5. Osmium 1992

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CONTENTS

INTRODUCTION

This review covers the coordination and selected organometallic and cluster chemistry of osmium published in the calendar year 1992 and continues the coverage published for the year 1991 in volume 127 of *Coordination Chemistry Reviews*. Coverage has been limited to the more well known journals and the emphasis is on the coordination and cluster chemistry of osmium. Organometallic chemistry is covered in less depth, and complex mechanistic details of transformations of organic ligands in such complexes are not discussed in depth.

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5.1 OSMIUM(VIII)

Gas phase PE spectroscopic studies and *ab initio* calculations have been used to calculate the ionisation energies of OsO_4. The results indicate ion state ordering to be: $^2T_1 < U_1(^2T_2) < E''(^2T_2) < {}^2A_1 < {}^2E < {}^2T_2$. The 1e and $2t_2$ MOs were shown to have significant 5*d* character, the $2a_1$ MO significant Os 6*s* character and the $3t_2$ MO significant Os 6*p* character [1].

The reaction of OsO_4 with KrF_2 in anhydrous HF yields *cis*-[OsO_2F_4] in contrast to a previous report in which the same reaction was reported to give [$OsOF_6$] [2].

There has been a report of evidence for stereoelectronic control of diastereoselectivity in OsO_4 catalysed *cis*-hydroxylation of sterically unbiased 3-(4-X-phenyl)-3-phenylcyclopentenes (X = NO_2, Br, Cl, OMe or NMe_2) [3].

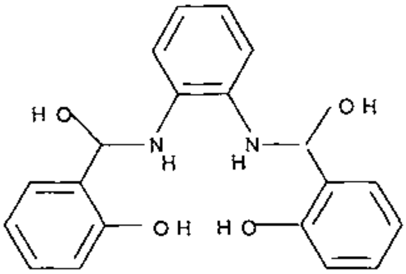
5.2 OSMIUM(VII)

The ESR spectrum of $OsOF_5$ has been reported and shows hyperfine coupling to ^{189}Os and four equivalent fluorine ligands. No coupling to the axial ligand is observed. Analysis of the spectrum indicates that 11.5% of the unpaired electron is delocallised from the Os d_{xy} orbital onto each equatorial fluorine [4].

5.3 OSMIUM(VI)

5.3.1 Nitrido and imido complexes

The osmium(VI) nitrido complex of the ligand HBA-B (**1**) is prepared by the action of trimethylsilyl azide on [$(Ph_3PO)_2Os(\eta^4$-HBA-B)] followed by base hydrolysis. The complex adopts a square based pyramidal geometry with an Os≡N distance of 1.639(6)Å [5].



(H_4**1**)

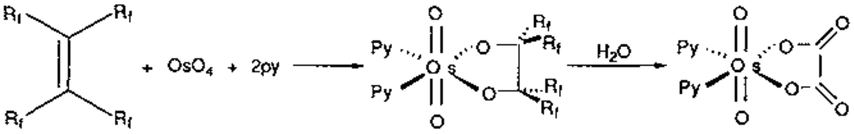
The one electron oxidation of $[Os(NH_3)_5Cl]^{2+}$ by aqueous Ce^{4+} yields the Os(VI) nitrido complex $[OsN(NH_3)_4]^{3+}$ which exhibits room temperature luminescence on irradiation in the 300-400 nm region. The excited state is found to be quenched by electron donors. Photolysis in

MeCN with donors such as C_6Me_6 or 1,4-dimethoxybenzene leads to self quenching and the formation of the μ-N_2 complex $[\{Os(NH_3)_4MeCN\}_2(\mu\text{-}N_2)]^{5+}$ [6].

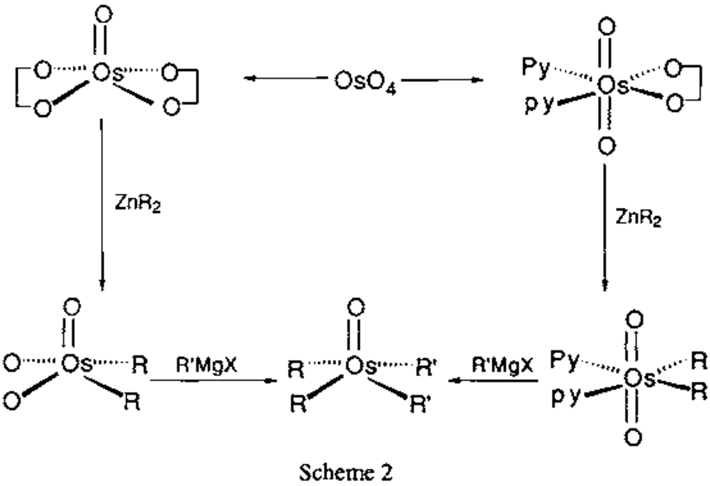
The complexes $[Os(P)(NH_2{}^tBu)_2]$ (P = porphyrin dianion) undergo oxidative deprotonation on stirring in thf solution under air to give a mixture of the bis-imido, imido/oxo and bis-oxo complexes $[Os(P)(N^tBu)_2]$, $[Os(P)(N^tBu)O]$ and $[Os(P)O_2]$ [7].

5.3.2 *Oxo complexs*

The reaction of fluorinated alkenes with OsO_4 in the presence of pyridine in hexane has been investigated and found to give osmate(VI) esters *trans*-$[OsO_2(py)_2(\eta^2\text{-}OC(R^F)_2C(R^F)_2O)]$. The X-ray crystal structure of the complex prepared by reaction with the alkene $(C_2F_5)FC{=}C(CF_3)_2$ has been determined. These products are sensitive to hydrolysis and yield carbonyl containing products on reaction with water (Scheme 1) [8]. Similarly, the reaction of OsO_4 with perfluoropinacol $[(CF_3)_2C(OH)]_2$ yields the water sensitive bis-glycolate complex $\{OsO[\eta^2\text{-}(CF_3)_2C(O)]_2\}$ (**2**) which may be stabilised with Lewis bases such as 4-^{t}butyl pyridine [9]. The increased water sensitivity of these complexes over those with nonfluorinated ligands is attributed to the greater Lewis acidity at the metal centre.

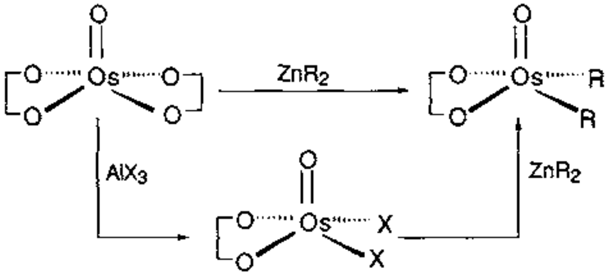


Scheme 1



Scheme 2

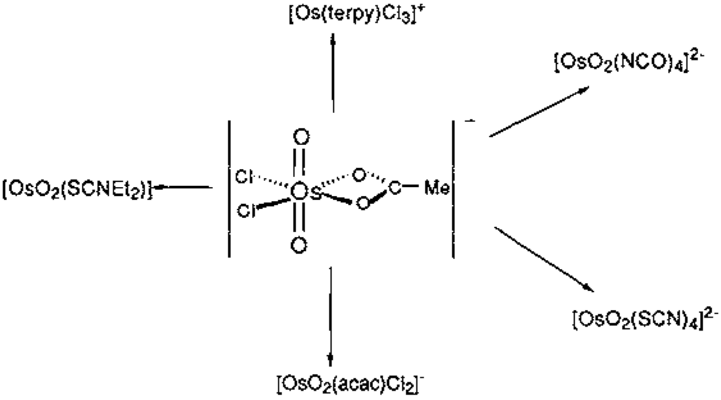
The synthesis of osmium oxo/alkyl/glycolate complexes has been reported in a series of publications. The general reaction scheme involves the alkylation of oxo-osmium glycolate complexes. The selective replacement of one glycolate ligand may be achieved by the use of dialkyl zinc reagents and subsequent alkylation may be achieved with Grignard reagents, thus making available mixed alkyl complexes of the type $[OsO(R)_2(R')_2]$ (Scheme 2) [10,11]. The replacement of one glycolate ligand may be achieved by reaction with aluminium trihalides yielding the dihalide complexes which may subsequently be alkylated with dialkyl zinc reagents (Scheme 3) [12].



Scheme 3

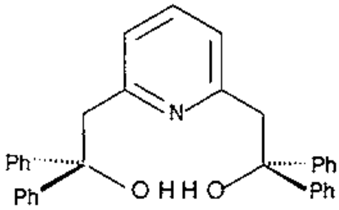
The synthesis and characterisation of $[OsO_2(dmp)_2]$ (dmpH = 1,2-dimethyl-3-hydroxy pyridine-4-one) (**3**) has been reported along with its complexes with a number of other transition metals [13].

The reaction of $K_2[OsO_2(OMe)_4]$ with carboxylic acids in the presence of $[PPh_4]Cl$ yields *trans*-$[OsO_2Cl_2(\eta^2\text{-}O_2CR)]$ (R = Me, Et, CH(Me)Et). These complexes catalyse the oxidation of many organic substrates with *N*-methylmorpholine-*N*-oxide as cooxidant, and in addition the ethanoate complex has been used as precursor for the synthesis of a number of new complexes (Scheme 4) [14].



Scheme 4

A number of complexes of the bulky chelating alkoxide 2,6-bis(2-hydroxy-2,2-diphenylethyl)pyridine (HL) (4) have been prepared. Dioxo complexes may be prepared from $K_2[OsO_2(OH)_4]$ while nitrido complexes are available from $[Bu_4N][OsNCl_4]$. The X-ray crystal structure of [OsN(L)Cl] is reported [15].

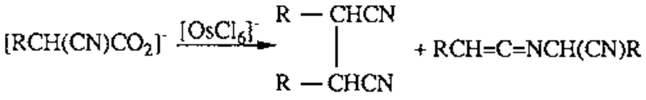


(4)

The regiochemistry of the bisosmylation of C_{60} has been analysed. Five regioisomers of $[C_{60}\{OsO_4(py)_2\}]$ have been separated by HPLC and these were characterised by NMR spectroscopy of their 4-^{t}butylpyridine analogues [16].

5.4 *OSMIUM(V)*

The Kolbe anodic oxidation of carboxylates has been simulated using $[OsCl_6]^-$ as a one electron oxidant. The complex reacts with carboxylates with electron withdrawing groups to give coupling products [17] as shown in equation (i). Magnetic susceptibility measurements have also

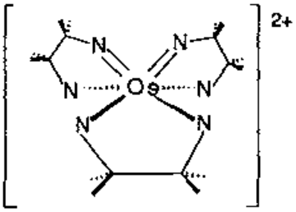


$$[RCH(CN)CO_2]^- \xrightarrow{[OsCl_6]^-} \begin{array}{l} R-CHCN \\ \quad\;\; | \\ R-CHCN \end{array} + RCH{=}C{=}NCH(CN)R \qquad (i)$$

been carried out on $[PPh_4][OsCl_6]$. Measurements were made at 1.0 T (4.5-300K) and between 0.25 and 5.0 T (2.5-20K). The results reveal the first example of one dimensional magnetic exchange in a heavy transition metal complex. A DV-X_α calculation on $[OsCl_6]^-$ which correlates well with the experimental results is also reported [18].

5.5 *OSMIUM(IV)*

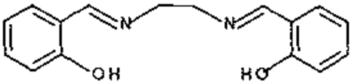
The reaction of either $OsCl_3.3H_2O$ or $[OsX_6]^-$ (X = Cl, Br) with tmen yields the complex $[Os(tmen\text{-}H)_2(tmen)]^{2+}$ (5) (tmen = 2,3-diamino-2,3-dimethylbutane). Reduction of (5) with Zn/H^+ yields the Os(III) complex $[Os(tmen)_3]^{3+}$ while protonation with triflic acid leads to $[Os(tmen\text{-}H)(tmen)_2]^{3+}$ (6) whose p*K*a has been determined to be 0.04. The solution structures of (5) and (6) have been determined by one and two dimensional NMR spectroscopic techniques, additionally the X-ray crystal structure of (5) is reported [19]. In a similar way the complexes *cis*-$[Os(en\text{-}H)_2(en)]^{2+}$ (7) and $[Os(en)_3]^{3+}$ are obtained by reaction of $[NH_4]_2[OsBr_6]$ with en. Protonation of (7) yields $[Os(en\text{-}H)(en)_2]^{3+}$. The complexes were characterised by IR, NMR and UV/VIS spectroscopies and their redox chemistry investigated [20].



(5)

Treatment of $K_2[OsCl_6]$ with 2-(2-hydroxyethyl)piperazine (L) (**8**) under reflx in 6MHCl/EtOH (1:1) does not lead to coordination of the ligand but rather the double salt {[bis-$(H_2L)][OsCl_6]\}Cl_2$ is obtained and has been characterised by X-ray crystallography [21].

Reduction of the *trans*-dioxoosmium complexes of the dianionic ligands salen (**9**), bpb (**10**) and bpc (**11**) with PPh_3 yields Os(IV) and Os(III) complexes of these ligands. Electrochemical and UV/VIS studies were carried out and the X-ray crystal structure of $[Os(salen)(O^iPr)_2]$ is reported. The osmium(III) complexes are catalysts for the oxidation of alkenes by iodosylbenzene [22].



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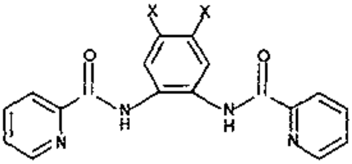
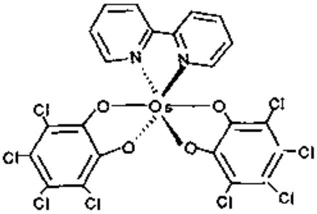


(10) X = H; **(11)** X = Cl

A series of dialkoxy osmium(IV) porphyrin (H_2Por) complexes $[Os(Por)(OR)_2]$ have been synthesised by treatment of $[Os(Por)(N_2)thf]$ with ROH in thf. The complexes were characterised by UV/VIS, IR and ^1H NMR spectroscopies. The X-ray crystal structures of the complexes $[Os(TPP)(OR)_2]$ (R = Et, ^iPr, Ph) are reported in which the Os-O bond lengths range from 1.909 to 1.938Å which is interpreted as indicating significant π-bonding [23].

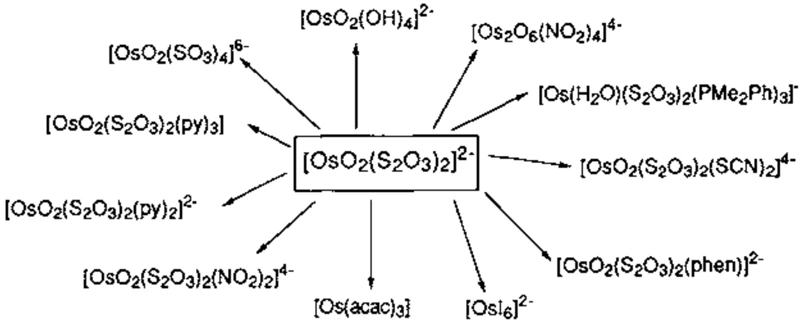
A series of bis(catecholato)(bpy)osmium(IV) complexes have been prepared and studied by electrochemical techniques and UV/VIS-near IR spectroscopy. The X-ray crystal structure of $[Os(bpy)(\eta^2\text{-}C_6Cl_4O_2)_2].2C_6H_6$ (**12**) is reported [24].



(12)

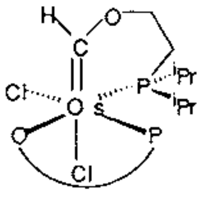
The reaction of $[M(SR)_3(MeCN)]$ (M = Ru, Os; HSR = HS-2,3,5,6-Me_4C_6H, HS-2,4,6-${}^iPr_3C_6H_2$) with HBF_4 or HPF_6 in MeCN gives cations $[M(SR)_3(MeCN)_2]^+$. The complexes may be reversibly reduced to the neutral complexes which may be achieved by Cp_2Co. X-ray crystal structures of one pair of the ruthenium complexes shows *trans*-MeCN ligands. The main differences are longer Ru-S but shorter Ru-N distances for the reduced species [25].

The reaction of $[OsO_2(S_2O_3)_2]^{2-}$ with a variety of ligands has been investigated (Scheme 5). The IR spectra of the products are discussed and the X-ray crystal structure of $[Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$ is reported [26].



Scheme 5

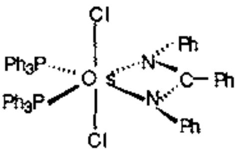
The reaction of $OsCl_3.3H_2O$ and $[OsCl_2(PPh_3)_3]$ with the alkoxyalkylphosphine ${}^iPr_2PCH_2CH_2OMe$ (**13**) has been investigated. The two starting materials provide different isomers of the Fischer carbene complex $[OsCl_2(=CHOCH_2CH_2P^iPr_2)(\eta^2\text{-}{}^iPrPCH_2CH_2OMe)]$ (**14**). The reaction of the nitrogen analogue ${}^iPr_2PCH_2CH_2NMe_2$ proceeds analogously. The reaction with ${}^iPr_2PCH_2CO_2Me$ is also reported [27].



(**14**)

5.6 *OSMIUM(III)*

The reaction of *N,N'*-diphenylamidines, PhN=CRNHPh (R = H, Me, Ph), with *trans*-$[Os(PPh_3)_3Cl_2]$ yields the osmium(III) complexes *trans*-$[Os(PPh_3)_2(\eta^2\text{-}PhNCRNPh)Cl_2]$ (**15**) (for R = Ph). Longer reaction times lead to complete substitution of the phosphine ligands and formation of the Os(IV) complexes *trans*-$[Os(\eta^2\text{-}PhNCRNPh)_2Cl_2]$ (**16**). The X-ray crystal structure of (**16**) (R = Et) is reported [28].



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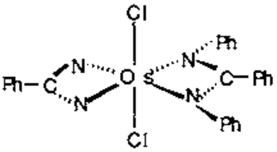


(16)

The oxidation of the complexes [Os(L-L)$_2$X$_2$] [X = Cl, Br; L-L = o-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(AsMe_2)_2$, *o*-$C_6H_4(PMe_2)(AsMe_2)$, *o*-$C_6F_4(AsMe_2)_2$, dppe, dmpe, $Ph_2AsCH{=}CHAsPh_2$, *o*-$C_6H_4(PPh_2)_2$, *o*-$C_6F_4(PPh_2)_2$] with dilute HNO_3 in aqueous HBF_4 provides the Os(III) complexes [Os(L-L)$_2$X$_2$]$^+$. Similar treatment with concentrated HNO_3 converts most of the complexes to Os(IV) species. Cyclic voltametry shows the Os(II)-Os(III) and Os(III)-Os(IV) couples to be mostly reversible. The electronic spectra of the Os(III) and Os(IV) complexes were assigned and the X-ray crystal structure of *trans*-[Os{*o*-$C_6H_4(AsMe_2)_2$}$_2$Cl$_2$][ClO$_4$] determined [29].

Electrochemical studies of $[Os_2Cl_8]^{2-}$ have been reported. At 235 K one electron oxidation (1.35V) is reversible and a second oxidation is observed at 'extreme potential' (2.05V) *vs* Ag/AgCl in CH_2Cl_2. The $[Os_2Cl_8]^-$ complex was characterised spectroelectrochemically [30].

The electrochemistry of the metallocenylmethyl carbonium ions $[(CpMC_5H_4)_nCPh_{3-n}]^+$ (M = Fe, Ru, Os; n = 1-3) have been investigated by cyclic voltametry. The stabilising effect of the metallocene substituents on the α-carbonium ion was found to be in the order Fe < Ru < Os. An increases in the number of metallocenyl groups at the α-carbonium ion hinders reduction [31]. The X-ray crystal structure of $[CpOs(C_5H_4CPh_2)][PF_6]$ has been determined, and its NMR spectra compared with those of the iron and ruthenium derivatives. These data also suggest that the stabilisation of the carbonium ion increases in the order Fe < Ru < Os [32].

5.7 *OSMIUM(II)*

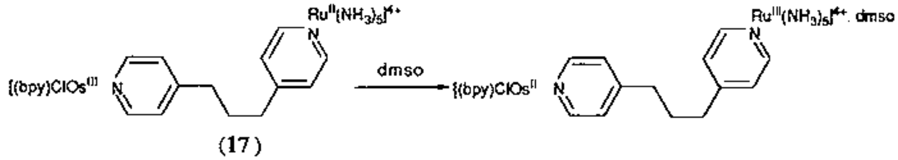
5.7.1 *Complexes with nitrogen ligands*

The complex *cis*-[Os(bpy)$_2$(CO)H]$^+$ has been found to be a catalyst for the reduction of CO_2 in MeCN containing 0.1M [Bu$_4$N]PF$_6$ at glassy carbon or Pt electrodes. In the absence of water the main product is CO, however, its presence provides 22% $[HCO_2]^-$. The catalytically active species was shown to be [Os(bpy)$_2$(CO)H]$^-$, and neither bound CO or H are involved in the reaction. For the complexes [M(bpy)$_2$(CO)R]$^-$ (M = Ru, Os; R = H, Me, Ph) a linear correlation between the initial rate determining step and the cone angle of R was established [33].

Electronic transitions in $[(bpy)ClOs(\mu\text{-}CN)Ru(NH_3)_5]^{3+/2+}$ have been studied by resonance Raman spectroscopy and band assignments made. In nitrobenzene all three intervalence transfer bands are observed for the first time and the existence of a remote MLCT previously proposed is supported. The results are used to demonstrate the utility of the technique for assigning electronic transitions in overlapping absorption spectra [34].

The electrochemical properties of complexes of the type $[OsQL_2]^{z+}$ [L = bpy, 2(*m*-tolylazo)py; Q = deprotonated forms of 8-quinolinol and 2-methyl-8-quinolinol; z = 1 for Os(II) and 2 for Os(III)] have been studied and exhibit (IV)-(III) and (III)-(II) couples in the range 0.1-1.6V dependant upon the π-acid properties of the ligand Q. Ligand reduction was observed between -0.3 and -2.3V [35].

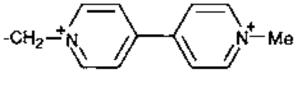
Intramolecular electron transfer within the bridged mixed metal complex (**17**), induced by addition of dmso to its nitromethane solution, has been studied by the technique of pulsed accelerated flow spectroscopy which enabled time resolution of the electron transfer process [36].



(**17**)

The synthesis, electrochemistry, spectroscopic and spectroelectrochemical properties of the complexes $[(bpy)_2Os(BL)Ru(bpy)_2][PF_6]_4$ [BL = 2,3-bis(2'-pyridyl)pyrazine, 2,3-bis(2'-pyridyl) quinoxaline and bis(2'pyridyl)benzoquinoxaline] have been reported. Addition of the $[Ru(bpy)_2]^{2+}$ moiety to the bridging ligand in $[Os(bpy)_2(BL)]^{2+}$ shifts the MLCT to the bridging ligand π-orbitals to lower energy and the bridging ligand electrochemical reductions to higher potentials. The lowest energy electronic transitions have been assigned to M(*d*π)-BL(π*) MLCT and the first and second reductions of the dimetallic complexes to sequential reductions of BL [37].

The complex $[Os(ttp)]^{2+}$ [ttp = 4'-(*p*-tolyl)-2,2':6,2"-terpyridine] has been used as a photosensitiser (P) linked to the$[MV]^{2+}$ (**18**) electron acceptor (A) and/or the PTZ (**19**) or DPAA (**20**) electron donors (D). Extensive electrochemical and luminescence investigations are reported for the P, P-A, D-P and D-P-A systems [38].



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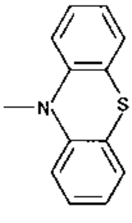

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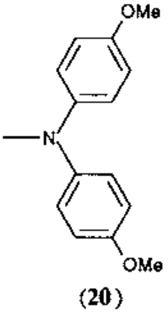

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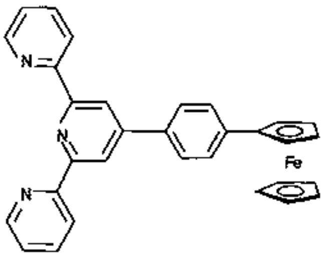

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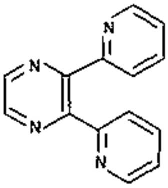
Complexes of the terpyridine ligand (**21**) of the type $[ML_2]^{2+}$ (M = Fe, Ru, Os) have been synthesised. Electrochemical and spectroscopic examination reveal a weak interaction between the Fc group and the metal centre, but strong intramolecular quenching of the excited state of the osmium complex is observed [39]. Four new hexanuclear complexes of the general formula $\{[ML_2(\mu\text{-}2,m\text{-dpp})]_2Ru(\mu\text{-}2,3\text{-dpp})Ru[(\mu\text{-}2,n\text{-dpp})M'L'_2]_2\}(PF_6)_{12}$ [M = M'+Ru, L = L' = biq, n = m = 3; M = M' = Ru, L = bpy, L' = biq, m = 5, n = 3; M = M = Os, L = L' = bpy, m = n = 3; M = Ru, M' = Os, L = L' = bpy, m = 5, n = 3 where dpp = bis(2-pyridyl)pyrazine (**22**) and biq = 2,2'-biquinoline (**23**)] have been synthesised using the complexes as ligands/metals methodology. A protection/deprotection procedure involving initial complexation with the monomethylated dpp ligand (formed by reaction of dpp with Me_3OBF_4) followed by secondary complexation and final deprotection with DABCO was also used in the syntheses [40]. Decanuclear homo- and



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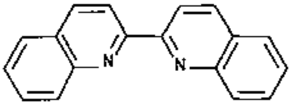

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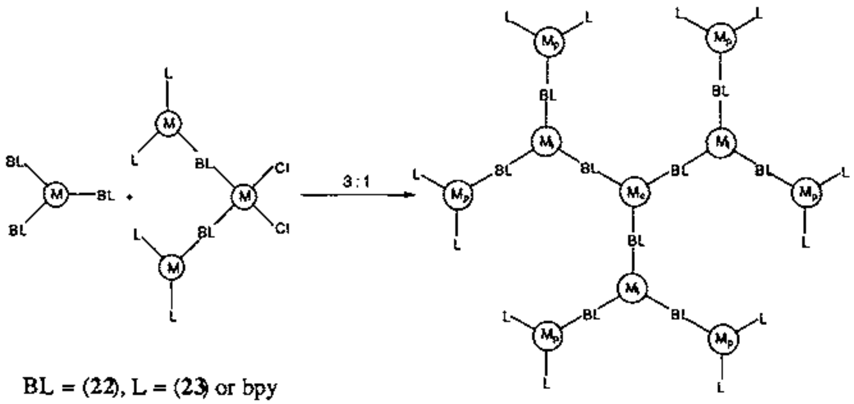
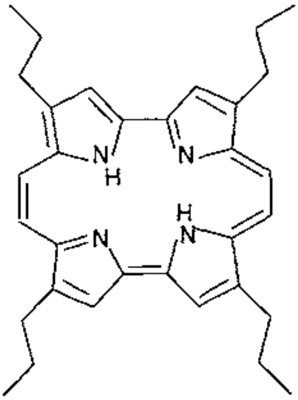


BL = (**22**), L = (**23**) or bpy

Scheme 6

heterometallic complexes $[M_c\{(BL)M_i[(BL)M_p(L)_2\}_3]^{20+}$ have also been prepared as PF_6^- salts using the complexes as ligands/metals methodology (Scheme 6). The central (M_c), intermediate (M_i) and peripheral (M_p) metal ions are Ru^{2+} or Os^{2+}, BL is the bridging ligand 2,3-bis(2-pyridyl)pyrazine (22) and L is either 2,2'-biquinoline (biq) (**23**) or bpy. The complexes show intense L and BL centred absorption bands in the UV spectrum, and intense M-L and M-BL bands in the visible regions. Electrochemical and luminescence experiments are also reported [41].

The reaction of $[Os_3(CO)_{12}]$ with 2,7,12,17-tetrapropylporphycene (H_2TPrPc) (**24**) at elevated temperatures yields [Os(TPrPc)(CO)]. Oxidation of this product with *m*-chloroperbenzoic acid in CH_2Cl_2 gives the *trans*-dioxo osmium(VI) complex $[Os(TPrPc)(O)_2]$ and this reacts with hydrazine hydrate in thf under nitrogen to give $[Os(TPrPc)(N_2)]$ ($\nu_{N\equiv N}$ = 2035 cm^{-1}) [42].



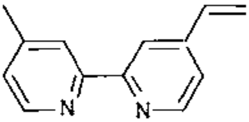
(**24**)

The reaction of $[Os(TTP)_2]$ with diazo alkanes N_2CRR' yields the alkylidene complexes [(TTP)Os=CRR'] (TTP = *meso*-tetra-*p*-tolylporphyrin, R = H, R' = $SiMe_3$; R = H, R' = CO_2Et). The catalytic conversion of ethyldiazoacetate to diethylmaleate by the osmium complexes was investigated [43].

The complexes $[M(OEP)(L)H_2)]$ [M = Ru, Os; L = thf, 1-^{t}butyl-5-phenylimadazole or (Im*)] have been synthesised. The H-H bond length was found to increase when Os was replaced by Ru and when Im* was replaced by thf (range 0.92-1.18Å) [44].

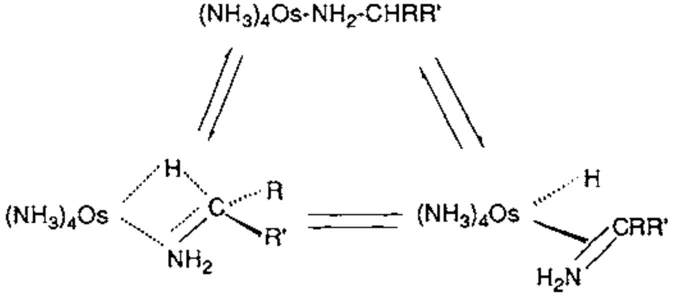
The complex [Os(Pc)] (Pc^{2-} = phthalocyanine) is prepared by thermal decomposition of $[Os(Pc)(py)_2]$ at 400°C and its reaction with ligands L = pyrazine or terrazine yields either $[Os(Pc)L_2]$ (L = pyrazine) or a mixture of $[Os(Pc)L_2]$ and $[Os(Pc)L]_n$ (L = terrazine). The polymeric $[Os(Pc)L]_n$ (L = pyrazine) could be prepared by thermal treatment of $[Os(PcL_2)]$ below 320°C. The polymers were found to be good and weak semiconductors respectively [45].

A number of papers have reported investigations of polymers derived from coordinated vinylbipyridines. Polymers of $[M(vbpy)_3][PF_6]_2$ (M = Ru, Os; vbpy = 4-vinyl-4'-methyl-2,2'-bipyridine) (**25**) were prepared by radical polymerisation and characterised by electrochemical and spectroscopic techniques. For the osmium polymers, the relative polymer size was found to vary in proportion to the number of vinyl groups consumed during polymerisation, while the same was not found to be the case for the Ru polymers [46]. Copolymers of $[Os(vbpy)_3][PF_6]_2$ and $[Ru(vbpy)_3][PF_6]_2$ have been prepared by solution and electropolymerisation and different ratios of Ru and Os were found to be incorporated depending on the polymerisation method, thus indicating fundamental differences between the two methods. Luminescence experiments at 77K and 298K indicate significant energy transfer from Ru-Os states in the polymer [47]. Photolysis of copolymer films of *cis*-$[Ru(Me_4Bpy)_2(vpy)_2]^{2+}$ and $[Os(vbpy)_3]^{2+}$ (Me_4bpy = 4,4',5,5'-bpy, vpy = 4-vinylpyridine) on Pt electrodes results in loss of $[Ru(Me_4bpy)_2]^{2+}$ and formation of molecular voids. The resulting binding sites were used to coordinate $[Os(PMe_2Ph)_3Cl_2]$ which could be incorporated with spatial control using masking techniques [48].



(25)

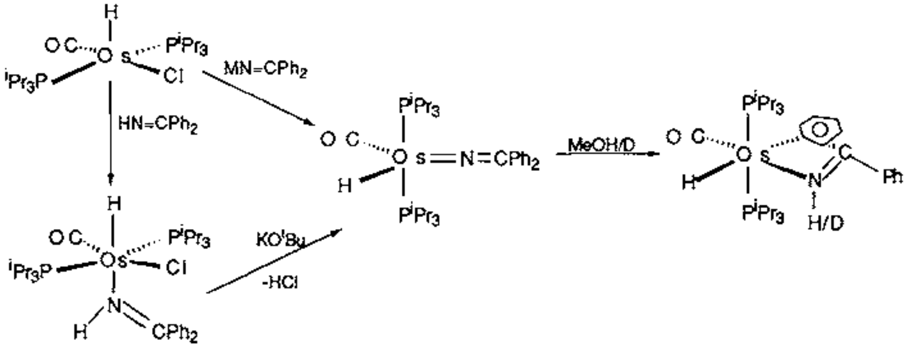
For the first time β-elimination from an amine ligand (analogous to β-elimination from an alkyl ligand) has been reported. The complexes $[Os(NH_3)_4(L)(NH_2CHRR')]$ (L = MeOH, $-CH_2OMe$; R = H, ^iPr; R' = Et, $-CH_2OMe$) undergo the reaction to form iminium-hydride complexes. Evidence for the microscopic reverse reaction is also presented (Scheme 7) [49]. An iminium complex $[Os(NH_3)_5(\eta^2\text{-}CH_3CH{=}NH_2)][OTf]_3$ is also formed by zinc amalgam reduction of $[Os(NH_3)_5(MeCN)][OTf]_3$ or $[Os(NH_3)_5(MeCN)][OTf]_2$ (HOTf = CF_3SO_3H), and may be deprotonated by proton sponge to the imine complex $[Os(NH_3)_5(CH_3CH{=}NH)][OTf]_2$. This complex disproportionates giving the acetonitrile complex as one of the products [50].



Scheme 7

The spectroscopically characterised azavinylidene complex $[OsH(=N=CPh_2)(CO)(P^iPr_3)_2]$ may be prepared by treatment of the five coordinate $[OsH(CO)(P^iPr_3)_2]$ (**26**) with an alkali metal imide $MN=CPh_2$ (M = Li, Na) or sequentially from (**26**) by treatment with $HN=CPh_2$ followed by elimination of HCl with KO^tBu (Scheme 8).

Treatment with MeOH leads to protonation at nitrogen and orthometallation of one of the phenyl rings. The use of MeOD leads to nitrogen deuteration [51].



Scheme 8

Osmium hydride and trifluoroacetate complexes ($L_nM\text{-}H/O_2CCF_3$) react with *N,N'*-diphenylamidines [PhN=C(R)NHPh] (R = H, Me, Et, Ph) giving the amidinato derivatives {L_{n-1}Os[PhNC(R)NPh]} and yielding H_2 or CF_3CO_2H. The complex [$OsH_4(PPh_3)_3$] reacts in the presence of EtOH to generate [OsH[PhNC(R)NPh](CO(PPh_3)$_2$] via an alcohol decarbonylation reaction [52].

The X-ray crystal structure of *cis*-[$Os(CO)_2(I)_2PPh_3(HNMe_2)$], formed by cleavage of [(μ-I)$Os_2(CO)_6$(μ-OCNHCHMe$_2$)(I)$_2$] with PPh_3, has been reported [53].

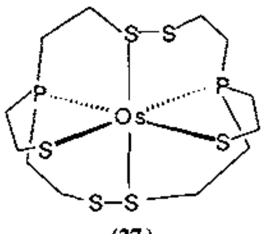
5.7.2 Complexes containing phosphorus ligands

The catalysis of the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one by the five coordinate complex [OsHCl(CO)(PR_3)$_2$] (PR_3 = P^iPr_3, PMe^tBu_2) has been studied. The reaction is first order with respect to the catalyst and substrate an independent of H_2 pressure, and a mechanism is deduced from kinetic and spectroscopic data [54].

The reaction of *cis*-[$OsBr_2(CO)_4$] with etherphosphine ligands gives *cis-*, *cis-*, *trans-*complexes [$OsBr_2(CO)_2$\{$R_2P(CH_2)_nOR$\}$_2$]. The X-ray crystal structure of the complex with $Ph_2PCH_2CH_2OMe$ ligands is reported. Irradiation of these complexes leads to ejection of one CO and coordination of one ether oxygen. Interconversion of isomers of these complexes is discussed [55].

Reaction of *trans*-[$OsCl_2(PPh_3)_3$] with the phosphine P(2-HSC$_6$H$_4$)$_3$ leads to the complex [Os\{P(C_6H_4S-2)$_3$\}$_2$] which on crystallisation undergoes linking of the two ligands via disulfur bonds to give octahedral (**27**) [56].

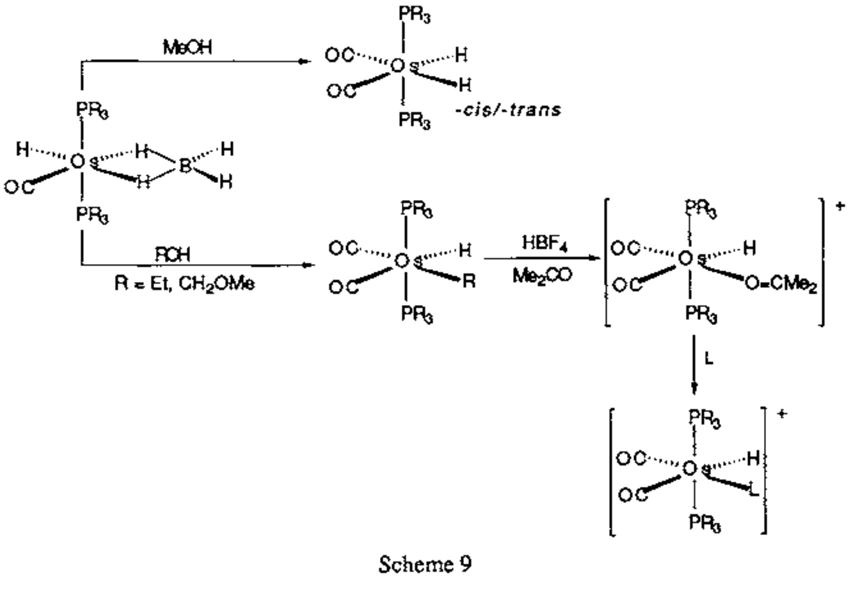
The dihydrogen ligand in [OsH(η^2-H_2)L_4][BF_4] (L = P(OEt)$_2$Ph) may be replaced by nitrosyl by reaction with [NO][PF_6] in CH_2Cl_2 which yields [OsH(NO)L_4][PF_6]$_2$ (**28**). The hydride ligand in (**28**) may be removed to yield the monocation [Os(NO)L_4]$^+$ whose reactions with CO, isonitriles and Br_2 have been investigated [57].



(27)

The X-ray crystal structure of *trans*-[OsH(η^2-H_2)(dppe)$_2$][BF_4] has been reported. Difficulty was experienced in refining the H positions, but an approximate Os-(η^2-H_2) distance of 1.7Å is given [58].

The η^2-BH_4 complex [OsH(CO)(P^iPr_3)$_2$(η^2-BH_4)] reacts with methanol to produce a mixture of *cis*- and *trans*-[OsH_2(CO)$_2$(P^iPr_3)$_2$] while with ROH (R = Et, CH_2OMe) the alkyl complexes [OsH(CO)$_2$(P^iPr_3)$_2$R] are formed. The reactions of these complexes with HBF_4 in acetone leads to elimination of R and coordination of Me_2C=O which is labile and may be replaced with other ligands to form the complexes [OsH(CO)$_2$(P^iPr_3)$_2$L]$^+$ (Scheme 9) [59].

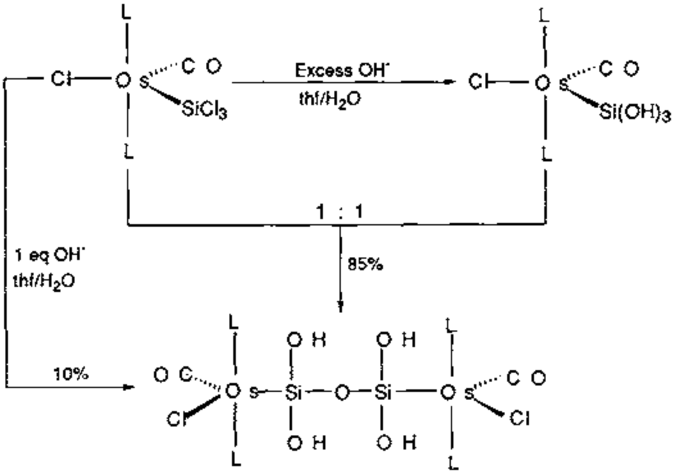


Scheme 9

The dinuclear complexes [(P^iPr_3)$_2$(CO)HM(μ-η^4-BH_4)MH(CO)(P^iPr_3)$_2$][BF_4], [MH(η^2-O_2CR^*)(CO)(P^iPr_3)$_2$] and [MH(pz)(CO)(Hpz)(P^iPr_3)$_2$] are prepared by reaction of [OsH(CO)(P^iPr_3)$_2$(η^2-BH_4)] with HBF_4, R^*CO_2H (R^* = various chiral groups) and pyrazole (Hpz) respectively (M = Ru, Os). Their reactions with H_2, tetrafluorobenzobarrelene, methylvinyl ketone, MeCN and Me_2CO and subsequent reactions are reported. The catalytic activity of some of the derived complexes in asymmetric H transfer from ^iPrOH to acetophenone is described. The osmium complexes give better optical yields than the ruthenium ones [60].

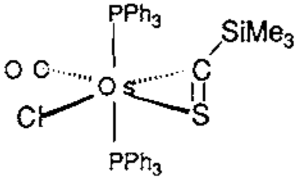
5.7.3 Other coordination complexes

Hydrolysis of $[Os(SiCl_3)Cl(CO)(PPh_3)_2]$ with $NaOH_{(aq)}$ in thf yields $[Os\{Si(OH)_3\}Cl(CO)(PPh_3)_2]$ whose X-ray crystal structure has been determined. If less than one molar equivalent of NaOH is present, some of the dinuclear complex $[\{OsCl(CO)(PPh_3)_2Si(OH)_2\}_2O]$ is formed which has also been the subject of an X-ray crystallographic study (Scheme 10) [61].



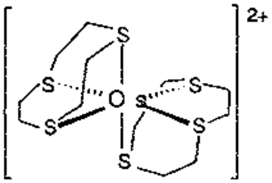
Scheme 10

Reaction of the unsaturated complex $[OsCl(PPh_3)_2(CS)SiR_3]$ with CO gives an intermediate 6-coordinate complex which undergoes migratory insertion of SiR_3 into the Os-CS bond to generate the silathioacyl complex $[OsCl(PPh_3)_2(CO)(\eta^2\text{-}S{=}CSiR_3)]$ (**29**). An X-ray crystal structure of the ruthenium analogue of (**29**) is reported [62].



(**29**)

The reaction of the chloro-bridged dimer $[\{[\eta\text{-}1,4\text{-}Me(^iPr)C_6H_4]OsCl_2\}_2]$ (**30**) with four molar equivalents of the tridentate sulfur macrocycle $[9]aneS_3$ (**31**) in the presence of $[NH_4][PF_6]$ generates the sandwich complex $[Os(\eta^3\text{-}[9]aneS_3)_2][PF_6]_2$ (**32**). Alternatively, (**32**) may be synthesised from $[OsCl_6]^{2-}$ and two molar equivalents of (**31**) in a water/dmf/MeOH mixture. The mixed sandwich complex $[\{\eta\text{-}1,4\text{-}Me(^iPr)C_6H_4\}Os(\eta^3\text{-}[9]aneS_3)]^{2+}$ (**33**) may be prepared by reaction of (**30**) with two molar equivalents of (**31**) in MeOH. The reaction of *mer*-$[OsH_2(CO)(PPh_3)_3]$ with one molar equivalent of (**31**) in 2-methoxyethanol generates the cation $[OsH(CO)(PPh_3)(\eta^3\text{-}[9]aneS_3)]^{2+}$ (**34**). X-ray crystal structures of (**32**), (**33**) and (**34**) are reported [63].



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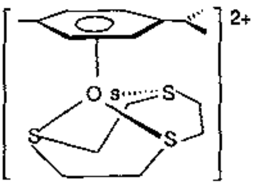

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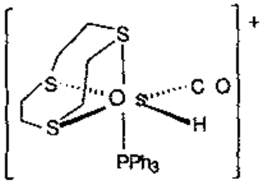
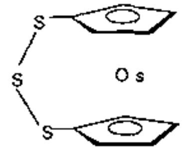


(34)

Complexes of the type $[Os(RSCS_2)_2(PPh_3)_2]^z$ (*cis-/trans*-Os(II), z = 0; *cis-/trans*-Os(III), z = +) have been prepared. The osmium(III) complexes display rhombic ESR spectra which have been analysed. The redox and isomerisation processes which link the complexes have been characterised by electrochemical and spectroscopic techniques [64].

5.7.4 *Organometallic complexes*

The first bridged osmocene has been obtained by reaction of 1,1'-dilithioosmocene with elemental sulfur giving 1,2,3-trithia[3]osmocenophane (**35**) [65].



(35)

The different effects of X^- ligands on the basicity of the metal in $[CpOs(PR_3)X]$ (X = Cl, Br, I, H; $PR_3 = PPh_3, PPh_2Me$) have been investigated. The complexes were examined calorimetrically and the basicity was found to increase in the order Cl < Br < I < H with the H complex being up to 23.2 kcal mol^{-1} more basic than the Cl complex [66].

The complexes $[(\eta\text{-}1,3,5\text{-}Me_3C_6H_3)Os(H)_2L]$ (L = MeCN, CO) have been prepared by reaction of $[(\eta\text{-}1,3,5\text{-}Me_3C_6H_3)OsCl_2L]$ with magnesium amalgam in the presence of EtOH. Comprehensive IR and Raman spectroscopic investigations and normal coordinate analyses are reported [67].

The complexes $[Os(C_6Me_6)(N^tBu)]$ and $\{Os[\eta\text{-}1,4\text{-}Me(^iPr)C_6H_4](N^tBu)\}$ have been the subject of a HeI and HeII PE spectroscopic study. The results show similarities between the bonding in these complexes and that in metallocenes [68].

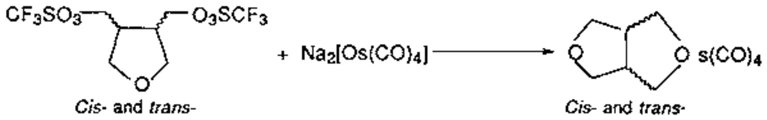
Dialkyl osmium(II) $[(Mes)OsR_2(CO)]$ (Mes = η-1,3,5-$Me_3C_6H_3$) and alkylhalogeno osmium(II) $[(\eta\text{-}1,3,5\text{-}Me_3C_6H_3)OsR(CO)X]$ complexes may be prepared by reaction of $[(Mes)OsCl_2(CO)]$ with Grignard reagents. The influence of the type of Grignard reagent has been investigated. Stepwise treatment of $[(Mes)OsR(CO)X]$ complexes with $AgBF_4$ and Al_2O_3 yields alkene complexes$[(Mes)Os(CH_2{=}CHR)(CO)]$. Alternatively, H^- abstraction with trityl followed by deprotonation gives the same products [69].

The X-ray crystal structure of $[Os(CO)_4(\eta^2\text{-}H_2C{=}CH_2)]$ has been reported. The ethene ligand occupies two coordination sites in an octahedral structure. The coupling constant $^1J(^{13}C\text{-}^{13}C)$ is 39.0(2). *Ab initio* calculations show that the structure is predominantly cyclopropane in character and explain the slight bending of the axial CO ligands towards the ethene [70].

The reaction of $[Os(NH_3)_5(OTf)][OTf]_2$ with arenes in the presence of Mg powder gives the complexes $[(NH_3)_5Os(\eta^2\text{-arene})]^{2+}$ (arene = phenol, 4-, 5-, 6-methylphenol, 4,5-dimethylphenol). Coordination in this way favours the keto-diene tautomer of the phenol, the keto-enol equilibrium constant approximating to unity at 20°C for the coordinated phenol [71].

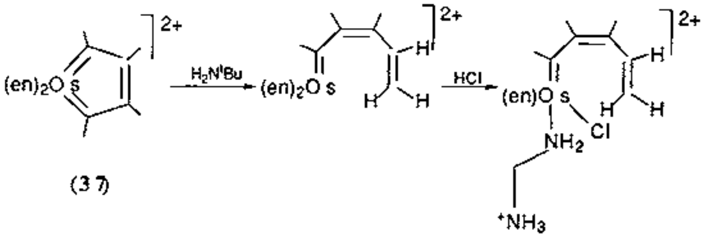
Protonation of the complexes $[Os(NH_3)_5(2,3\text{-}\eta^2\text{-pyrrole})]^{2+}$ (pyrrole = pyrrole and alkylated pyrroles) has been found to occur exclusively at the β-carbon. Depending on the substitution of the pyrrole the ligand may also be (i) converted to the 2-*H*-pyrrolium tautomer, (ii) deprotonated at N or (iii) deprotonated at the α-carbon [72].

The reaction of $Na_2[Os(CO)_4]$ with *cis*- and *trans*-3-4-bis(trifluoromethylsulfonyloxymethyl)oxolane gives a mixture of the *cis*- and *trans*-3-oxa-7-osmabicyclo[3.3.0]octanes (**36**). The X-ray crystal structure of the *cis*-isomer has been determined [73].



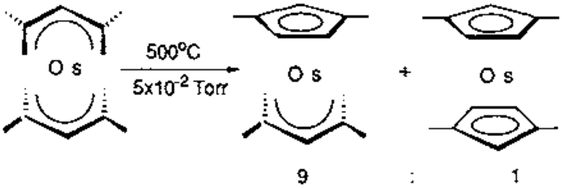
(**36**)

The metallacyclopentatrienes *cis*-$[Os(C_4Me_4)(en)_2]^{2+}$ (**37**) and *cis*-$[Os(C_{10}H_{14})(en)_2]^{2+}$ (**38**) have been prepared by reaction of $[Os(en)_2(H_2O)(H_2)][OTf]_2$ with the appropriate alkyne [74]. The reaction of (**37**) with $^tBuNH_2$ followed by HCl leads to cleavage of the metallacycle and quaternisation of one (en) nitrogen (Scheme 11) [75].



Scheme 11

The low pressure gas phase thermolysis of $[Os(\eta^5\text{-}2,4\text{-}Me_2\text{-pentadienyl})]$ yields $[Os(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)(\eta^5\text{-}2,4\text{-}Me_2\text{-pentadienyl})]$ and $[Os(\eta^5\text{-}1,3\text{-}Me_2C_5H_3)_2]$ in a 9:1 ratio (Scheme 12) [76].



Scheme 12

5.8 OSMIUM(I)

The halide induced disproportionation of the 17 electron complexes $[M(CO)_3(PCy_3)_2]^+$ (M = Fe, Ru, Os) has been probed by a number electrochemical techniques. The periodic effect on reactivity showed only slight variation in contrast to the 18 electron systems [77].

5.9 OSMIUM(0)

Protonation of [(η-arene)Os(diene)] complexes (arene = benzene, mesitylene; diene = 1,3-cyclohexadiene, *cis*-2,3-dimethylbutadiene) leads to systems in which a hydrido-diene complex is in equilibrium with an allyl complex. This equilibrium was studied by NMR spectroscopy and compared with the similar [MHCp*(diene)] (M = Rh, Ir) and $[ArRuH(diene)]^+$ systems [78].

5.10 IONIC LATTICES

The compounds Y_4Br_4Os and Er_4Br_4Os have been prepared from Y or Er, YBr_3 or $ErBr_3$ and Os in Nb containers at 850-1020°C. An X-ray crystal structure Y_4Br_4Os shows the structure to consist of Os centred square antiprisms sharing opposite faces (*C2/c*; Z = 8; a = 12.514(5), b = 12.381(4), c = 6.567(2)Å, β = 90.96(3)°; R, R_w = 3.5, 3.9%) [79].

5.11 OSMIUM CARBONYL CLUSTERS

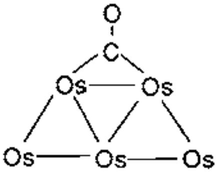
5.11.1 Clusters with only carbonyl and hydride ligands

Variable temperature ^{13}C and ^1H NMR and $\{^1H\}^{13}C$ Exchange Spectroscopy (EXSY) has been used to probe the fluxional processes occurring in $[HM_{10}C(CO)_{24}]^-$ (M = Ru, Os). Results are interpreted in terms of both locallised and global intramolecular exchange of both CO and H ligands which occurs by the same mechanism in both clusters [80].

A new synthesis of the insoluble $[H_2Os_{10}C(CO)_{24}]$ which enables crystal formation has been reported. The synthesis involves heating $[Os_3(CO)_{12}]$ in cyclohexane at 300°C for one hour.

The resulting crystal structure shows both hydride ligands to be in μ_2-coordination modes on the surface of the cluster [81].

The pyrolysis of $[Os_5(CO)_{19}]$ in CH_2Cl_2 at 50-55°C in a sealed tube for three days yields $[Os_5(CO)_{18}]$ **(38)** which an X-ray crystal structure determination shows to have a planar structure. Further pyrolysis at 70°C leads to ejection of two further CO ligands and formation of $[Os_5(CO)_{16}]$ [82].

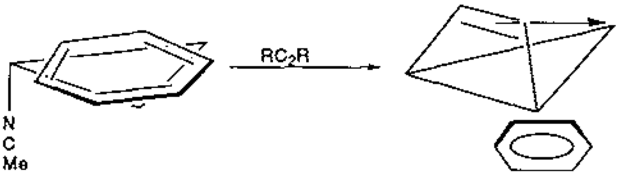


(38)

Detailed study of the X-ray crystal structures of $[M_3(CO)_{12}]$ (M = Fe, Ru, Os) and a series of their substituted derivatives $[M_3(CO)_{12-n}L_n]$ has revealed good evidence in support of the intermediacy of an anticuboctahedral ligand shell geometry in ligand fluxional processes for these clusters [83].

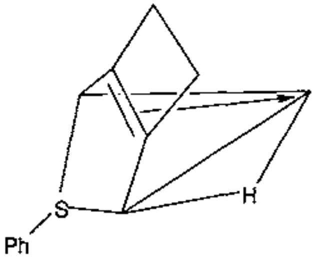
5.11.2 Clusters with additional C, Si or Sn ligands

A paper comprehensively describing the chemistry of the "face-capping" (μ_3-η^2:η^2:η^2-) benzene ligand on a triosmium cluster framework has appeared. X-ray crystal structures of $[Os_3(CO)_8(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)L]$ (L = PPh_3, C_2H_4) are reported and the preparation of $[Os_3(CO)_8(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(NCMe)]$ (39) is given. Semi-empirical calculations on the Os_3-(μ_3-η^2:η^2:η^2-C_6H_6) bonding are also reported [84]. The reaction of **(39)** with alkynes results in a shift of the benzene ligand coordination to η^6- and the alkyne coordinates in a typical μ_3-η^2-fashion (Scheme 13). This reactivity is compared with that of the ruthenium analogue [85]. A further publication on this topic reports an extensive investigation of the stereochemical non-rigidity of $[Os_3(CO)_8(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\eta^2\text{-}CH{=}CHR)]$ by one and two dimensional and CPMAS NMR techniques. Results show spinning of the benzene and alkene ligands and $Os(CO)_3/Os(CO)_2$(alkene) polytopal rotation. Similar processes are evident in the solid state [86].



Scheme 13

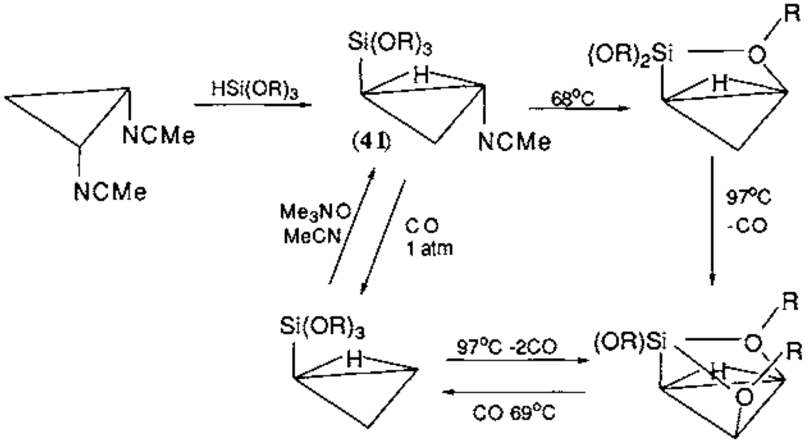
The triosmium cyclobutyne complex $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_4H_4)(\mu\text{-}SPh)(\mu\text{-}H)]$ (**40**) is synthesised by reaction of $[Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C_4H_5)(\mu\text{-}SPh)]$, prepared by reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with 1-(phenylthio)cyclobutene, with Me_3NO in CH_2Cl_2 followed by reflux for 30 hours. The cyclobutyne is bonded as a typical alkyne [87].



(40)

Various transformations of the alkyne H-C≡C-$SiMe_3$ on a triosmium core have been reported [88]. The structure of $[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}DMAD)]$ (DMAD = dimethylacetylene dicarboxylate) has been reported and compared in detail with those of nine other related Os and Ru clusters, deviations from C_s symmetry are accounted for [89].

The reaction of $[Os_3(CO)_{11}(NCMe)]$ with PhCOCH=CHCOPh leads to substitution of the MeCN ligand and coordination of the new ligand via the C=C bond in an equatorial position [90]. The reaction of $\{Os_3(CO)_9[\mu_3\text{-}C(Et)N(Me)CH](\mu\text{-}H)_2\}$ with PhC≡CPh at 125°C yields six products, four of which were characterised by X-ray crystallography [91].

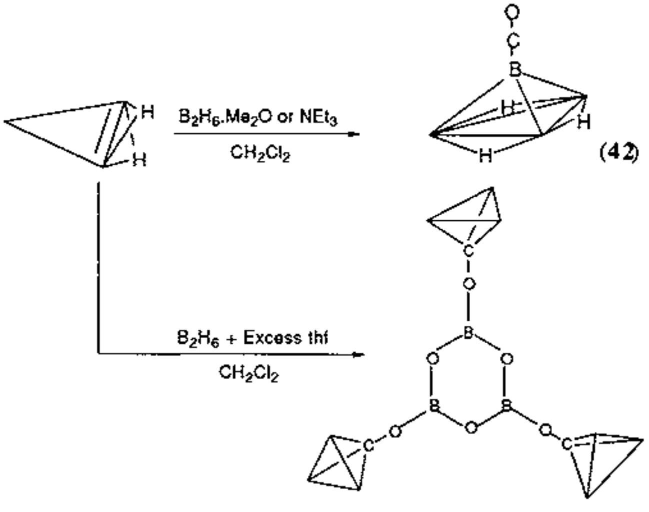


Scheme 14

The reaction of $[Os_3(CO)_{10}(NCMe)_2]$ and $[Os_3(CO)_{11}(NCMe)]$ with $HSi(OR)_3$ (R = Et, Me) gives $[Os_3(CO)_{10}(NCMe)[Si(OR)_3](\mu\text{-}H)]$ (**41**) and $[Os_3(CO)_{11}[Si(OR)_3](\mu\text{-}H)]$. Thermolysis of (41) gives two products in which one or two of the alkoxy oxygens are coordinated to osmium (Scheme 14) [92]. The reaction of $[Os_3(CO)_{10}(NCMe)[Si(OMe)_3](\mu\text{-}H)]$ with alkynes

HC≡CR (R = ^{t}Bu, *p*-tolyl) yields complexes which, on treatment with CO, give silyl alkenes *trans*-R(H)C=C(H)Si(OMe)$_3$. One intermediate in this reaction was characterised by X-ray crystallography which showed it to contain a μ-η^2-^{t}Bu-vinyl ligand thus indicating that the hydrosilation reaction occurs by H-insertion [93].

Hydroboration of [Os$_3$(CO)$_{10}$(μ-H)$_2$] with B_2H_6 yields [Os$_3$(CO)$_9$(μ-H)$_3$(μ$_3$-BCO)] **(42)** or [{Os$_3$(CO)$_9$(μ-H)$_3$(μ$_3$-C-)}$_3$(O$_3$B$_3$O$_3$)] **(43)** depending on conditions (Scheme 15); **(42)** is an analogue of a ketenylidene cluster. The boron-bound CO is readily displaced by PMe$_3$, but no exchange is observed with ^{13}CO. Mechanisms are proposed for the formation of **(42)** and **(43)**. The reaction of **(43)** with halogens (X$_2$) is reported to give [Os$_3$(CO)$_9$(μ$_3$-CX)(μ-H)$_3$] and the reaction of [Os$_3$(CO)$_{10}$(μ-H)$_2$] with cathechol borane is also reported [94].



Scheme 15

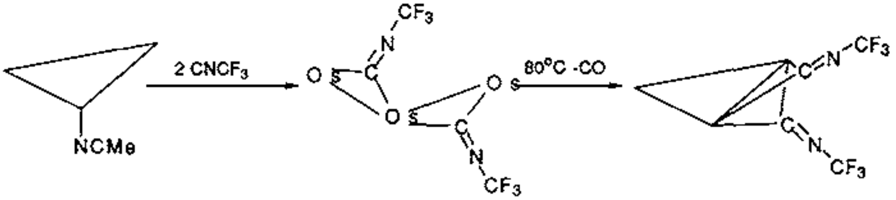
The reaction of (triphenylphosphoranylidene)ethenal (Ph$_3$PCHCHO) with [Os$_3$(CO)$_{10}$(NCMe)$_2$] has been investigated in detail [95]. The reaction of [Os$_3$(CO)$_{12}$] the phosphinimines Ph$_3$P=NR (R = Pr, ^{i}Pr, Ph) has also been studied and found to proceed in a Wittig manner with elimination of Ph$_3$P=O and formation of [Os$_3$(CO)$_{11}$(CNR)]. The reaction of the isonitrile products with primary amines were investigated [96].

The reaction of [Os$_3$(CO)$_{11}$(NCMe)] with trifluoromethylisonitrile (CF$_3$NC) leads to addition of two moles of the new ligand and opening of the cluster core. At elevated temperatures the cluster recloses with elimination of CO (Scheme 16). Both isonitrile ligands in [Os$_3$(CO)$_{10}$(CNCF$_3$)$_2$] bridge the same Os-Os edge reminiscent of the structure of [Fe$_3$(CO)$_{12}$]. Two further minor products were identified: [Os$_3$(CO)$_9$ (NCMe)(CNCF$_3$)$_2$] (2%) and [Os$_3$(CO)$_{10}$(NCMe)(CNCF$_3$)] (17%) [97].

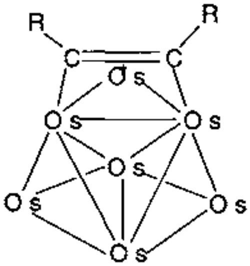
Deprotonation of [Os$_3$(CO)$_9$(μ$_3$-COMe)(μ-H)$_3$] with DBU followed by reaction with Au(PPh$_3$)Cl in the presence of TlPF$_6$ leads to replacement of one of the hydride ligands by a μ-

$AuPPh_3$ fragment. A similar reaction of $[Os_3(CO)_9(\mu_3\text{-CCl})(\mu\text{-H})_3]$ with DBU yields an intermediate deprotonated anion which will then react with added nucleophiles to substitute the chloride giving the clusters $[Os_3(CO)_9(\mu_3\text{-C-Nuc})(\mu\text{-H})_2]$ [Nuc = py, quinoline, isoquinoline, $P(OMe)_3$, DBU]. X-ray crystal structures of the $P(OMe)_3$ and quinoline derivatives are reported. Data for these compounds are consistent with a zwitterionic formulation [98].

Reaction of $[Os_7(CO)_{20}H_2]$ with MeC≡CMe at 90-100°C yields $[Os_7(CO)_{19}(Me_2C_2)]$ (**44**) [99].



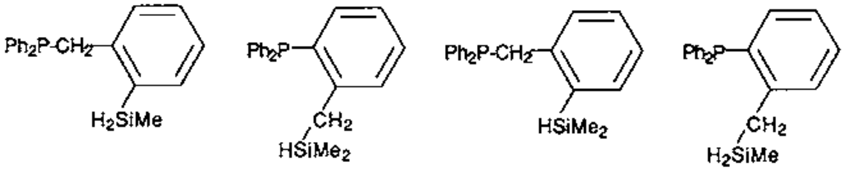
Scheme 16



(**44**)

5.11.3 *Clusters with additional N, P, As or Sb ligands*

Systems based upon $[Os_3(CO)_{12}]$ have been used effectively for homogeneous selective hydrogenation of α,β-unsaturated carbonyl compounds. Mixtures of $[Os_3(CO)_{12}]$ and various phosphines or $P(OPh)_3$ were used [100].

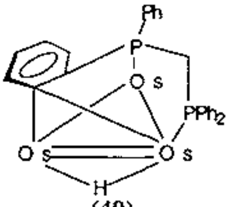


(**45**)-(**48**)

The new didentate ligands (**45**)-(**48**) have been synthesised from Ph_2PCl and Grignard reagents RMgBr (R = $C_6H_4CH_2SiMe_2\text{-}o$, $C_6H_4CH_2SiMeH_2\text{-}o$). Their reaction with

$[Os_3(CO)_{10}(NCMe)_2]$ yields the clusters $[Os_3H(CO)_{10}(L\text{-}L)]$ in which the didentate ligand bridges an Os-Os edge [101].

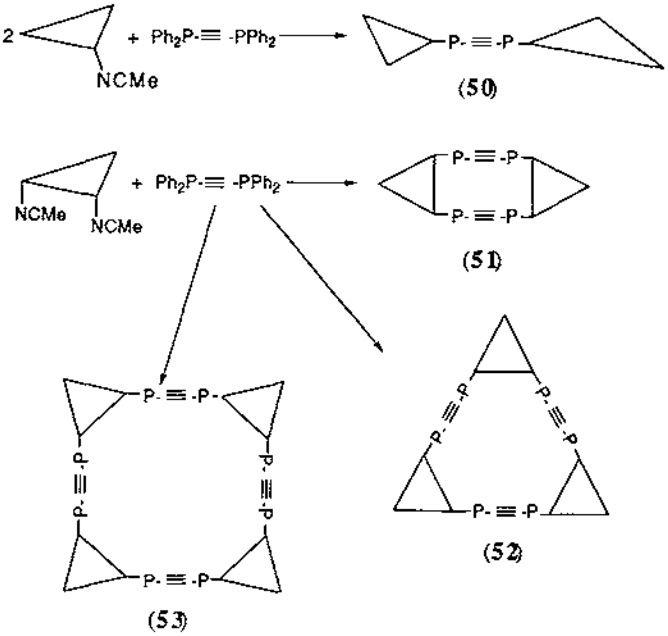
The unsaturated cluster $[Os_3H(CO)_8\{Ph_2PCH_2P(Ph)C_6H_4\}]$ **(49)** has been studied electrochemically and spectroscopically. The transformation of **(49)** into the saturated clusters $[Os_3H(CO)_9\{Ph_2PCH_2P(Ph)C_6H_4\}]$ and $[Os_3(CO)_{10}(Ph_2PCH_2PPh_2)]$ by CO addition is followed by cyclic voltametry [102].



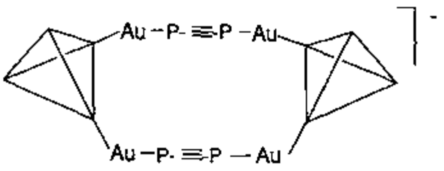
(49)

The synthesis of the dppm linked cluster $[Os_3(CO)_{11}(Ph_2PCH_2PPh_2)Rh_6(CO)_{15}]$ has been reported and its structure discussed on the basis of its IR and ^{31}P NMR spectra [103].

The bis-phosphine $Ph_2P\text{-}C{\equiv}C\text{-}PPh_2$ (dppa) has been used to link triosmium clusters. The reaction with $[Os_3(CO)_{11}(NCMe)]$ yields $[Os_3(CO)_{11}(\mu\text{-}Ph_2P\text{-}C{\equiv}C\text{-}PPh_2)Os_3(CO)_{11}]$ **(50)** while with $[Os_3(CO)_{10}(NCMe)_2]$ a number of cyclic species containing two **(51)**, three **(52)** and four **(53)** Os_3 units linked by the dppa ligand are formed (Scheme 17). An extension of this study involved the reaction of ClAu-dppa-AuCl with $[Os_4H_3(CO)_{12}]^-$ in the presence of $TlPF_6$ and Et_3N which gave the linked species $\{[Os_4H(CO)_{12}(Audppa)]_2\}^-$ **(54)** [104].



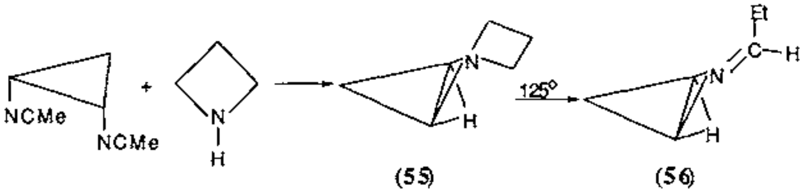
Scheme 17



(54)

The thermolysis of $[Os_3(CO)_{11}PPhFc_2]$ [Fc = $CpFe(\eta\text{-}C_5H_4\text{-})$] has been found to lead to two trinuclear products in which either benzyne or ferrocyne ligands are present. A structure in which two Os_3 units are linked by a ferrodicyne $[Fe(C_5H_3)]$ is obtained on similar treatment of $\{[Os_3(CO)_{11}]_2[Fe(C_5H_4P^iPr_2)_2]\}$. X-ray crystal structures of all three new products are reported [105].

The reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with azetidine results in the addition of the N-H bond to the cluster to give $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NCH_2CH_2CH_2)]$ **(55)** which on thermolysis at 125°C yields the μ-imido cluster $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}N{=}CHEt)]$ **(56)** (Scheme 18) [106].



Scheme 18

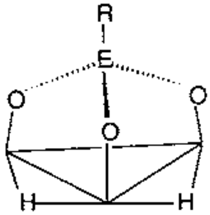
Reaction of Os_3-clusters containing the μ_3-imidoyl ligands $\mu_3\text{-}\eta^2\text{-}MeCH_2C{=}NCH_2CH_2Me$ and $\mu_3\text{-}\eta^2\text{-}C{=}NCH_2CH_2CH_2$ with diazomethane leads to insertion of CH_2 into the Os-C bond and C-H oxidative addition [107].

The μ_3-imido cluster $[Os_3(CO)_{10}(\mu_3\text{-}NPh)]$ **(57)** reacts with halides to give a mixture of two products in which the added halide behaves as a terminal one electron ligand or a bridging three electron ligand, the heavier halides favouring the former. The parent **(57)** is inert to CO, but in the presence of halide insertion of CO into the Os-N bond takes place to eventually eliminate PhN=C=O and leave $[Os_3(CO)_{11}Cl]^-$. The oxygen of the intermediate ($\mu_3\text{-}\eta^2$-PhNCO) cluster is susceptible to electrophilic attack [108].

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

The reaction of the clusters $[Os_3(CO)_{10}(RC_2R)]$ (R = Me, Ph) with EtOH at 80°C has been found to yield $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}RC_2R)(\mu\text{-}OEt)]$ [109]. The reaction of $[Os_3(CO)_{10}(CNR)(NCMe)]$ with propynoic acid ($HC{\equiv}CCO_2H$) in CH_2Cl_2 gives $[Os_3(CO)_{10}(CNR)(\mu\text{-}OC(O)C{\equiv}CH)]$ in which the carboxylate oxygen bridges an Os-Os edge [110]. The reaction of $[Os_3(\mu\text{-}H)_2(CO)_{10}L]$ (L = NCMe, NCPh) with the radical $(CF_3)_2NO$ yields $[Os_3(CO)_{10}(\mu\text{-}H)L\{ON(CF_3)_2\}]$ and $(CF_3)_2NOH$ [111].

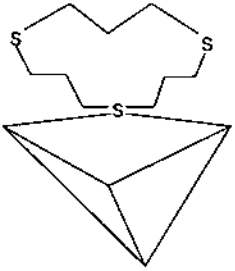
Treatment of $[Os_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CH)]$ sequentially with triflic acid and REO_3H_2 (R = Ph, E = P, As; R = Me, E = P) gives the clusters $[Os_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}O_3ER)]$ (**58**). Infra red and ^{13}C NMR spectroscopic studies of the new species are reported [112].



(**58**)

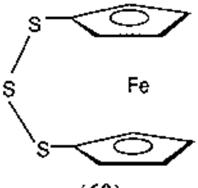
The cluster $[Os_3(CO)_9(\mu\text{-}H)_2(\mu_3\text{-}S)]$ reacts with dppm to give $[Os_3(CO)_7(\mu\text{-}H)_2(\mu_3\text{-}S)(dppm)]$ which has been characterised by X-ray crystallography. Thiols react with $[Os_3(CO)_{10}\text{-}(dppm)]$ to give $[Os_3(CO)_8(\mu\text{-}H)_2(\mu\text{-}SR)(dppm)]$. Investigation of the sites of protonation and the mobility of the resulting hydrides was made [113].

The reaction of $[Os_3(CO)_{12}]$ with [12]aneS_3 $\{[(CH_2)_3S]_3\}$ gives $[Os_3(CO)_{11}([12]aneS_3)]$ and the bridged butterfly cluster $[Os_4(CO)_{13}([12]aneS_3)]$ (**59**) [114].



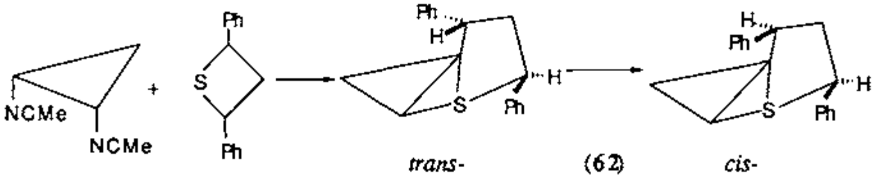
(**59**)

The reaction of 1,2,3-trithia[3]ferrocenophane (**60**) with $[Os_3(CO)_{12}]$ yields a total of five Os_2, Os_3 and Os_4 clusters in which the $(C_5H_4S)_2Fe$ ligand bridges Os centres in different modes. This reactivity is compared with that of $[M_3(CO_{12}]$ (M = Fe, Ru) [115].



(**60**)

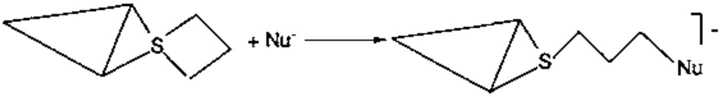
A series of publications dealing with the reaction of small ring sulfur heterocycles with osmium clusters have appeared. Treatment of $[Os_3(CO)_{10}(NCMe)_2]$ with *trans*-2,4-diphenyl dithietane (**61**) leads to ring opening of the ligand and formation of *cis*- and *trans*- isomers of $\{Os_3(CO_{10}[\mu\text{-}SCH(Ph)CH_2CH(Ph)\}$ (**62**) (Scheme 19) [116].



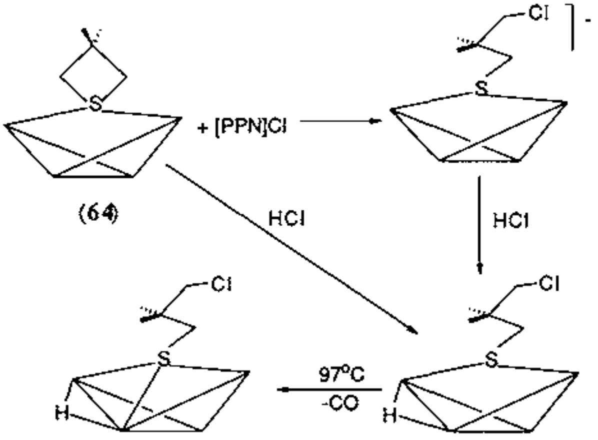
trans- (**62**) *cis*-

Scheme 19

The Os_3 thietane cluster $[Os_3(CO)_{10})(\mu\text{-}SCH_2CH_2CH_2)]$ (**63**) undergoes ring opening addition of nucleophiles (Scheme 20) [117].



Scheme 20



(**64**)

(**65**)

Scheme 21

The thermal and photochemical transformations of Os_3 clusters containing the bridging and terminal 3,3-dimethylthietane ligand have been investigated [118]. The structures of two of the products are reported along with further reactions with CO and PPh_3 [119]. The reaction of $[Os_3(CO)_9(\mu_3\text{-}S)]$ with thietanes promoted by Me_3NO has also been investigated and yields the 50 electron clusters $[Os_3(CO)_8(\mu_3\text{-}S)(\mu\text{-thietane})]$ with two Os-Os bonds which also undergo ring opening addition of nucleophiles [120]. The tetraosmium thietane cluster $[Os_4(CO)_{13}(\mu\text{-}3,3\text{-dimethylthietane})]$ (**64**) also undergoes the ring opening with Cl^-. Subsequent protonation, or direct reaction of **(64)** with HCl, generates the neutral cluster **(65)**. Addition and elimination of CO are reported (Scheme 21) [121].

The reaction of $[Os_3(CO)_{10}(NCMe)_2]$ with RSeSeR (R = Me, Ph) gives $[Os_3(CO)_{10}(\mu RSe_2R)]$ which isomerises with Se-Se bond cleavage to give $[Os_3(CO)_{10}(\mu\text{-}SeR)_2]$ which gives a number of minor products on thermolysis [122].

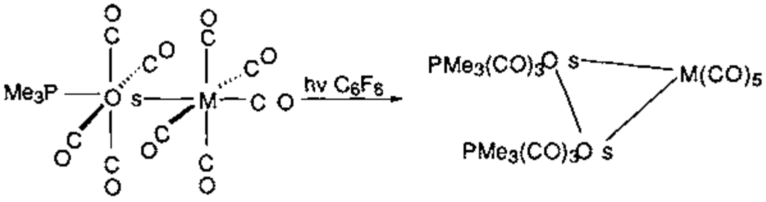
5.11.5 Clusters with additional halide ligands

The reaction of $[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}OCNHCHMe_2)]$ **(66)** with halogens (X_2) (X = Br, I) yields dinuclear *cis*-$[Os_2(\mu\text{-}X)(CO)_6)(\mu\text{-}OCNHCHMe_2)(X)_2]$ **(67)**. These are kinetic products and slowly isomerise to *trans*-isomers. The kinetics of this process were studied. UV photolysis of the complexes results in ejection of CO and gives $[Os_2(\mu\text{-}X)(CO)(\mu\text{-}OCNHCHMe_2)X]$ **(68)** [123].

5.12 OSMIUM CLUSTERS CONTAINING OTHER TRANSITION METALS

5.12.1 Groups 6 and 7

Photolysis of $[Os(CO)_4(PR_3)\text{-}M(CO)_5]$ **(69)** in C_6F_6 leads to the trinuclear $\{[Os(CO)_3(PR_3)]_2M(CO)_5\}$ **(70)** (M = Cr, PR_3 = PMe_3; M = Mo, P = $P(OMe)_3$; M = W, PR_3 = PMe_3). The reaction of **(70)** (M = W, PR_3 = PMe_3) with H_2 gives $[\{Os(CO)_3PMe_3\}_2W(CO)_4]$ (Scheme 22) [124].



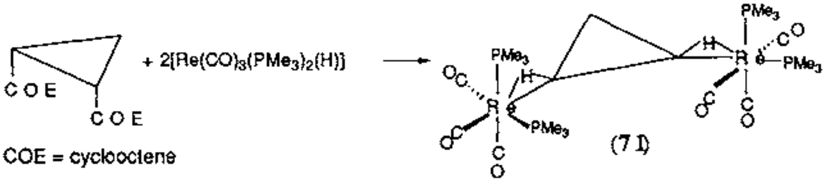
(69) **(70)**

Scheme 22

Condensation of $[Os(CO)_4(CN^tBu)]$ with $[W(CO)_5thf]$ yields $[(CO)_4(^tBuNC)Os\text{-}W(CO)_5]$ as the major product. In addition, a 20% yield of a 1:1 ratio of the trinuclear complexes $[(CO)_4(^tBuNC)Os\text{-}Os(CO)_3(CN^tBu)W(CO)_5]$ and $[(CO)_4(^tBuNC)Os\text{-}Os(CO)_4W(CO)_5]$ are formed. The metal-metal bonds in these systems are regarded as dative [125]. Ab-initio calculations on the metal bonds in $[(CO)_5Os\text{-}M(CO)_5]$ dimers (M = Cr, Mo, W) indicate the presence of dative M-M bonds as suggested experimentally. Calculated ΔH_f energies are 20.9 and 7.7 kcal mol^{-1} for W and Cr respectively. Comparisons with the isoelectronic $[M_2(CO)_{10}]$ dimers (M = Mn, Re) are made [126].

The reaction of the alkyne clusters $[Os_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}RC_2R)]$ (R = tolyl, Me) with $[LW(CO)_3(C{\equiv}CR)]$ (L = Cp, Cp*; R = Ph, ^tBu) gives a mixture of six WOs_3 clusters four of which were characterised by X-ray crystallography. The structures and their interconversions are described in detail [127]. Similarly, the reaction of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with $[Cp(CO)_2Mo{\equiv}Ctol]$ gives three Os_3Mo products which were characterised spectroscopically [128]. The reaction of one of the products containing a μ-acyl ligand with H_2/Me_3NO is reported [129].

The synthesis and structure of $[\{(CO)_3(PMe_3)_2Re(\mu\text{-}H)\}_2\{Os_3(CO)_{10}\}]$ **(71)** has been reported (Scheme 23), the reasons for the hydride ligands bridging the Re-Os bonds are discussed [130].



Scheme 23

5.12.2 *Groups 8, 9 and 10*

An investigation into the catalytic activity of $[PPN][MRh_4(CO)_{15}]$ (M = Fe, Ru, Os) for the carbonylation of nitrobenzene to methyl phenylcarbamate in the presence of MeOH has been undertaken. The addition of bpy enhances the rate and selectivity. Examination of the effects of the different metals revealed the Ru was most effective, but $[Rh_5(CO)_{15}]^-$ and $[Rh(CO)_4]^-$ were better still [131].

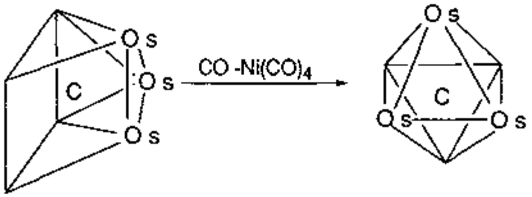
The acidification of $[OsRh_4(CO)_{15}]^{2-}$ **(72)** yields a 1:1 mixture of the octahedral $[OsRh_5(CO)_{16}]^-$ **(73)** and the tetrahedral $[OsRh_3(CO)_{12}]^-$ **(74)**. Alternative preparations of **(72)** are condensation of Rh(I) derivatives with **(72)** or via a one-pot synthesis from $[Os_3CO)_{12}]$ and $[Rh_4(CO)_{12}]$. The tetrahedral **(74)** may also be obtained by oxidative degradation of **(72)** with I_2 [132].

The ionic coupling of $[Os_5(CO)_{15}]^{2-}$ with $[(\eta\text{-}C_6H_6)Ru(NCMe)_3]^{2+}$ or $[Cp^*Rh(NCMe)_3]^{2+}$ gives two isomers of $[RuOs_5(CO)_{15}(\eta\text{-}C_6H_6)]$ and three isomers of $[RhOs_5(CO)_{15}(Cp^*)]$ respectively. The structures of one isomer of each cluster have been crystallographically determined and shown to consist of an Os_5 trigonal bipyramid with a Os_3 face capped by $Ru(\eta\text{-}C_6H_6)$ or $RhCp^*$ thus generating the bicapped tetrahedral metal core [133].

The reaction of $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ with $[CpIr(CO)_2]$ yields the tetrahedral cluster $[CpIrOs_3(CO)_{10}(\mu\text{-}H)_2]$ [134].

The thermolysis reactions of $[Os_3(CO)_{10}L_2]$ [$L = CpFe(\eta\text{-}C_5H_4PPh_2)$], $[Os_3(CO)_{10}L\text{-}L]$ [$L\text{-}L = Fe(\eta\text{-}C_5H_4P^iPr_2)_2$] and $[Os_3(CO)_{11}L]$ ($L = PPhFc_2$) have been investigated. The products have complex structures in which Fe-Os bonds are present [135]. Similar direct Os-Fe bonds are present in the products obtained from the thermolysis of $[Os_3(CO_{11}L]$ ($L = PFc^iPr_2$, $PEtFc_2$) [136].

The capped trigonal prismatic carbido cluster $[Os_3Ni_4C(CO)_{13}]^{2-}$ **(75)** is obtained from the condensation of the ketenylidene cluster $[Os_3(CO)_9(CCO)]^{2-}$ with $[Ni(CO)_4]$. Under CO **(75)** loses $[Ni(CO)_4]$ forming the octahedral $[Os_3Ni_3C(CO)_{13}]^{2-}$ **(76)** [137].



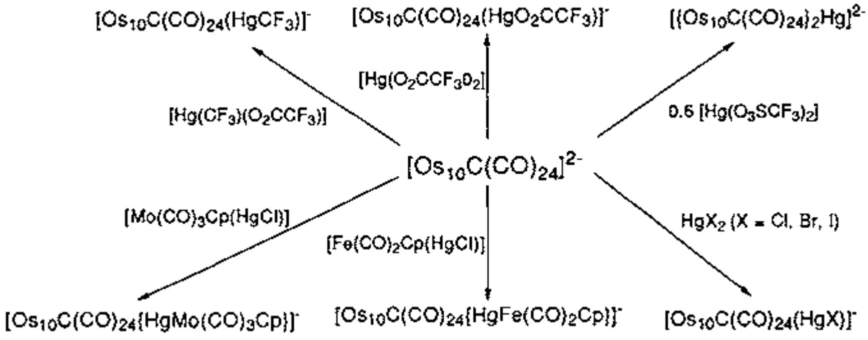
(75) (76)

The pyrolysis of $[Pt_2Os_3(CO)_{10}(COD)_2]$ at 128°C under CO yields $[Pt_4Os_6(CO)_{22}(COD)]$ (77) (17%), $[Pt_5Os_6(CO)_{21}(COD)_2]$ (13%) and $[Pt_4Os_6(CO)_{19}(COD)_2]$ (9%). All were fully characterised by Ir, NMR and X-ray crystallography. A further new cluster $[Pt_7Os_6(CO)_{21}(COD)_2]$ was generated by reaction of (77) with Me_3NO and two equivalents of $[Pt(COD)_2]$ [138].

5.12.3 Groups 11 and 12

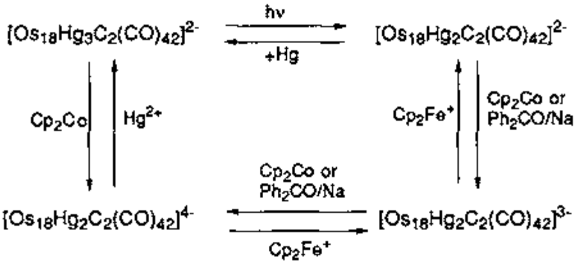
The reaction of *trans*-$[Os(CO)_3(PPh_3)_2]$ with $[Ag(O_2CCF_3)]$ in thf followed by extraction with benzene yields $[(CO)_3(PPh_3)_2Os\text{-}Ag(O_2CCF_3)]$, an apparent intermediate in the Os(O)-Ag(I) electron transfer reaction. In CH_2Cl_2 metallic silver is generated and the Os(I) complex $[Os(CO)_3(PPh_3)_2]^+$ was detected by ESR spectroscopy [139].

A number of papers detailing the synthesis and reactivity of high nuclearity Os/Hg clusters derived from $[Os_{10}C(CO)_{24}]^{2-}$ (**78**) have appeared. The reaction of Hg(II) electrophiles with (**78**) provides either capped or linked products depending on the choice of mercury reagent (Scheme 24) [140].



Scheme 24

The dynamic behaviour of Hg-capped $[Os_{10}C(CO)_{24}(HgY)]^-$ [Y = Cl, Br, I, CF_3, $Mo(CO)_3Cp$] clusters in solution have been examined by variable temperature NMR spectroscopy. A high degree of mobility is observed and a model for the process is proposed [141]. A redox/photochemical cycle involving extrusion and reinsertion of Hg into the $[Os_{18}Hg_3(C)_2(CO)_{42}]^{2-}$ cluster has been illucidated (Scheme 25). The redox-chemical results are reflected in cyclic voltametric studies [142].



Scheme 25

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