in the triangular clusters $[(\eta^5\text{-}C_5R_5)(CO)Ir\{Os(CO)_4\}_2]$ (R = H, Me) was examined by NMR spectroscopy [157].

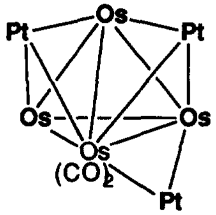
The crystal structures of the butterfly clusters $[Os_3Pt(\mu\text{-H})_2(CO)_{10}(PCy_3)(P^iPr_3)]$ [158] and $[Os_3Pt(CO)_{11}(PPh_3)_2]$ [159] were determined. Both have a Pt-PR_3 group at one wingtip, with the other phosphine bound to the Os atom at the other wingtip. Isomerisation and fluxional processes of the tetrahedral clusters $[Os_3Pt(\mu\text{-H})(CO)_9(PR_3)(PCy_3)]$ (where the PCy_3 is attached to Pt and the PR_3 attached to Os) were studied by ^{13}C EXSY NMR spectroscopy. The structures adopted depend on the bulk of PR_3. For PR_3 = PMe_2Ph, PMe_3, PPh_3 one isomer predominates, and H^- migration occurs. For PR_3 = P^iPr_3, $PCy_2{}^iPr$ the clusters axist as a 1:1 mixture of two isomers in solution which interconvert rapidly at room temperature. Several independent CO exchange pathways may be present [160]. *Nido*-$[OsB_5H_9(CO)(PPh_3)_2]$ may be converted to $[(CO)(PPh_3)_2Os(\mu\text{-H})PtCl(PMe_2Ph)B_5H_7]$ according to Scheme 8. Thermolysis of this yields a variety of other platina-osmaboranes [161].

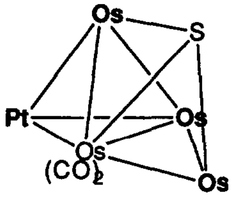


Scheme 8: Preparation of a new platina-osmaborane [Os = $Os(CO)(PPh_3)_2$]

Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with $Pt(cod)_2$ gives two products, $[Pt_2Os_3(CO)_{10}(cod)_2]$ (comprising a tetrahedral Pt_2Os_2 core with an $Os(CO)_4$ group bridging the Os-Os edge) and $[PtOs_3(CO)_8(cod)(\mu\text{-}C_8H_{11})(\mu\text{-H})]$ (comprising a tetrahedral $PtOs_3$ core in which one cod ligand bridges an Os-Os edge due to C-H cleavage). The former product is electron deficient, and reacts with CO to give *inter alia* the truncated raft cluster $[Pt_2Os_3(CO)_{14}]$ [162]. The crystal structures of $[Pt_2Os_4(CO)_{11}(cod)_2]$ and $[Pt_2Os_4(CO)_{12}(cod)_2]$ (from reaction of $[Pt_2Os_4(CO)_{18}]$ with cod) were determined; both have tetrahedral Os_4 cores with two Pt(cod) face-capping groups, and differ only by the presence of an additional μ-CO in the latter case. They may be interconverted by gain and loss of CO [163, 164]. $[Pt_2Os_4(CO)_{11}(cod)_2]$ is unsaturated, and reacts with $Pt(cod)_2$ and H_2S to give $[Pt_3Os_4(CO)_{11}(cod)_3]$ **(61)** and $[PtOs_4(CO)_{11}(cod)(\mu_3\text{-S})(\mu\text{-H})_2]$ **(62)** respectively [164].

By contrast ***photochemical*** reaction of $[Pt_2Os_4(CO)_{18}]$ with cod affords a mixture of $[Pt_2Os_4(CO)_{17}]$ (29%, which undergoes two reversible one-electron reductions), $[Pt_2Os_4(CO)_{15}(cod)]$ (25%, which has a raft-like structure), $[Pt_2Os_4(CO)_{12}(cod)_2]$ (6%) and $[PtOs_2(CO)_8(cod)]$; the latter two products are already known [165].





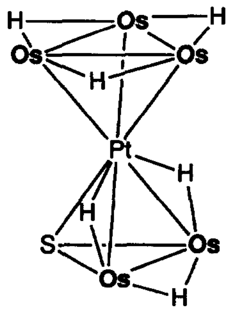
[Pt= Pt(cod); Os= Os(CO)$_3$]

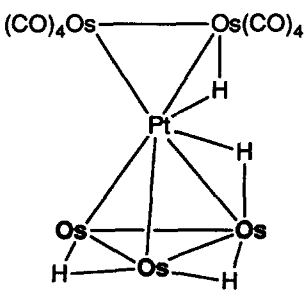
(61)

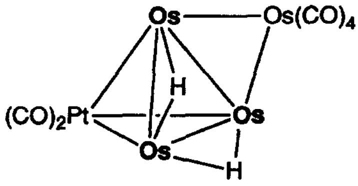
(62)

The two bridging hydrides were not located crystallographically, but probably lie along Os–Os edges.

Reaction of $[Pt_2Os_4(CO)_{18}]$ with H_2 at 25°C/100 atm. affords the four new hydrogen-rich clusters $[PtOs_5(CO)_{16}(\mu\text{-}H)_6]$ (a $PtOs_3$ tetrahedron and a $PtOs_2$ triangle fused at a shared Pt vertex), $[Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6]$ ($PtOs_3$ and Pt_2Os_2 tetrahedra fused at a shared Pt vertex), $[Pt_2Os_7(CO)_{23}(\mu\text{-}H)_8]$ ($PtOs_3$ and Pt_2Os_2 tetrahedra and a $PtOs_2$ triangle, fused at shared Pt vertices) and $[PtOs_6(CO)_{18}(\mu\text{-}H)_8]$ (two $PtOs_3$ tetrahedra fused at the shared Pt vertex). All hydrides were located unambiguously by crystallography and ^1H NMR spectroscopy. The first three clusters are electron deficient and are readily degraded by CO [166]. Further reactions of $[Pt_2Os_5(CO)_{17}(\mu\text{-}H)_6]$ with H_2S, to give $[PtOs_5(CO)_{15}(\mu\text{-}H)_6(\mu_3\text{-}S)]$ (**63**), and with $Os(CO)_5$ to give $[PtOs_5(CO)_{18}(\mu\text{-}H)_4]$ (**64**) and $[PtOs_4(CO)_{15}(\mu\text{-}H)_2]$ (**65**) were carried out. Again, all products were characterised by X-ray crystallography and the hydrides located both indirectly from their bond-lengthening effects and directly from NMR spectroscopy. The dynamic behaviour of the species in solution was studied [167].







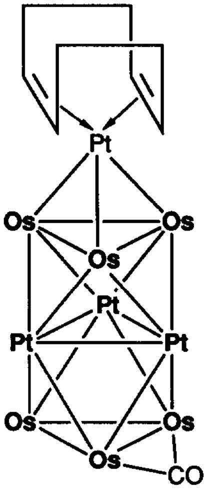
[O s= Os(CO)$_3$]

(63)

(64)

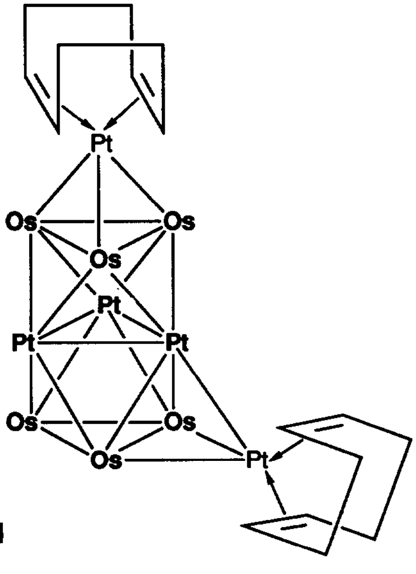
(65)

Small mixed-metal Pt-Os clusters have been used as precursors to prepare high-nuclearity species; bimetallic clusters containing Pt are of interest for modelling the surface behaviour of Pt-alloy catalysts used in petroleum reforming. Thermolysis of $[Pt_2Os_3(CO)_{10}(cod)_2]$ under N_2 in hexane produced $[Pt_4Os_6(CO)_{22}(cod)]$ (**66**) and $[Pt_5Os_6(CO)_{21}(cod)_2]$ (**67**), both of which contain alternating layers of Os and Pt atoms [168]. Likewise, thermolysis of $[Pt_2Os_3(CO)_9(cod)_2(\mu\text{-}H)_2]$ in the presence of CO affords $[Pt_4Os_6(CO)_{21}(cod)(\mu\text{-}H)_2]$ which has a similar alternating-layer structure to (**66**) [169].



[Pt = Pt(CO); Os = Os(CO)$_3$]

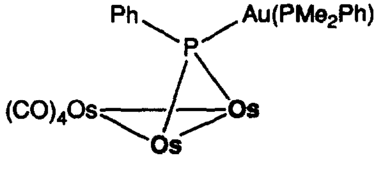
(66)



(67)

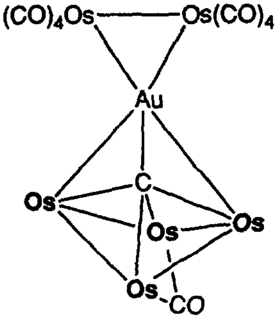
1.11.3 Groups 11 and 12

The allyl ligand in the new cluster $[Os_3(CO)_{10}(\mu_2\text{-}\eta^3\text{-}C_3H_5)(\mu_2\text{-}AuPEt_3)]$ shows a hitherto unobserved coordination mode, bridging one Os–Os edge. Fenske-Hall calculations were used to probe the bonding [170]. The nucleophilic P atom in $[Os_3(CO)_{10}(H)(\mu\text{-}PPh)]^-$ reacts with electrophiles such as $[AuCl(PMe_2Ph)]$ to give $[Os_3(CO)_{10}(H)\{\mu\text{-}P(Ph)Au(PMe_2Ph)\}]$ (**68**) and with [HgClR] to give analogous species with P–Hg bonds. The reactions occur at the more accessible side of the nucleophilic P atom, *exo* to the $Os(CO)_4$ group [171]. Reaction of $[Os_3(CO)_9(R^1C{\equiv}CR^2)]^{2-}$ with $[AuCl(PPh_3)]$ gives $[Os_3(CO)_9(R^1C{\equiv}CR^2)XY]$ (X = Y = $AuPPh_3$; X = H, Y = $AuPPh_3$) [154]. The structure of $[Os_6AuC(CO)_{20}(\mu\text{-}OMe)]$ (**69**), prepared by reaction of $[Os_3(CO)_{10}(\mu\text{-}AuPEt_3)(\mu\text{-}COMe)]$ with $[Os_3(CO)_{10}(MeCN)_2]$, was determined [172].



[Os = Os(CO)$_3$]

(68)



(69)

The crystal structures of [$Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}{}^tBu_2C_2)(\mu_3\text{-}Hg)\{Mo(Cp)(CO)_3\}$], [$Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}{}^tBu_2C_2)(\mu_3\text{-}Hg)\{Co(CO)_4\}$] and [$\{Os_3(CO)_9(\mu_3\text{-}S)(\mu_2\text{-}H)\}_2(\mu_4\text{-}Hg)$] were determined [173]. The preparation and crystal structure of the giant cluster anion [$Os_{18}Hg_3C_2(CO)_{42}$]$^{2-}$ have been reported (Fig. 4). The structure comprises two tricapped-octahedral Os_9 fragments linked by a Hg_3 triangle. Ejection of one Hg atom to give [$Os_{18}Hg_2C_2(CO)_{42}$]$^{2-}$ may be induced photochemically; the Hg atom may then be re-inserted thermally [174].

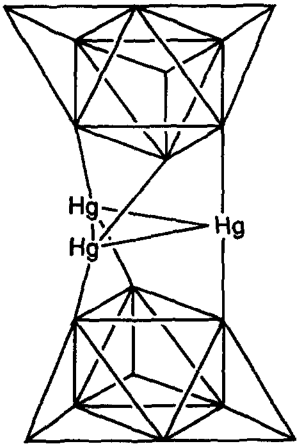


Figure 3: Core structure of [$Os_{18}Hg_3C_2(CO)_{42}$]$^{2-}$; each unlabelled vertex represents an Os atom.

REFERENCES

1. S. Sattar and K. Kustin, *Inorg. Chem.*, 30 (1991) 1668.
2. J. Hussain, S. K. Mishra and P. D. Sharma, *J. Chem. Soc., Dalton Trans.*, (1991) 89.
3. A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1991) 269.
4. A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1991) 1855.

5. M. Bakir, P. S. White, A. Dovletoglou and T. J. Meyer, *Inorg. Chem.*, 30 (1991) 2835.
6. D. C. Ware and H. Taube, *Inorg. Chem.*, 30 (1991) 4598.
7. D. C. Ware and H. Taube, *Inorg. Chem.*, 30 (1991) 4605.
8. J. J. Schwab, E. C. Wilkinson, S. R. Wilson and P. A. Shapley, *J. Am. Chem. Soc.*, 113 (1991) 6124.
9. W.-H. Leung, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1991) 2791.
10. M. H. Schofield, T. P. Kee, J. T. Anhaus, R. R. Schrock, K. H. Johnson and W. M. Davis, *Inorg. Chem.*, 30 (1991) 3595.
11. R. W. Marshman, J. M. Shusta, S. R. Wilson and P. A. Shapley, *Organometallics*, 10 (1991) 1671.
12. K. Rydpal, W. A. Herrmann, S. J. Eder, R. W. Albach, P. Watzlowik, H. Bock and B. Solouki, *Organometallics*, 10 (1991) 1331.
13. W. A. Herrmann, S. J. Eder and P. Kiprof, *J. Organometal. Chem.*, 412 (1991) 407.
14. W. A. Herrmann, S. J. Eder and P. Kiprof, *J. Organometal. Chem.*, 413 (1991) 27.
15. C. F. Edwards and W. P. Griffith, *Polyhedron*, 10 (1991) 61.
16. T. L. Groy, R. F. Hartman and S. D. Rose, *Acta Cryst., Sect. C*, 47 (1991) 273.
17. J.-H. Lin, C.-M. Che, T.-F. Lai, C.-K. Poon and Y. X. Cui, *J. Chem. Soc., Chem. Commun.*, (1991) 468.
18. W. E. Lynch, R. L. Lintvedt and X. Q. Shui, *Inorg. Chem.*, 30 (1991) 1014.
19. C.-M. Che, J.-S. Huang, Z.-Y. Li and C.-K. Poon, *Inorg. Chim. Acta*, 190 (1991) 161.
20. J. M. Hawkins, S. Loren, A. Meyer and R. Nunlist, *J. Am. Chem. Soc.*, 113 (1991) 7770.
21. J. M. Hawkins, A. Meyer, S. Loren and R. Nunlist, *J. Am. Chem. Soc.*, 113 (1991) 9394.
22. A. C. Dengel and W. P. Griffith, *Inorg. Chem.*, 30 (1991) 869.
23. K. Irmer and W. Preetz, *Z. Naturforsch.*, B46 (1991) 1200.
24. J. Halpern, L. Cai, P. J. Desrosiers and Z. Lin, *J. Chem. Soc., Dalton Trans.*, (1991) 717.
25. P. J. Desrosiers, L. Cai, Z. Lin, R. Richards and J. Halpern, *J. Am. Chem. Soc.*, 113 (1991) 4173.
26. Z.-W. Li and H. Taube, *J. Am. Chem. Soc.*, 113 (1991) 8946.
27. M. Aracama, M. Esteruelas, F. J. Lahoz, J. A. Lopez, U. Meyer, L. A. Oro and H. Werner, *Inorg. Chem.*, 30 (1991) 288.
28. D. Strand, R. Linder and H.-H. Schmidtke, *Inorg. Chim. Acta*, 182 (1991) 205.
29. H. Zhang and R. W. Murray, *J. Am. Chem. Soc.*, 113 (1991) 5183.
30. R. Sarala, S. B. Rabin and D. M. Stanbury, *Inorg. Chem.*, 30 (1991) 3999.
31. D. H. Macartney, *Inorg. Chem.*, 30 (1991) 3337.
32. G. A. Heath and D. G. Humphrey, *J. Chem. Soc., Chem. Commun.*, (1991) 1668.
33. T. W. Johnson, S. M. Tetrick, P. E. Fanwick and R. A. Walton, *Inorg. Chem.*, 30 (1991) 4146.
34. F. A. Cotton, T. Ren and J. L. Eglin, *Inorg. Chem.*, 30 (1991) 2559.
35. A. M. El-Hendawy, *Inorg. Chim. Acta*, 179 (1991) 223.
36. A. Hills, D. L. Hughes, R. L. Richards, M. Arroyo, D. Cruz-Garritz and H. Torrens, *J. Chem. Soc., Dalton Trans.*, (1991) 1281.
37. A. Pramanik, N. Bag, D. Ray, G. K. Lahiri and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, (1991) 139.
38. A. Pramanik, N. Bag, D. Ray, G. K. Lahiri and A. Chakravorty, *Inorg. Chem.*, 30 (1991) 410.
39. M. M. Richter, B. Scott, K. J. Brewer and R. D. Willett, *Acta. Cryst., Sect. C*, 47 (1991) 2443.
40. F. C. Anson, D. N. Blauch, J.-M. Savéant and C.-F. Shu, *J. Am. Chem. Soc.*, 113 (1991) 1922.
41. Z. Murtaza, A. P. Zipp, L. A. Worl, D. Graff, W. E. Jones, Jr., W. D. Bates and T. J. Meyer, *J. Am. Chem. Soc.*, 113 (1991) 5113.
42. S. Gould and T. J. Meyer, *J. Am. Chem. Soc.*, 113 (1991) 7442.
43. M. M. Richter and K. J. Brewer, *Inorg. Chim. Acta*, 180 (1991) 125.
44. M. Furue, T. Yoshidzumi, S. Kinoshita, T. Kushida, S. Nozakura and M. Kamachi, *Bull. Chem. Soc. Jpn.*, 64 (1991) 1632.
45. M. Beley, J.-P. Collin, J.-P. Sauvage, H. Sugihara, F. Heisel and A. Miehé, *J. Chem. Soc., Dalton Trans.*, (1991) 3157.
46. F. Barigelletti, L. De Cola, V. Balzani, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Inorg. Chem.*, 30 (1991) 641.
47. L. De Cola, F. Barigelletti, V. Balzani, R. Hage, J. G. Haasnoot, J. Reedijk and J. G. Vos, *Chem. Phys. Lett.*, 178 (1991) 491.
48. M. Haga, T. Ano, K. Kano and S. Yamabe, *Inorg. Chem.*, 30 (1990) 3843.
49. M. Haga and A. M. Bond, *Inorg. Chem.*, 30 (1990) 475.
50. P. D. Robinson, I. A. Ali and C. C. Hinckley, *Acta Cryst., Sect. C*, 47 (1991) 651.
51. P. D. Robinson, I. A. Ali and C. C. Hinckley, *Acta Cryst., Sect. C*, 47 (1991) 1397.

52. M. A. Esteruelas, C. Valero, L. A. Oro, U. Meyer and H. Werner, *Inorg. Chem.*, 30 (1991) 1159.
53. M. A. Esteruelas, L. A. Oro and C. Valero, *Organometallics*, 10 (1991) 462.
54. D. S. Bohle, G. R. Clark, C. E. F. Rickard, W. R. Roper and W. B. Shepard, *J. Organometal. Chem.*, 402 (1991) 375.
55. K. A. Earl, G. Jia, P. A. Maltby and R. H. Morris, *J. Am. Chem. Soc.*, 113 (1991) 3027.
56. A. Mezzetti, A. D. Zotto, P. Rigo and E. Farnetti, *J. Chem. Soc., Dalton Trans.*, (1991) 1525.
57. N. R. Champness, W. Levason, R. A. S. Mould, D. Pletcher and M. Webster, *J. Chem. Soc., Dalton Trans.*, (1991) 2777.
58. S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 30 (1991) 2906.
59. L. A. Gentil, A. Navaza, J. A. Olabe and G. E. Rigotti, *Inorg. Chim. Acta*, 179 (1991) 89.
60. D. P. Workman, W. Quintana and S. G. Shore, *Acta Cryst., Sect. C*, 47 (1991) 6.
61. R. Bhattacharya, A. M. Saha, P. N. Ghosh, M. Mukherjee and A. K. Mukherjee, *J. Chem. Soc., Dalton Trans.*, (1991) 501.
62. J. E. Ferguson, W. T. Robinson and R. K. Coll, *Inorg. Chim. Acta*, 181 (1991) 37.
63. W. Lewandowski, L. M. Proniewicz and K. Nakamoto, *Inorg. Chim. Acta*, 190 (1991) 145.
64. L. K. Woo, D. A. Smith and V. G. Young, Jr., *Organometallics*, 10 (1991) 3977.
65. T. Hasegawa, M. Sekine, W. P. Schaefer and H. Taube, *Inorg. Chem.*, 30 (1991) 449.
66. M. E. Kopach, J. Gonzalez and W. D. Harman, *J. Am. Chem. Soc.*, 113 (1991) 8972.
67. W. D. Harman, T. Hasegawa and H. Taube, *Inorg. Chem.*, 30 (1991) 453.
68. W. H. Meyers, M. Sabat and W. D. Harman, *J. Am. Chem. Soc.*, 113 (1991) 6682.
69. H. Werner, R. Weinand, W. Knaup, K. Peters and H. G. von Schnering, *Organometallics*, 10 (1991) 3967.
70. W. Knaup and H. Werner, *J. Organometal. Chem.*, 411 (1991) 471,
71. H. Werner, W. Knaup and M. Schulz, *Chem. Ber.*, 124 (1991) 1121.
72. T. Daniel, M. Müller and H. Werner, *Inorg. Chem.*, 30 (1991) 3118.
73. H. Werner, U. Wecker, M. Schulz and S. Stahl, *Organometallics*, 10 (1991) 3278.
74. H. Werner, S. Stahl and M. Schulz, *Chem. Ber.*, 124 (1991) 707.
75. S. Stahl and H. Werner, *J. Am. Chem. Soc.*, 113 (1991) 2944.
76. H. Werner, S. Stahl and W. Kohlmann, *J. Organometal. Chem.*, 409 (1991) 285.
77. D. M. Heinekey and T. G. P. Harper, *Organometallics*, 10 (1991) 2891.
78. L. Dahlenburg, S. Kerstan and D. Werner, *J. Organometal. Chem.*, 411 (1991) 457.
79. R. I. Michelman, R. A. Andersen and R. G. Bergman, *J. Am. Chem. Soc.*, 113 (1991) 5100.
80. D. Dai and K. Balasubramanian, *Chem. Phys. Lett.*, 185 (1991) 165.
81. S. Y. Ketkov and G. A. Domrachev, *J. Organometal. Chem.*, 420 (1991) 67.
82. E. W. Abel, N. J. Long, K. G. Orrell, A. G. Osborne and V. Sik, *J. Organometal. Chem.*, 419 (1991) 375.
83. A. Z. Kreindlin, E. I. Fedin, P. V. Petrovskii, M. I. Rybinskaya, R. M. Minyaev and R. Hoffmann, *Organometallics*, 10 (1991) 1206.
84. E. S. Shubina, L. M. Epstein, T. V. Timofeeva, Y. T. Struchkov, A. Z. Kreindlin, S. S. Fadeeva and M. I. Rybinskaya, *J. Organometal. Chem.*, 401 (1991) 133.
85. E. S. Shubina, L. M. Epstein, A. Z. Kreindlin, S. S. Fadeeva and M. I. Rybinskaya, *J. Organometal. Chem.*, 401 (1991) 145.
86. E. S. Shubina, L. M. Epstein, Y. L. Slovokhotov, A. V. Mironov, Y. T. Struchkov, V. S. Kaganovich, A. Z. Kreindlin and M. I. Rybinskaya, *J. Organometal. Chem.*, 401 (1991) 155.
87. H. Werner, A. Michenfeldner and M. Schulz, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 596.
88. A. F. Hill, G. R. Clark, C. E. F. Rickard, W. R. Roper and M. Herberhold, *J. Organometal. Chem.*, 401 (1991) 357.
89. B. Niemer, J. Bremair, T. Völkel, B. Wagner, K. Polborn and W. Beck, *Chem. Ber.*, 124 (1991) 2237.
90. M. A. Bennett, S. Pelling, G. B. Robertson and W. A. Wickramasinghe, *Organometallics*, 10 (1991) 2166.
91. M. W. Payne, P. K. Dorhout and J. D. Corbett, *Inorg. Chem.*, 30 (1991) 1467.
92. A. Filipponi, A. DiCicco, R. Zanoni, M. Bellatreccia, V. Sessa, C. Dossi and R. Pisaro, *Chem. Phys. Lett.*, 184 (1991) 485.
93. M. S. Corraine and J. D. Atwood, *Organometallics*, 10 (1991) 2985.
94. A. J. Amoroso, B. F. G. Johnson, J. Lewis, P. R. Raithby and W.-T. Wong, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 1505.
95. A. Amoroso, L. H. Gade, B. F. G. Johnson, J. Lewis, P. R. Raithby and W.-T. Wong, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 107.
96. M. W. Payne, D. L. Leussing and S. G. Shore, *Organometallics*, 10 (1991) 574.

97. C. E. Anson, U. A. Jayasooriya, S. F. A. Kettle, P. L. Stanghellini and R. Rossetti, *Inorg. Chem.*, 30 (1991) 2282.
98. B. F. G. Johnson, J. Lewis, M.-A. Pearsall and L. G. Scott, *J. Organometal. Chem.*, 402 (1991) C27.
99. A. J. Amoroso, B. F. G. Johnson, J. Lewis, P. R. Raithby and W.-T. Wong, *J. Chem. Soc., Chem. Commun.*, (1991) 814.
100. A. Bashall, L. H. Gade, J. Lewis, B. F. G. Johnson, G. McIntyre and M. McPartlin, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 1164.
101. S. J. Heyes, M. A. Gallop, B. F. G. Johnson, J. Lewis and C. M. Dobson, *Inorg. Chem.*, 30 (1991) 3850.
102. H. Chen, B. F. G. Johnson, J. Lewis, D. Braga, F. Grepioni and E. Parisini, *J. Chem. Soc., Dalton Trans.*, (1991) 215.
103. D. Braga, F. Grepioni, B. F. G. Johnson, H. Chen and J. Lewis, *J. Chem. Soc., Dalton Trans.*, (1991) 2559.
104. H. Chen, B. F. G. Johnson, J. Lewis, D. Braga, F. Grepioni and P. Sabatino, *J. Organometal. Chem.*, 405 (1991) C22.
105. O. P. Anderson, B. R. Bender, J. R. Norton, A. C. Larson and P. J. Vergamini, *Organometallics*, 10 (1991) 3145.
106. B. F. G. Johnson, J. Lewis, J. Lunniss, D. Braga and F. Grepioni, *J. Organometal. Chem.*, 412 (1991) 195.
107. D. Braga, F. Grepioni, B. F. G. Johnson, J. Lewis and J. Lunniss, *J. Chem. Soc., Dalton Trans.*, (1991) 2233.
108. N. Hadj-Bagheri, D. S. Strickland, S. R. Wilson and J. R. Shapley, *J. Organometal. Chem.*, 410 (1991) 231.
109. R. D. Adams and G. Chen, *Organometallics*, 10 (1991) 3020.
110. R. D. Adams and G. Chen, *Organometallics*, 10 (1991) 3028.
111. A. J. Deeming, N. I. Powell and C. Whittaker, *J. Chem. Soc., Dalton Trans.*, (1991) 1875.
112. M. W. Day, S. Hajela, S. E. Kabir, M. Irving, T. McPhillips, E. Wolf, K. I. Hardcastle, E. Rosenberg, L. Milone, R. Gobetto and D. Osella, *Organometallics*, 10 (1991) 2743.
113. A. J. Arce, Y. De Sanctis, A. J. Deeming, K. I. Hardcastle and R. Lee, *J. Organometal. Chem.*, 406 (1991) 209.
114. D. A. Strickland and J. R. Shapley, *J. Organometal. Chem.*, 401 (1991) 187.
115. E. C. Constable, B. F. G. Johnson, F. K. Khan, J. Lewis, P. R. Raithby and P. Mikulcik, *J. Organometal. Chem.*, 403 (1991) C15.
116. E. V. Anslyn, M. Green, G. Nicola and E. Rosenberg, *Organometallics*, 10 (1991) 2600.
117. R. D. Adams, J. E. Cortopassi and M. P. Pompeo, *Inorg. Chem.*, 30 (1991) 2960.
118. C. J. Cardin, D. J. Cardin, M. A. Convery and M. M. Devereux, *J. Chem. Soc., Chem. Commun.*, (1991) 687.
119. B. Hansert, M. Tasi, A. Tirpicchio, M. T. Camellini and H. Vahrenkamp, *Organometallics*, 10 (1991) 4070.
120. S. E. Kabir, M. Day, M. Irving, T. McPhillips, H. Minassian, E. Rosenberg and K. I. Hardcastle, *Organometallics*, 10 (1991) 3997.
121. M. Langenbahn, H. Stoeckli-Evans and G. Süss-Fink, *J. Organometal. Chem.*, 402 (1991) C12.
122. M. Day, D. Espitia, K. I. Hardcastle, S. E. Kabir, E. Rosenberg, R. Gobetto, L. Milone and D. Osella, *Organometallics*, 10 (1991) 3550.
123. A. J. Arce, J. Manzur, M. Marquez, Y. De Sanctis and A. J. Deeming, *J. Organometal. Chem.*, 412 (1991) 177.
124. J. B. Keister, U. Frey, D. Zbinden and A. E. Merbach, *Organometallics*, 10 (1991) 1497.
125. B. F. G. Johnson, L. Heuer, J. Lewis and C. N. Kenney, *Polyhedron*, 10 (1991) 1955.
126. H. Chen, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Organometal. Chem.*, 406 (1991) 219.
127. B. F. G. Johnson, J. Lewis, J. Lunniss, D. Braga and F. Grepioni, *J. Organometal. Chem.*, 401 (1991) C46.
128. B. J. Bobbie, N. J. Taylor and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, (1991) 1511.
129. H. G. Ang, Y. M. Cai, W. L. Kwik, W. K. Leong and D. A. Tocher, *Polyhedron*, 10 (1991) 881.
130. H. G. Ang, Y. M. Cai, W. L. Kwik, E. C. Morrison and D. A. Tocher, *J. Organometal. Chem.*, 403 (1991) 383.
131. A. J. Arce, Y. De Sanctis, J. Manzur, A. J. Deeming and N. I. Powell, *J. Organometal. Chem.*, 408 (1991) C18.
132. A. J. Deeming, N. I. Powell, A. J. Arce, Y. De Sanctis and J. Manzur, *J. Chem. Soc., Dalton Trans.*, (1991) 3381.

133. B. F. G. Johnson, J. Lewis, M.-A. Pearsall and L. G. Scott, *J. Organometal. Chem.*, 413 (1991) 337.
134. D. Osella, E. Stein, C. Nervi, P. Zanello, F. Laschi, A. Cinquantini, E. Rosenberg and J. Fiedler, *Organometallics*, 10 (1991) 1929.
135. K. Guldner, B. F. G. Johnson, J. Lewis, A. D. Massey and S. Bott, *J. Organometal. Chem.*, 408 (1991) C13.
136. H. G. Ang, W. L. Kwik, C. H. Koh, W. K. Leong, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Organometal. Chem.*, 420 (1991) 289.
137. T. H. Walter, G. R. Frauenhoff, J. R. Shapley and E. Oldfield, *Inorg. Chem.*, 30 (1991) 4732.
138. B. F. G. Johnson, J. Lewis, P. R. Raithby and W. T. Wong, *J. Organometal. Chem.*, 401 (1991) C50.
139. B. F. G. Johnson, J. Lewis, P. R. Raithby, V. P. Saharan and W. T. Wong, *J. Chem. Soc., Chem. Commun.*, (1991) 365.
140. G. R. Frauenhoff, S. R. Wilson and J. R. Shapley, *Inorg. Chem.*, 30 (1991) 78.
141. M. P. Diebold, B. F. G. Johnson, J. Lewis, V. P. Saharan, M. McPartlin and H. R. Powell, *J. Organometal. Chem.*, 405 (1991) C25.
142. R. D. Adams and M. P. Pompeo, *J. Am. Chem. Soc.*, 113 (1991) 1619.
143. R. D. Adams, J. A. Belinski and M. P. Pompeo, *Organometallics*, 10 (1991) 2539.
144. A. J. Arce, P. Arrojo, A. J. Deeming and Y. De Sanctis, *J. Chem. Soc., Chem. Commun.*, (1991) 1491.
145. G. Süss-Fink, M. Langenbahn, H. Stoeckli-Evans and D. Naumann, *J. Chem. Soc., Chem. Commun.*, (1991) 447.
146. S.-H. Chuang, Y. Chi, F.-L. Liao, S.-L. Wang, S.-M. Peng, G.-H. Lee, J.-C. Wu and K.-M. Horng, *J. Organometal. Chem.*, 410 (1991) 85.
147. J. A. Shipley, R. J. Batchelor, F. W. B. Einstein and R. K. Pomeroy, *Organometallics*, 10 (1991) 3620.
148. M.-H. Cheng, G.-H. Lee, S.-M. Peng and R.-S. Liu, *Organometallics*, 10 (1991) 3600.
149. Y. Chi, C.-H. Wu, S.-M. Peng and G.-H. Lee, *Organometallics*, 10 (1991) 1676.
150. Y. Chi, H.-F. Hsu, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Chem. Commun.*, (1991) 1019.
151. Y. Chi, H.-F. Hsu, S.-M. Peng and G.-H. Lee, *J. Chem. Soc., Chem. Commun.*, (1991) 1023.
152. S. P. Best, R. J. H. Clark, A. J. Deeming, R. C. S. McQueen, N. I. Powell, C. Acuña, A. J. Arce and Y. De Sanctis, *J. Chem. Soc., Dalton Trans.*, (1991) 1111.
153. J. Bremair, B. Niemer, K. Raab and W. Beck, *Chem. Ber.*, 124 (1991) 1059.
154. A. T. Brooker, P. A. Jackson, B. F. G. Johnson, J. Lewis and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1991) 707.
155. R. W. Hilts, R. A. Franchuk and M. Cowie, *Organometallics*, 10 (1991) 304.
156. R. W. Hilts, R. A. Franchuk and M. Cowie, *Organometallics*, 10 (1991) 1297.
157. A. Riesen, F. W. B. Einstein, A. K. Ma, R. K. Pomeroy and J. A. Shipley, *Organometallics*, 10 (1991) 3629.
158. L. J. Farrugia, *Acta. Cryst., Sect. C*, 47 (1991) 1310.
159. D. H. Farrar, R. R. Gukathasan and J. A. Lunniss, *Inorg. Chim. Acta*, 179 (1991) 271.
160. L. J. Farrugia and S. E. Rae, *Organometallics*, 10 (1991) 3919.
161. J. Bould, J. E. Crook, N. N. Greenwood and J. D. Kennedy, *J. Chem. Soc., Dalton Trans.*, (1991) 185.
162. R. D. Adams, G. Chen, J.-C. Lii and W. Wu, *Inorg. Chem.*, 30 (1991) 1007.
163. R. D. Adams and W. Wu, *Organometallics*, 10 (1991) 35.
164. R. D. Adams and W. Wu, *Inorg. Chem.*, 30 (1991) 3605.
165. R. D. Adams, M. S. Alexander, I. Arafa and W. Wu, *Inorg. Chem.*, 30 (1991) 4717.
166. R. D. Adams, M. P. Pompeo and W. Wu, *Inorg. Chem.*, 30 (1991) 2425.
167. R. D. Adams, M. P. Pompeo and W. Wu, *Inorg. Chem.*, 30 (1991) 2899.
168. R. D. Adams, J.-C. Lii and W. Wu, *Inorg. Chem.*, 30 (1991) 2257.
169. R. D. Adams, J.-C. Lii and W. Wu, *Inorg. Chem.*, 30 (1991) 3613.
170. C. E. Housecroft, B. F. G. Johnson, J. Lewis, J. A. Lunniss, S. M. Owen and P. R. Raithby, *J. Organometal. Chem.*, 409 (1991) 271.
171. A. J. Deeming, S. Doherty, M. W. Day, K. I. Hardcastle and H. Minassian, *J. Chem. Soc., Dalton Trans.*, (1991) 1273.
172. C. M. Hay, B. F. G. Johnson, J. Lewis, N. D. Prior, P. R. Raithby and W. T. Wong, *J. Organometal. Chem.*, 401 (1991) C20.
173. E. Rosenberg, K. I. Hardcastle, M. W. Day, R. Gobetto, S. Hajela and R. Muftikian, *Organometallics*, 10 (1991) 203.
174. L. H. Gade, B. F. G. Johnson, J. Lewis, M. McPartlin, T. Kotch and A. J. Lees, *J. Am. Chem. Soc.*, 113 (1991) 8698.