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# 3. OSMIUM

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CONTENTS

## INTRODUCTION

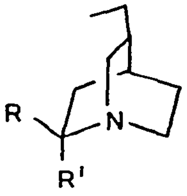
The scope and aims of this review are very similar to those of the companion review (Section 2) on ruthenium. Not only does the chemistry of osmium differ, in ways that are becoming increasingly more apparent each year, from that of ruthenium, but the emphasis in the work reported differs. Thus for osmium, this year, nearly half of the papers published have been concerned with carbonyl cluster chemistry, whereas for ruthenium only about 15% of the papers were concerned with that area. In contrast, the development of the coordination chemistry of osmium, particularly of oxidation states ≥III, has lagged significantly behind that of ruthenium, although the greater stability of those oxidation states for osmium promises a rich and exciting chemistry, which is hinted at in Sections 3.4–3.6. It is undoubtedly true that certain areas of osmium chemistry, notably the chemistry of $[Os(bipy)_3]^{2+}$, are experiencing an upsurge in interest in response to interest in the ruthenium chemistry, but the chemistry of osmium deserves more than a reflected glory.

## 3.1 OSMIUM(VIII)

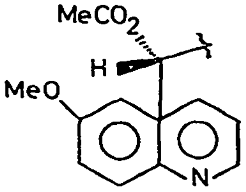
The $\nu_3$ IR band of $[OsO_4]$ has been studied using high-resolution saturation spectroscopy with $CO_2$ lasers; fine and hyperfine structure was detected [1,2].

An excellent review of the uses of $OsO_4$ for the *cis*-hydroxylation of alkenes and alkynes has been published [3]. The oxidations of α,β-unsaturated ethers [4] and cyclopropylidenecycloalkenes [5] by $[OsO_4]$ have been investigated; the latter substrates yield the expected diols, apart from cyclopropylidenecyclopropane, which gives a mixture of cyclohexanedione and formylcyclopropane derivatives [5].

The hydroxylation of sterically hindered alkenes by $[OsO_4]$ is catalysed by $Me_3NO$ and pyridine [6]. $[OsO_4]$, in the presence of (1), can cause asymmetric induction in the reaction [7]:



(1; R = H, R' = (2);
R = (2), R' = H)



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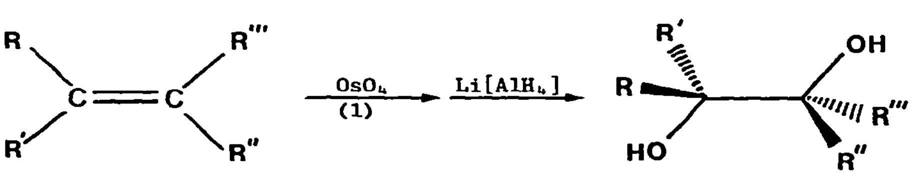
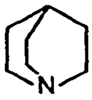


Improved oxyamination procedures for alkenes with $[\mathrm{O_3Os{=}NCMe_3}]$ have been reported. Originally, pyridine was used as a solvent, but now the tertiary alkyl bridgehead amine adducts $[\mathrm{O_3Os{=}NCMe_3(L)}]$ {L = (3)-(6)} or $[\{\mathrm{O_3Os{=}NCMe_3}\}_2\mathrm{L}]$ {L = (7) or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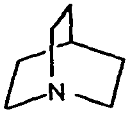
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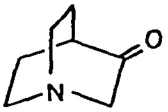
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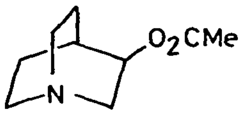
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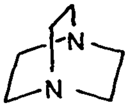
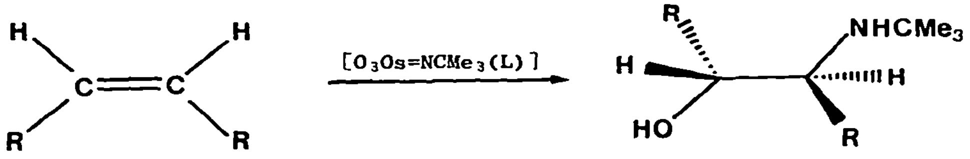
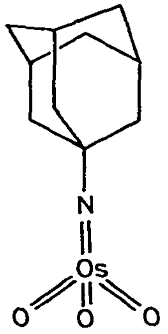

(7)

hmta} are used in non-coordinating solvents [8]:

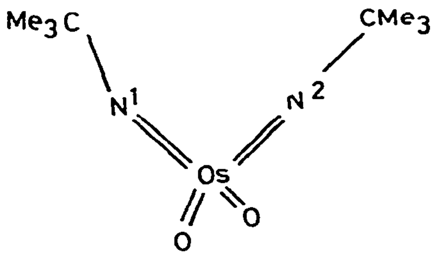


Good yields of amine, and very little diol, were obtained; the complex with (3) was particularly efficient [8]. The molecular structures of the compounds $[\mathrm{O_3Os{=}NR}]$ (8; R = *N*-1-adamantyl) and $[\mathrm{O_2Os({=}NCMe_3)_2}]$ (9) have been recently



(8)

$\bar{r}(\mathrm{Os{=}O}) = 0.1715$ nm
$r(\mathrm{Os{=}N}) = 0.1697$ nm
$\mathrm{Os\hat{N}C} = 171.4^\circ$

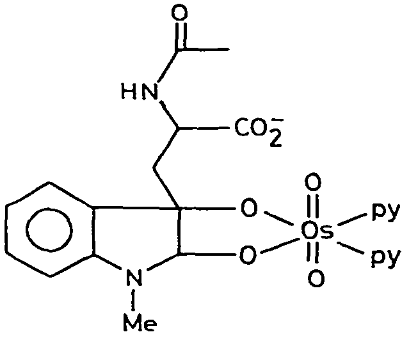


(9)

$\bar{r}(\mathrm{Os{=}O}) = 0.1744$ nm
$\bar{r}(\mathrm{Os{=}N}) = 0.1715$ nm
$\mathrm{Os\hat{N}^1C} = 155.1^\circ$
$\mathrm{Os\hat{N}^2C} = 178.9^\circ$

determined: the R-N-Os unit in (8) is essentially linear but one of the two units in (9) is significantly bent [9].

A series of indole derivatives related to tryptophan react with $[\mathrm{OsO_4(py)_2}]$, by addition to the 2,3-positions of the indole ring, to give osmium(VI) esters. With 1-methyl-$\alpha$-*N*-acetyl-DL-tryptophan, the complex (10) was isolated [10]. The



(10)

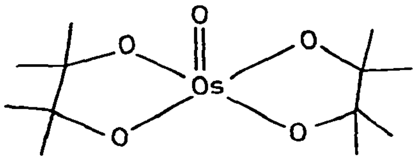
reactions of $[OsO_4]$ with derivatives of model systems (L) for the side chains of tissue proteins have been studied, alone and in the presence of unsaturated lipids (R), as part of a general study of the fixation of biological tissue with $[OsO_4]$. This resulted in the isolation and characterisation of the following complexes: $[Os_2^{VI}O_6L_4]$ (L = $\alpha$-*N*-benzoyl-L-histidine isobutyl ester, imidH, 1-Meimid, 5,6-dimethylbenzimidazole, butylamine or $\alpha$-*N*-benzoyl-DL-methionine), $[Os_2^{VI}O_6L_3L']$ (L = 1-Meimid; L' = L-proline methyl ester or $\alpha$-*N*-benzoyl-L-arginine ethyl ester), $[Os^{IV}L_2]$ ($LH_2$ = glutathione or L-cysteine), $[Os^{II}LL'_n]$ ($n$ = 2 or 3; L = 1-Meimid; L′ = $\alpha$-*N*-benzoyl-L-cysteine or $\alpha$-*N*-acetyl-L-cysteine), $[Os^{VI}O_2(O_2R)L_2]$ (R = cyclohexene, oleic acid, methyl oleate or cholesteryl ethanoate; L = 1-Meimid, 5,6-dimethylbenzimidazole, $\alpha$-*N*-benzoyl-L-histidine isobutyl ester or pyridine), $[Os_2^{VI}O_4(O_4R)L_4]$ and $[Os_3^{VI}O_6(O_6R')L_6]$ (R = methyl linoleate; R' = methyl linolenate; L = 1-Meimid) [11]. The reduction of $[OsO_4]$ by $Na[BH_4]$ in acidic aqueous solution has also been investigated [12].

## 3.2 OSMIUM(VII)

Force constants have been calculated for $[OsOF_5]$ [13].

## 3.3 OSMIUM(VI)

Further details are emerging [14] of the fascinating chemistry of the osmium(VI) ester complexes with (3), and related amines, which were discussed last year [15; p.66]. The crystal structure of $[O{=}Os(O_2C_2Me_4)_2]$ (11) reveals the constituent molecules to be a five-coordinate complex, based on a square pyramidal geometry about the metal [16].



(11)

The complexes [$OsO_2(OEP)$] and [$Os{\equiv}N(X)(OEP)$] (X = [OMe], F or [$ClO_4$]) have been prepared, and characterised, by $^1H$ NMR, UV-VIS and fluorescence spectroscopy, and have been the subject of EHMO calculations [17].

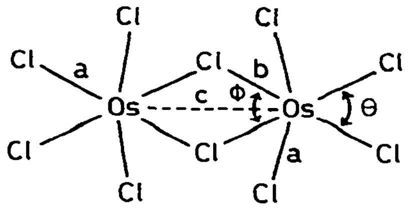
## 3.4 OSMIUM(V)

[NO][$OsF_6$] has been prepared by treating [$OsF_6$] with NO, or a large excess of NOF, at room temperature and characterised by Raman spectroscopy [18].

One of the most exciting papers to be published this year describes the preparation and properties of a new halide of osmium, [$Os_2Cl_{10}$]. This interesting new species was prepared by halide exchange, according to [19]:

$$OsF_6 + 2BCl_3 \longrightarrow OsCl_5 + 2BF_3 + \tfrac{1}{2}Cl_2$$

[$Os_2Cl_{10}$] is a black solid, extremely moisture sensitive, which gives [$OsO_4$] in moist air and [$OsOCl_4$] in moist solvents: in basic solution, $OsO_2.xH_2O$ is slowly precipitated. [$Os_2Cl_{10}$] is insoluble in non-polar solvents (*e.g.* $CCl_4$ or $C_6H_{12}$) but dissolves slightly in $CHCl_3$ or $CH_2Cl_2$ to give essentially non-conducting solutions. It is stable at room temperature *in vacuo* or under an inert atmosphere but decomposes above 160 °C to give $OsCl_4$ and $Cl_2$. [$Os_2Cl_{10}$] is isomorphous with [$Re_2Cl_{10}$] and its structure is shown in (12); its IR spectrum has been recorded and assigned analogously to [$M_2Cl_{10}$] (M = Nb, Ta or Re), and its diffuse reflectance electronic spectrum was also reported. The compound gives a broad (several hundred Gauss) EPR signal at $g$ ~2.0 and has a room temperature magnetic moment per Os atom of $\mu_{eff}$ = 2.55 $\mu_B$. The magnetic



(12)

$a$ = 0.224 nm
$b$ = 0.242 nm
$c$ = 0.363 nm
$\theta$ = 95°
$\phi$ = 83°

susceptibility obeys the Curie-Weiss law (80–293 K; $\theta_W$ = 230 K), and any direct Os...Os interaction was considered unlikely, rather the antiferromagnetic coupling was thought to occur by a superexchange interaction through the bridging chloride atoms [19].

## 3.5 OSMIUM(IV)

### *3.5.1 Halides and oxohalides*

$^{35}$Cl NQR spectra have been measured for crystals of $K_2[OsCl_6]$; the results support the theory that the high electrical conductivity of these crystals is associated with $H^+$ ion mobility [20]. The IR, structural, and magnetic properties of the solid solutions $K_2[(Pt,Os)Cl_6]$ have been determined; for $K_2[OsCl_6]$, $\mu_{eff}$ = 1.49 $\mu_B$ and $\nu$(OsCl) = 325 cm$^{-1}$ [21]. Low temperature NIR absorption and MCD spectra have been measured for $Os^{4+}$ doped into cubic crystals of $Cs_2[ZrCl_6]$ and $Cs_2[ZrBr_6]$; the electronic *d*↔*d* transitions for the osmium(IV) $(t_{2g})^4$ configuration have been identified and assigned in this excellent study. All six excited states were identified (10 *Dq* = 22400 cm$^{-1}$; *B* = 500 cm$^{-1}$) [22]. Earlier data [23] concerning the low temperature specific heat variations of $K_2[OsCl_6]$ have been reinterpreted, to allow for the presence of a low-lying rotary mode in the crystal at 29.1 cm$^{-1}$ [24].

The preparation of *trans*-$[OsCl_4FI]^{2-}$, by the interaction of tridodecylammonium fluoride with $[(C_{12}H_{25})_3NH]_2[OsCl_5I]$ in non-polar solvents, has been reported and this anion has been characterised by IR and UV-VIS spectroscopy [25]. Electronic spectral studies of $A_2[OsCl_4FI]$ (A = $(C_{12}H_{25})_3NEt$ or $(C_{12}H_{25})_3NH$) in various organic solvents indicate that intimate ion pairs form between $[(C_{12}H_{25})_3NH]^+$ and $[OsCl_4FI]^{2-}$ in non-polar solvents, that loosely-bound ion pairs form between $[(C_{12}H_{25})_3NEt]^+$ and $[OsCl_4FI]^{2-}$ in polar or non-polar solvents, or between $[(C_{12}H_{25})_3NH]^+$ and $[OsCl_4FI]^{2-}$ in polar solvents, and that solvent-separated ion pairs are present in protic solvents [26].

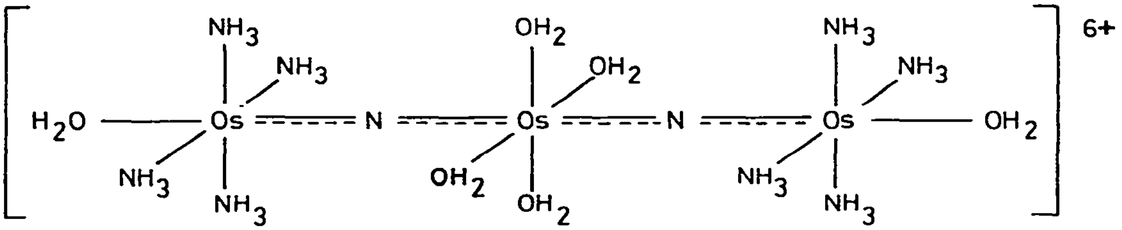
The isolation of the salt $[SCl_3]_2[OsCl_6]$ has been reported [27]. Acidic hydrolysis of $[OsCl_6]^{2-}$ (and controlled reduction of $OsO_4$ in hydrochloric acid with Fe(II)) gives products which have been separated by column chromatography on cellulose: they were characterised by determination of their Os:Cl ratio, ionic charge (as deduced from elution behaviour), and absorption spectroscopy. The species thus identified include: $[OsCl_5(H_2O)]^-$, *cis*-$[OsCl_4(OH)(H_2O)]^-$, *fac*-$[OsCl_3(OH)_2(H_2O)]^-$, *mer*-$[OsCl_3(OH)(H_2O)_2]$, $[Os_2OCl_{10}]^{4-}$, $[Os_2OCl_8(H_2O)_2]^{2-}$ and $[Os_2OCl_6(OH)_2(H_2O)_2]^{2-}$ [28]. $[OsX_6]^{2-}$ reacts with bidentate sulphur-donor ligands to give $[OsX_4(LL)]$ (X = Cl, LL = $RS(CH_2)_2SR$, RSCH=CHSR or 1,2-$C_6H_4(SR)_2$, R = Me or Ph; X = Br, LL = $MeS(CH_2)_2SMe$ or MeSCH=CHSMe) [29].

### *3.5.2 Ammines*

*Trans-* and *cis-*$[Os(NH_3)_4X_2]^{2+}$ (X = Cl, Br or I), *mer-*$[Os(NH_3)_3X_3]^+$ and $[Os(NH_3)Cl_5]^-$ have been prepared by the oxidation of their osmium(III) analogues with $[Fe(H_2O)_6]^{3+}$. Acidic solution aquation and disproportionation reactions (both of which readily occur) are sufficiently slow to allow ion-exchange separation, isolation of the solids, and characterisation of the solution species. ν(OsCl) is *ca.* 40 $cm^{-1}$ higher than for the osmium(III) analogues and the LMCT transitions occur at lower energies for the osmium(IV) complexes. At high acidity, the Os(IV)/Os(III) couples are reversible on the CV time scale, at (for X = Cl) 0.73, 0.83, 0.61 and 0.37 V (*vs.* SHE), respectively, and the complexes show $pK_a$'s of 4.0, *ca.* 1.0, 4.9 and 6.5. These osmium complexes all show weak, sharp NIR absorption bands [30]. At lower acidities, disproportionation, according to the following equation, occurs [30]:

$$3\textit{trans}\text{-}[Os(NH_2)(NH_3)_3Cl_2]^+ + 3H_2O \rightarrow 2\textit{trans}\text{-}[Os(NH_3)_4Cl_2]^+ + [OsO_2(NH_3)_4]^{2+} + H_3O^+ + 2Cl^-$$

Treatment of $[OsO_4]$, $[OsCl_6]^{2-}$ or $[Os(NH_3)_5Cl]^{2+}$ with aqueous ammonia in air generates a new, violet coloured complex, $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$, which has appropriately been named "osmium violet" (by analogy with "ruthenium red", see Section 2.5). This complex is believed to have the structure illustrated in (13)



(13)

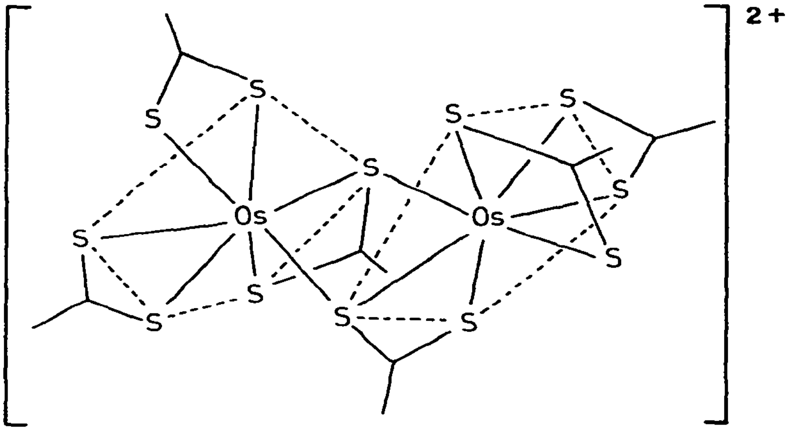
and appears to be a better cell staining reagent than ruthenium red. Related complexes prepared include $[Os_3N_2(NH_3)_8(OH_2)_6]^{7+}$, $[Os_3N_2(NH_3)_8(OH)(OH_2)_5]^{5+}$ $[Os_3N_2(NH_3)_6(OH)_4(OH_2)_2]^{2+}$, $[Os_3N_2(NH_3)_4(OH)_8(OH_2)_2]$, $[Os_3N_2(CN)_{10}(OH_2)_4]^{4-}$ and $[Os_3N_2(CN)_8(OH)_4(OH_2)_2]$, and all were characterised by IR, resonance Raman, and XPES spectroscopy [31].

### *3.5.3 Other complexes*

The cation of the salt $[Os(S_2CNEt_2)_3][PF_6]$ (prepared by oxidation of $[Os(S_2CNEt_2)_3]$ electrochemically, or by $BF_3$ under aerobic conditions) undergoes a novel monomer $\rightleftharpoons$ dimer equilibrium in $CH_2Cl_2$ solution:

$$2[Os(S_2CNEt_2)_3]^+ \rightleftharpoons [Os_2(S_2CNEt_2)_6]^{2+}$$

In the solid state, it exists solely as the dimer, (14), possessing a distorted pentagonal bipyramidal geometry about each Os atom {$r$(OsOs) = 0.3682 nm} [32].



(14)

With MeCN or $Cl^-$, it forms $[Os(S_2CNEt_2)_3(NCMe)]^+$ or $[Os(S_2CNEt_2)_3Cl]$, respectively, both of which are believed, also, to be seven-coordinate [32]. A new Schiff base complex of osmium(IV) has also been reported [33].

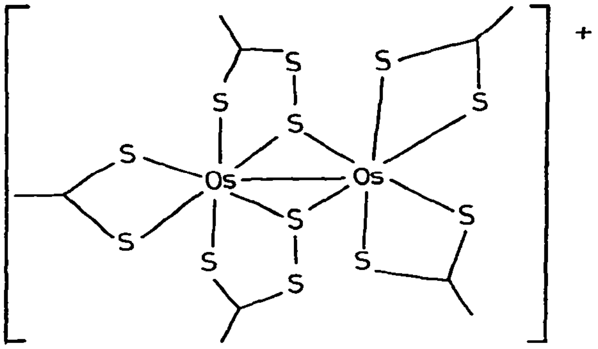
## 3.6 OSMIUM(III)

### 3.6.1 *Halides and pseudohalides*

Treatment of $OsCl_3$ in benzene with cyclopropane and CO gives a mixture of $C_6H_5CHMe_2$ (95%), methyl 2-chlorobutanoate (2%) and methyl 3-chlorobutanoate (3%) [34]. EXAFS has been used to study the complexes $[Os(NCS)_n(SCN)_{6-n}]^{3-}$ ($n$ = 1, 2, 3, 5 or 6): $r$(OsS) is invariant at 0.250 nm within the series, whereas $r$(OsN) decreases from 0.226 nm ($n$ = 1) to 0.213 nm ($n$ = 6). For these measurements, $[Os(py)_4Br_2]$ was used as a reference, to determine the nitrogen backscattering amplitude and phase shifts of the PE wave for the Os-N pair [35].

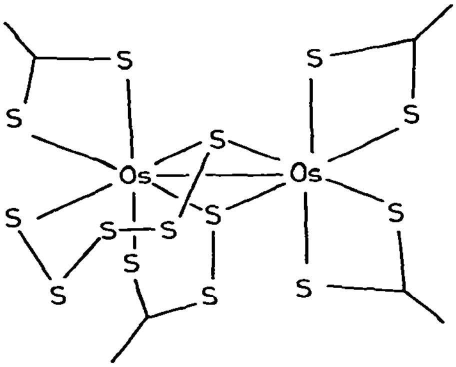
### 3.6.2 *Dithiocarbamate complexes*

The novel complex $[Os_2(\mu\text{-}S_3CNEt_2)_2(S_2CNEt_2)_3]^+$, isolated as its $[BPh_4]^-$ salt, is the first characterised example of a complex of the elusive sulphur-rich trithiocarbamate ligand. The species was isolated as a by-product in the normal preparation of $[Os(S_2CNEt_2)_3]$ and $[Os_2(S_2CNEt_2)_5]^+$, but the reason for its formation, and its properties, are not yet clear. Its structure (15) has



(15)

been determined crystallographically, however, and has an Os–Os separation of 0.2791 nm [36]. Similar complexes have been prepared, by treatment of $[Os(S_2CNR_2)_3]$ (R = Me or Et) with elemental sulphur in dmf to yield $[Os_2(\mu\text{-}S_5)(\mu\text{-}S_3CNR_2)(S_2CNR_2)_3]$ (16), along with some $[Os_2(\mu\text{-}S_3CNR_2)_2(S_2CNR_2)_3][PF_6]$



(16)

(17). (16) can be converted into (17) by reaction with tetraalkylthiuram disulphide. The structure of (17; R = Me) is essentially similar to (15), with $r(OsOs) = 0.2792$ nm. The structure of (16; R = Et) shows the unusual bonding rôle of the $(\mu\text{-}S_5)$ ligand, and reveals an Os–Os separation of 0.2785 nm. (17) reacts with $PBu_3$ or $P(OMe)_3$ to give $[Os_2(\mu\text{-}S_2CNR_2)_2(S_2CNR_2)_3][PF_6]$ [37].

### *3.6.3 Ammine and diimine complexes*

Good new synthetic routes to $[Os(NH_3)_5(OH_2)][ClO_4]_3$, $[Os(NH_3)_5X]X_2$ (X = Cl, Br or I), $[Os(NH_3)_6][ClO_4]_3$, *trans*-$[Os(NH_3)_4X_2]X$ (X = Cl, Br or I) and $Cs_2[OsCl_5(NH_3)]$ have been developed; their NIR spectra show weak, sharp absorptions [30]. Treatment of amminehaloosmium(III) complexes with $HNO_2$ yields such complexes as *cis*-$[Os(NH_3)_4I(N_2)]^{2+}$, *cis*- or *trans*-$[Os(NH_3)_3X_2(N_2)]^+$ (X = Cl, Br or I), *mer*-$[Os(NH_3)_2X_3(N_2)]$ and $[Os(NH_3)_5(N_2)]^{3+}$. Typically [38]:

$$[Os(NH_3)_4I_2]^+ + HNO_2 \longrightarrow [Os(NH_3)_3I_2(N_2)]^+ + 2H_2O$$

The mechanism for this reaction is believed to involve an osmium(IV) intermediate:

$$\begin{tikzcd}
{[Os(NH_3)_4I_2]^+} \arrow[r, "HNO_2", "H_3O^+"'] & {[Os(NH_3)_4I_2]^{2+} + NO + H_2O} \arrow[d, shift left] \\
{[Os(NH_3)_3I_2(N_2)]^+} & {[Os(NH_3)_3I_2(NH_2)]^+ + H_3O^+} \arrow[u, shift left] \arrow[l, "NO"']
\end{tikzcd}$$

The coordinated $N_2$ considerably enhances the acidity of the coordinated ammonia. Thus the p$K_a$ of $[Os(NH_3)_6]^{3+}$ is *ca.* 16, whereas the p$K_a$ of $[Os(NH_3)_5(N_2)]^{3+}$ is *ca.* 6.6. In basic conditions, the osmium(III) complexes disproportionate to give the corresponding osmium(II) complex and an unidentified osmium(VI) species [38]. The ruthenium(II) analogues of the above complexes have been prepared and $[Os(NH_3)_5(N_2)]^{2+}$ can be converted into $[Os(NH_3)_4(N_2)_2]^{2+}$ with $HNO_2$, but this time involving an osmium(III) intermediate [38].

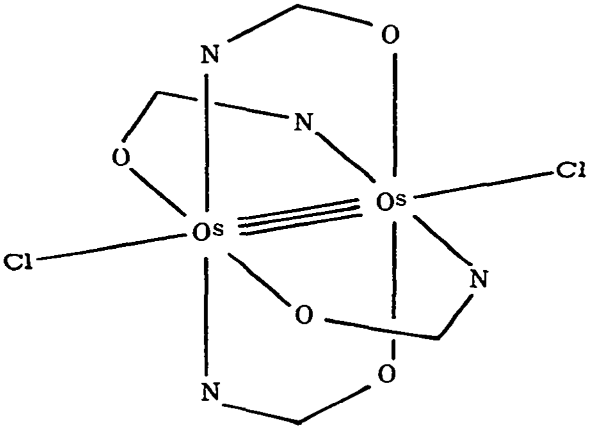
A correlation between the half-wave reduction potentials of $[Os(LL)_3]^{3+}$ (LL = bipy, 4,4'-Me$_2$bipy, 5,5'-Me$_2$bipy or phen) and the rate constant for their reduction by $[Fe(H_2O)_6]^{2+}$, in the presence or absence of sodium dodecyl sulphate, has been proposed [39].

### *3.6.4 Phosphine and arsine complexes*

$[OsX_6]^{2-}$ (X = Cl or Br) reacts with $AsPh_2R$ (R = Me, Et, Pr or Bu) in basic conditions to give $[OsX_3(AsPh_2R)_3]$ [40]. Treatment of $Na_2[OsCl_6]$ with $PPh_3$ in ethanol yields a green precipitate of $[OsCl_2(PPh_3)_3]$. However, if this reaction mixture is filtered, and the filtrate heated and treated with MeCN, then $[OsCl_3(MeCN)(PPh_3)_2]$ can eventually be isolated. This complex was characterised crystallographically {$r$(OsCl) = 0.236 nm} and shown to have a *mer,trans* configuration [41].

### *3.6.5 Osmium-osmium triple bonded complexes*

The first complex of this type, the purple compound $[Os_2(py\text{-}2\text{-}O)_4Cl_2]$ (18), has been prepared by treating $OsCl_3$ with 2-hydroxypyridine in ethanol, and has the familiar "lantern" structure [42]. It has been isolated, both as mono(diethyl ether) and as bis(ethanenitrile) solvates, and the molecular structures of both forms have been determined. For the former complex, $r(Os{\equiv}Os)$ = 0.2344 nm and



(18)

$r$(OsCl) = 0.2483 nm; for the latter, $r$(Os≡Os) = 0.2357 nm and $r$(OsCl) = 0.2503 nm [43].

## 3.7 OSMIUM(II)

### *3.7.1 Complexes with sulphur donor ligands*

$[OsL_2]$ and $[Os(HL)_2][BPh_4]$ (HL = thiodiglycol) have been prepared and characterised [44].

### *3.7.2 Ammine and pyridine complexes*

A new synthetic route to $[Os(NH_3)_5(N_2)]Cl_2$ has been published [30]. Other osmium(II) dinitrogen complexes have been discussed in Section 3.6.3.

Dark red, *trans*-$[Os(py)_4I_2]$ has been prepared by the reaction of $K_2[OsI_6]$ with pyridine (in the presence of glycerin). It is volatile at 360 °C, and soluble in organic solvents but not in water. Solutions of the complex in non-polar solvents react with HX (X = Cl or Br) to give blue complexes, tentatively formulated as $[Os(py)_4I_2]$.2HX [45]. Similarly, $K_2$[*fac*-$OsX_3I_3$] (X = Cl or Br) reacts with pyridine and glycerin to give the dark red, *trans*-$[Os(py)_4XI]$ complexes, which are soluble in organic solvents and sublime *in vacuo* at 300 or 320 °C; they also react with HX, to give violet "*trans*-$[Os(py)_4XI]$.2HX" [46].

### *3.7.3 Diimine complexes*

In the wake of the current interest in $[Ru(bipy)_3]^{2+}$ (*cf*. Sections 2.8.4, 2.15, 2.16 and 2.17), attention is being turned towards $[Os(bipy)_3]^{2+}$. Thus, the electronic absorption and CD spectra of $[Os(bipy)_3]^{2+}$ have been studied and provide strong evidence, even for osmium where the spin-orbit coupling constant is large, that there is some real meaning to the singlet and triplet manifold [47]. Lifetime measurements for $[Os(LL)_3]^{2+}$ (LL = bipy, phen, 4,4'-$Me_2$bipy, 5,6-$Me_2$phen, 5-Mephen, 5-Clphen, 4,4'-$Ph_2$bipy or 4,7-$Ph_2$phen), and rate constants for the quenching of $\{[Os(5\text{-}Clphen)_3]^{2+}\}^*$ by $[M(LL)_3]^{2+}$ (M = Fe, Ru or Os; LL = various diimines) have been reported [48]. Complexes with sterically hindered ligands, $[Os(LL)_3]Cl_2$ (LL = 6-Mebipy, 6,6'-$Me_2$bipy, 2-Mephen or 2,9-$Me_2$phen) have also been prepared, and characterised by absorption and emission spectroscopy (including $\varphi$ and $\tau$ measurements) [49]. In an independent study, the complexes $[Os(LL)_3]I_2$ (LL = bipy, 4,4'-$Me_2$bipy, phen, 5,6-$Me_2$phen or 4,7-$Me_2$phen), $[Os(bipy)_2X_2]$ (X = Cl or CN), $[Os(bipy)_2(en)]I_2$, $[Os(bipy)_2(py)_2]I_2$ and $[Os(terpy)_2]I_2$ have been prepared, and characterised by electronic absorption spectroscopy and low temperature emission spectroscopy (including $\varphi$ and $\tau$ data) [50,51]. The quenching of $\{[Os(LL)_3]^{2+}\}^*$ (LL = bipy, phen, 5,5'-$Me_2$bipy or 5-Clphen) by $[Fe(H_2O)_6]^{3+}$ has been studied by an electrochemical transient method and rate constants for the quenching reaction, and for the reverse thermal reaction, determined [52]. The electrochemistry of $[Os(bipy)_3]^{2+}$ in dmf has also been investigated by polarography and CV; six reduction waves were observed, corresponding to five successive one-electron reductions to the species $[Os(bipy)_3]^{3-}$, which decomposes at the sixth wave [53].

The complexes $[Os(LL)_2L_2]^{2+}$ (LL = bipy, L = MeCN; LL = phen, L = $PMe_2Ph$) and $[Os(LL)_2(L'L')]^{2+}$ (LL = bipy or phen; L'L' = dppm or $Ph_2PCH{=}CHPPh_2$) were prepared according to [54]:

*e.g.* $$cis\text{-}[Ru(phen)_2Cl_2] \xrightarrow[\Delta;\ glycerol]{dppm} [Ru(phen)_2(dppm)]^{2+}$$

These complexes, along with $[Os(LL)_3]^{2+}$ (LL = bipy or phen), were characterised by CV, UV-VIS, $\lambda_{em}$ and $\tau_o$ measurements, and it was found that the lifetime of the excited state was considerably enhanced by the introduction of strong $\pi$-acceptor ligands. Thus, for $\{[Os(phen)_3]^{2+}\}^*$, $\tau = 8 \times 10^{-8}$ $s^{-1}$ (MeCN; 25 °C), but for $\{[Os(phen)_2(Ph_2PCH{=}CHPPh_2)]^{2+}\}^*$, $\tau = 1.84 \times 10^{-6}$ $s^{-1}$ (MeCN; 25 °C) [54].

### *3.7.4 Porphyrin and phthalocyanine complexes*

The complexes $[Os(OEP)L_2]$ {L = $NH_3$, py or $P(OMe)_3$}, $[Os(OEP)(L)(L')]$ (L = $N_2$, L' = thf; L = CO, L' = py; L = CS, L' = py) and $[Os(OEP)(NO)X]$ (X = OMe, F, $[ClO_4]$ or NO) have been prepared and characterised by electronic absorption and emission spectroscopy; the bonding was discussed in terms of EHMO calculations [17].

[Os(Pc)(CO)(py)] has been prepared by the reaction of $OsO_4$ with molten 1,2-dicyanobenzene under CO, or by treating $[Os_3(CO)_{12}]$ with 1,2-dicyanobenzene in air, followed by reaction with pyridine; [Os(Pc)(CO)(thf)] was prepared in a similar manner. The molecular structure of [Os(Pc)(CO)(py)] reveals that the Os atom is 0.015 nm out of the plane of the phthalocyanine group towards the CO $\{r(OsN_{py}) = 0.2202$ nm; $r(OsN_{Pc}) = 0.198$, 0.203 nm; $r(OsC) = 0.1873$ nm$\}$ [55].

### 3.7.5 *Phosphine and arsine complexes*

$[OsX_6]^{2-}$ (X = Cl, Br or I) reacts with diars in $MeOH/Me_2CO$ under CO to give $[OsX_2(CO)_2(diars)]$; one *cis* and two *trans* isomers were formed according to the reaction conditions. The isomers are interconvertible, the all *cis* isomer being the most stable and the *trans* carbonyl isomer being the least stable [56]. $[OsX_3(AsPh_2R)_3]$ (X = Cl or Br; R = Me, Et, Pr or Bu) reacts with CO to give $[OsX_2(CO)_2(AsPh_2R)_2]$, whereas treatment of $[OsX_6]^{2-}$ with $AsPh_2R$ in the presence of methanal yields $[OsX_2(CO)(AsPh_2R)_3]$ [40].

Full details of the reactions of RNCO (R = $C_6H_4$-4-Me) with $[OsHX(CO)(PPh_3)_3]$ (X = Cl or Br), $[OsH_2(CO)(PPh_3)_3]$, or $[OsH_4(PPh_3)_3]$ to give the formamido, ureylene and formamidinato complexes reported last year [15; p.70] have now appeared [57]. $[OsH(O_2CCF_3)(CO)(PPh_3)_2]$ and $[Os(O_2CCF_3)_2(CO)(PPh_3)_2]$ react with both terminal and internal alkynes to give oligomerisation and hydrogenation products, respectively, along with some vinyl complexes. For phenylethyne, the process is catalytic, one mole of complex producing 100 moles of oligomer (*cf.* Section 2.8.6.2) [58].

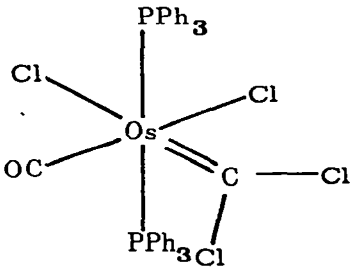
### 3.7.6 *Carbonyl complexes*

*cis*-$[Os(CO)_4(CH_2C_6F_5)_2]$ has been prepared by treating $C_6H_5CH_2Cl$ with $[Os(CO)_4]^{2-}$ and its molecular structure determined $\{\bar{r}(OsC_{Bz}) = 0.218$ nm; $\bar{r}(OsC_{CO}) = 0.194$ nm$\}$ [59]. The reaction between $[H_4Os_4(CO)_{12}]$ and $N_2O_4$ yields $[H_4Os_4(CO)_{12}(OH)]^+$ $[Os(CO)_3(NO_3)_3]^-$ (see also Section 3.9.2): the anion is a *facial* osmium(II) complex, containing three monodentate nitrato ligands, and has been crystallographically characterised [60].

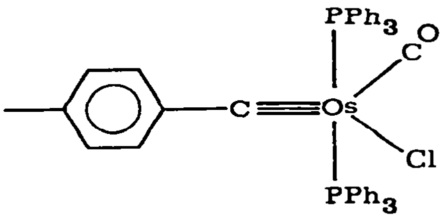
The $pK_a$ of $[H_2Os(CO)_4]$ is 12.8 [61].

### 3.7.7 *Carbene and carbyne complexes*

$[Os(CO)(PPh_3)_3HCl]$ reacts with $[Hg(CCl_3)_2]$ to give the fascinating dichlorocarbene complex $[OsCl_2(CCl_2)(CO)(PPh_3)_2]$ (19) which has been characterised crystallographically [62]. (19) reacts with LiR (R = Ph, $C_6H_4$-4-Me, $C_6H_4$-4-$NMe_2$ or $C_6H_4$-4-OMe) to generate the five-coordinate carbyne complex,

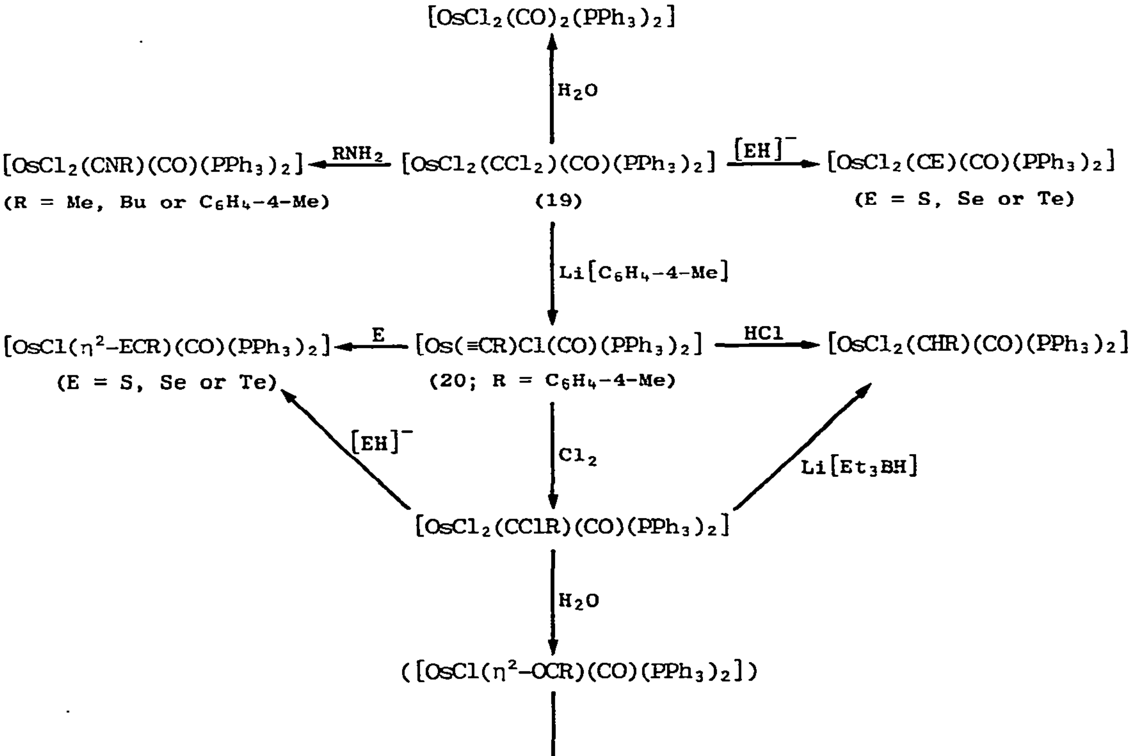


(19)



(20)

[$Os(\equiv CR)Cl(CO)(PPh_3)_2$]: [$Os(\equiv CC_6H_4$-4-Me)$Cl(CO)(PPh_3)_2$] (20) was crystallographically characterised {$r(Os\equiv C)$ = 0.177 nm; $r(OsCl)$ = 0.2506 nm} [63]. The reactions of (19) and (20) are summarised in Scheme I [62,63].



SCHEME I: Some reactions of (19) and (20) [62,63].

### 3.7.8 *Trichlorosilyl and trichlorostannyl complexes*

*cis*-$[Os(CO)_4(SiCl_3)_2]$ has been prepared from the photochemical reaction between $[Os_3(CO)_{12}]$ and $Cl_3SiH$; upon heating at 120 °C, it is quantitatively converted to the *trans* isomer (*cf*. Section 2.8.8). *cis*-$[Os(CO)_4(SiCl_3)_2]$ reacts with $PPh_3$ at 130 °C, to give *mer*-$[Os(CO)_3(PPh_3)(SiCl_3)_2]$, and with 1,3,5-$C_6H_3Me_3$ (200 °C; sealed tube), to give low yields of $[\{C_6H_3Me_3\}Os(CO)(SiCl_3)_2]$ [64,65].

The molecular structure of a salt of $[OsCl(SnCl_3)_5]^{4-}$ $\{\bar{r}(OsCl) = 0.243$ nm; $r(OsSn) = 0.2530$–$0.2582$ nm$\}$ has been determined [66,67], although the nature of the cation, nominally $[NMe_4]^+$, appears to be in some doubt.

## 3.8 OSMIUM(0)

The reduction of $[\{OsCl_2(1,5\text{-cod})\}_n]$ with potassium amalgam, in the presence of excess $CNCMe_3$, yields $[Os(CNCMe_3)_3(1,5\text{-cod})]$ [68], whereas treatment of $[OsH_2(CO)_4]$ with $[Fe(CNCMe_3)_5]$ gives $[FeH(CNCMe_3)_5]^+$ $[OsH(CO)_4]^-$ [69].

## 3.9 OSMIUM CARBONYL CLUSTERS

The introduction to the section on ruthenium carbonyl clusters (Section 2.13) is essential background to the following discussion, as it outlines the notation which has been used to represent the cluster structures and reviews the general background literature common to both ruthenium and osmium.

An excellent review of the syntheses, structures and reactivities of osmium carbonyl cluster complexes has been published, with particular emphasis being placed upon bonding and reaction pathways [70]; it is highly recommended to any workers interested in this area.

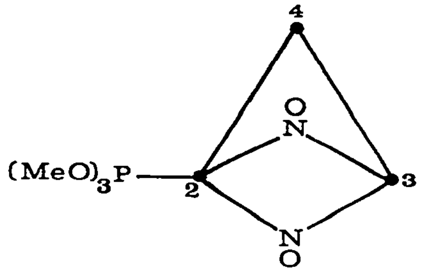
### 3.9.1 *Trimeric clusters*

The high resolution IR and Raman spectra and a complete vibrational analysis of $[Ru_nOs_{3-n}(CO)_{12}]$ ($n$ = 0, 1, 2 or 3) have been reported [71,72], and a further study of the UVPES of $[Os_3(CO)_{12}]$ has been published [73]. Electrochemical or alkali-metal reduction of $[Os_3(CO)_{12}]$ generates $[Os_3(CO)_{12}]^{\dot{-}}$, which has been characterised by EPR spectroscopy [74].

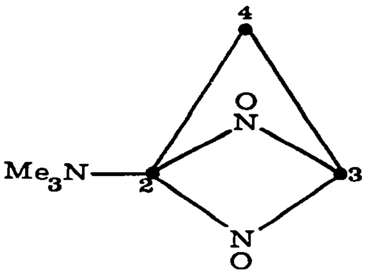
The reduction of CO by $H_2$ using $[M_3(CO)_{12}]$ (M = Ru or Os) in 2-methoxyethanol (below 200 °C and 200 atm) gives MeOH and $Me_2CO$ (when M = Ru) or MeOH, $HCO_2Me$, $Me_2CO$ and $HCO_2C_2H_4OH$ (when M = Os) [75]. It is not clear from this communication how the possibility of these products arising from the solvent was eliminated, but this may become clear when fuller details are published. $[M_3(CO)_{12}]$ (M = Ru or Os) is also reported to be an active catalyst for the water gas shift reaction ($CO + H_2O \rightleftharpoons H_2 + CO_2$), showing a high degree of sulphur tolerance [76], and to be a homogeneous catalyst for the alkyl exchange reactions of tertiary amines [77].

Some photochemical reactions of $[Os_3(CO)_{12}]$ with common reagents have been investigated. Thus, UV irradiation of $[Os_3(CO)_{12}]$ in $CCl_4$, $CHCl_3$ or $CH_2Cl_2$ yields $[Os(CO)_4Cl_2]$, *via* a proposed intermediate of $[Os_3(CO)_{12}Cl_2]$. No reaction was observed with CO, but UV irradiation of $[Os_3(CO)_{12}]$ in the presence of $PPh_3$ gave $[Os_3(CO)_{12-n}(PPh_3)_n]$ ($n$ = 1, 2 or 3): prolonged irradiation of $[Os_3(CO)_9(PPh_3)_3]$ with $PPh_3$ generated $[Os(CO)_3(PPh_3)_2]$ [78].

$[Os_3(CO)_9(NO)_2\{P(OMe)_3\}]$ (21) has been structurally characterised and the phosphite ligand is equatorial [79]. Treatment of $[Os_3(CO)_{10}(NO)_2]$ with $Me_3NO$ yields $[Os_3(CO)_9(NO)_2(NMe_3)]$ (22); the very long Os-$NMe_3$ bond (0.222 nm) reflects the utility of $NMe_3$ as a good leaving group in cluster chemistry [80].



(21)



(22)

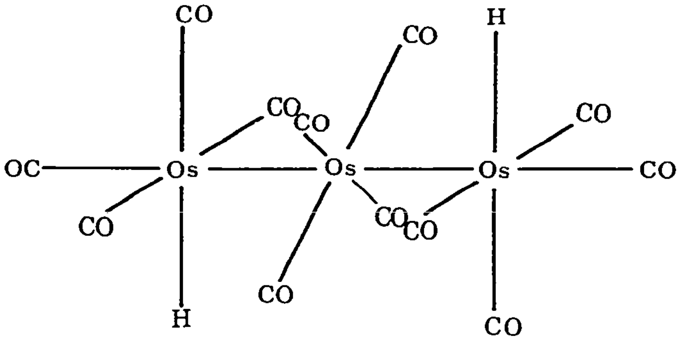
Appropriate treatment of $[Os_3(CO)_{12}]$ with CNR yields $[Os_3(CO)_{12-n}(CNR)_n]$ (R = Me or $C_6H_4$-4-OMe, $n$ = 1 or 2; R = Bu or $CMe_3$, $n$ = 1, 2, 3 or 4) which have been studied by VT $^{13}C$ NMR spectroscopy [81]. Indeed, $[Os_3(CO)_{11}(NCMe)]$, which is

$$\begin{tikzcd}
{[Os_3(CO)_{12}] + MeCN + Me_3NO} \arrow[r] & {[Os_3(CO)_{11}(NCMe)] + CO_2 + NMe_3} \arrow[d, "NH_3"] \\
{\underset{(24)}{[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NH_2)]}} & {\underset{(23)}{[Os_3(CO)_{11}(NH_3)] + MeCN}} \arrow[l, "\Delta"'] \arrow[d, "\text{cyclohexanone}"] \\
{\underset{(26)}{[Os_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}NC_6H_{10})]}} & {\underset{(25)}{[Os_3(CO)_{11}(NH{=}C_6H_{10})]}} \arrow[l, "\Delta"']
\end{tikzcd}$$

SCHEME II: The synthesis of ammonia derivatives of $[Os_3(CO)_{12}]$ [82].

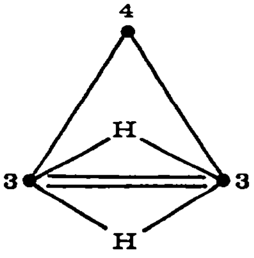
isomeric with the CNMe complex, is the basis of the interesting chemistry illustrated in Scheme II. The complexes (23)-(26) were characterised by IR and $^{1}$H NMR spectroscopy; the conversion of (25)→(26) is more facile than that of (23)→(24) [82].

Turning, now, to hydride derivatives, IR, Raman and $^{13}$C NMR spectral studies upon [$H_2Os_3(CO)_{12}$] are all consistent with it possessing the structure (27),

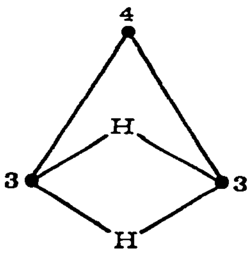


(27)

with terminal hydrides and a linear skeleton [83]. The UVPES (He-I and He-II) study of [$H_2Os_3(CO)_{10}$] and [$H_4Os_4(CO)_{12}$] which was reported this year [84] has a very important conclusion. The results are totally inconsistent with the conventional bonding scheme for [$H_2Os_3(CO)_{10}$], (28), in which a formal double

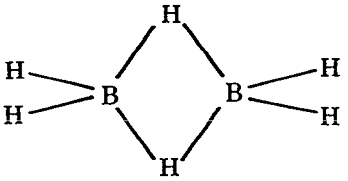


(28)

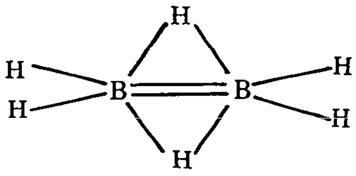


(29)

bond is normally written between the two bridged Os atoms. Instead, they clearly point to a localised 4-centre, 4-electron bonding (or, alternatively, two 3-centre, 2-electron bonding) situation, (29), analogous to that found in diborane (30): to



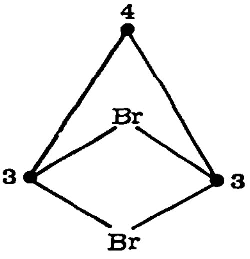
(30)



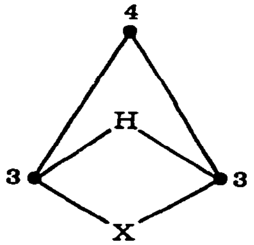
(31)

write $[H_2Os_3(CO)_{10}]$ with structure (28) is as misleading as to write diborane with structure (31). Similarly, there is no direct metal-metal interaction between the singly hydride bridged metal centres in $[H_4Os_4(CO)_{12}]$. Thus, in all of the structures in this review (and in the companion review on ruthenium), the $M_2(\mu\text{-}H)$ situation is represented as $M\overset{\diagup H \diagdown}{\quad}M$ and *not* as $M\overset{\diagup H \diagdown}{\overline{\quad\quad}}M$.

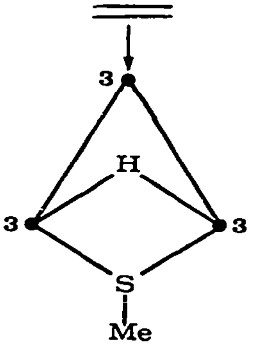
The molecular structures of $[Os_3(CO)_{10}Br_2]$ (32) [85], $[HOs_3(CO)_{10}Br]$ (33) [86],



(32)



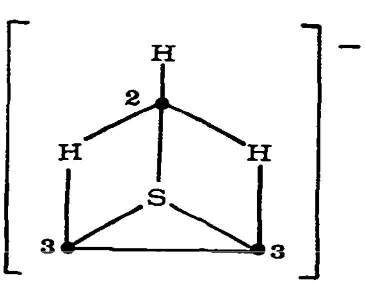
(33; X = Br)
(34; X = OMe)
(35; X = $NHSO_2C_6H_4$-4-Me)



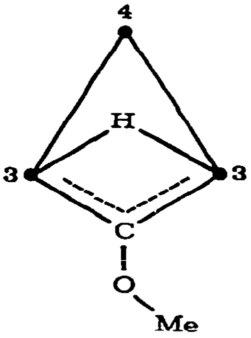
(36)

$[HOs_3(CO)_{10}(OMe)]$ (34) [87], $[HOs_3(CO)_{10}(NHSO_2C_6H_4\text{-4-Me})]$ (35) [88] and $[HOs_3(CO)_9(C_2H_4)(SMe)]$ (36) [89] have been reported. (32) was prepared by treating $[Os_3(CO)_{12}]$ with 2-bromomethylnaphthalene [85], and (35) by treating $[H_2Os_3(CO)_{10}]$ with $N_3SO_2C_6H_4$-4-Me [88]. The hydride was directly located in (33), and its structure was compared with a number of related molecules, $[HOs_3(CO)_{10}X]$ (X = H, Cl, $CHCH{=}NEt_2$, SEt, *etc.*); the Os–Os distance in the $\{Os_2(\mu\text{-}H)(\mu\text{-}X)\}$ moiety seems to be determined more by the Os-H-Os unit then by the Os-X-Os unit [86]. In (36), the ethene molecule is equatorial [89]. $[HRu_3(CO)_{10}(NO)]$ has been prepared by treating $Na[HRu_3(CO)_{11}]$ with $[NO][PF_6]$ [90].

Treatment of $[Os_3(CO)_{12}]$ with $Li[Et_3BH]$ in thf at -30 °C yields a deep red solution, believed (on the basis of IR and $^1H$ NMR spectral evidence) to contain the formyl complex, $[Os_3(CO)_{11}(CHO)]^-$: the complex decomposes at room temperature

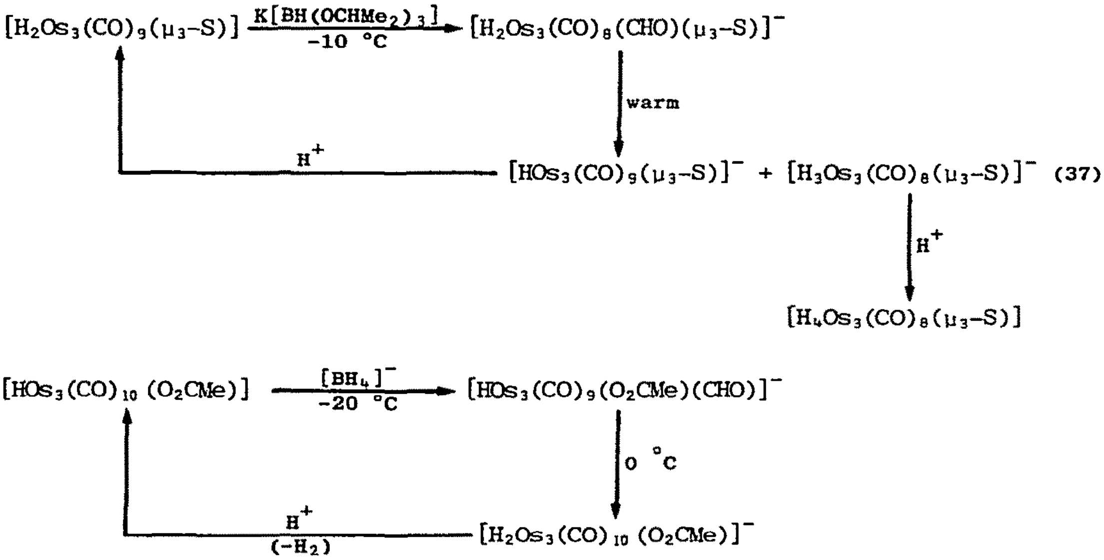


(37)

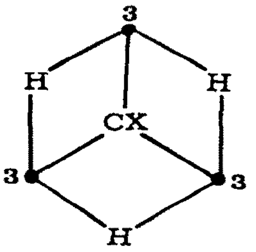


(38)

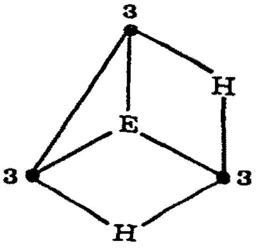
[91]. Formyl intermediates, $[H_2Os_3(CO)_8(CHO)S]^-$ and $[HOs_3(CO)_9(O_2CMe)(CHO)]^-$, are also generated in the reactions illustrated in Scheme III [92]. The novel trihydrido species, (37), contains a terminal hydride ligand. In another reaction involving attack on a coordinated carbonyl group, a novel carbyne cluster, $[HOs_3(CO)_{10}\{C(OMe)\}]$ (38), has been prepared by methylation of $[HOs_3(CO)_{11}]^-$ {*cf*. Section 2.13.1} with $MeSO_3F$. Treatment of (38) with dihydrogen generates $[H_2Os_3(CO)_9\{\mu_3\text{-}C(OMe)\}]$ (39) [93], which reacts with $BX_3$ (X = Cl or Br) to yield the structurally related $[H_3Os_3(CO)_9(\mu_3\text{-}CX)]$ (40) complex [94].



SCHEME III: Some reactions involving formyl intermediates [92].

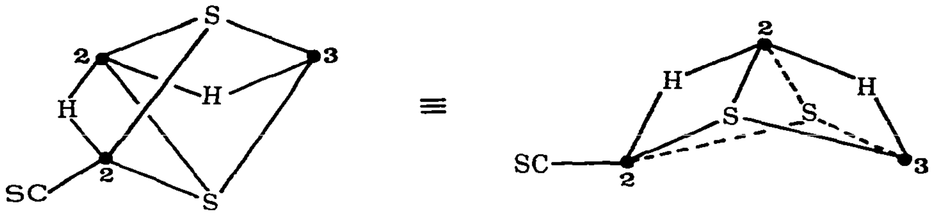


(39; X = OMe)
(40; X = Cl or Br)



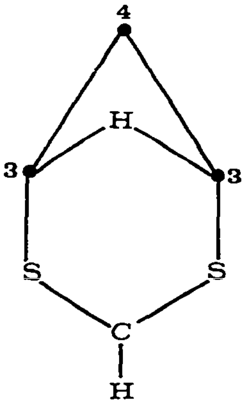
(41; E = S, Se or Te)

$[Os_3(CO)_{12}]$ reacts with $E_n$ (E = S, Se or Te), in octane at reflux, to give $[H_2Os_3(CO)_9E]$ (41) and $[H_2Os_4(CO)_{12}E_2]$ (see Section 3.9.2) [95]. $[H_2Os_3(CO)_8(MeCN)(\mu_3\text{-}S)]$, a derivative of (41; E = S), reacts with $CS_2$ in cyclohexane to give $[H_2Os_3(CO)_7(CS)(\mu_3\text{-}S)_2]$ (42), in which the CS group is



(42)

terminal and equatorial $\{r(OsC)_{CS} = 0.190$ nm$\}$, and two of the osmium atoms contain no direct bonding interaction between them $\{r(OsOs) = 0.370$ nm$\}$ [96]. Treatment of $[Os_3(CO)_{10}(C_6H_8)]$ with $K[S_2CH]$, or $[H_2Os_3(CO)_9(PMe_2Ph)]$ with $CS_2$, yields the related complexes $[HOs_3(CO)_{10}(S_2CH)]$ (43) or $[HOs_3(CO)_9(PMe_2Ph)(S_2CH)]$



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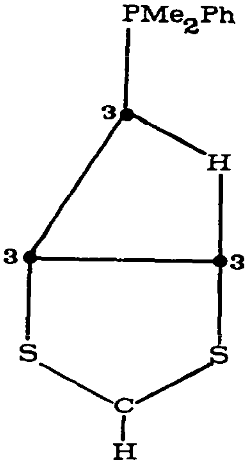
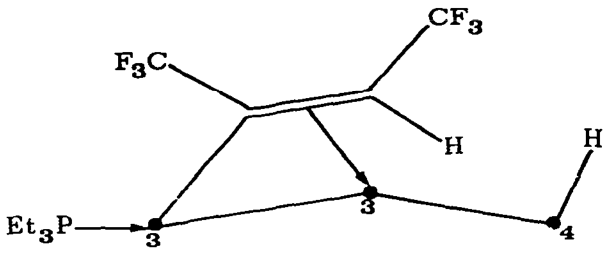


(44)

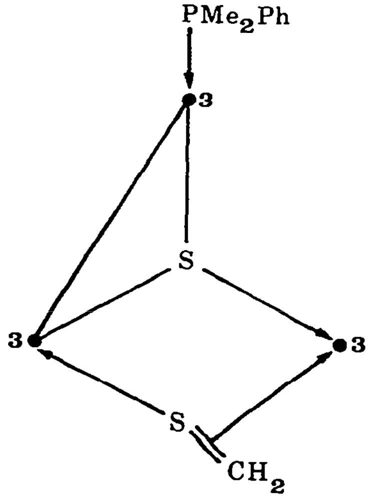
(44), respectively. The structures of (43) and (44) contain different hydride distributions (although it should be noted that the hydrides were not directly located), and it is clear from the structural results that, for both the $(\mu\text{-}S_2CH)$ bridged Os-Os bond, and the unbridged Os-Os bond, addition of a hydride ligand caused an *increase* in Os-Os separation [97].

Although strictly organometallic (and many other examples of organometallic cluster chemistry have been omitted from this review), the last two papers to be discussed in this section reveal interesting bonding features which reflect upon cluster chemistry in general. Treatment of $[HOs_3(CO)_{10}(CF_3C{=}CHCF_3)]$ with $PEt_3$ yields $[HOs_3(CO)_{10}(PEt_3)(CF_3C{=}CHCF_3)]$ (45), which shows the remarkable feature of the triangular cluster of the reactant having opened to an almost linear chain ($Os\hat{O}sOs = 162.3^\circ$), with the terminal osmium atoms showing no bonding interaction, either directly or *via* bridging ligands (other, of course, than the

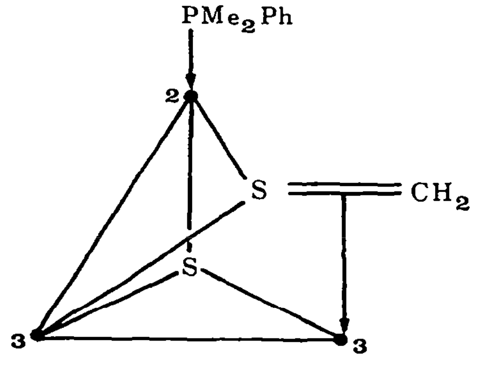


(45)

central osmium moiety!), between each other [98]. A similar, albeit less dramatic, example of this kind was found in the formation of (42). This cluster breakdown is promoted by the coordination of an additonal two-electron donor, in a reaction type which is not so uncommon in the reactions of higher nuclearity clusters (*e.g.* $[Os_6(CO)_{18}]$) [98]. Another example of Os-Os bond cleavage by the creation of an electron-rich complex is in the formation of the thioformaldehyde derivative $[Os_3(CO)_9(PMe_2Ph)(\mu_3\text{-}S)(\mu\text{-}S{=}CH_2)]$ (46), by treatment of



(46)

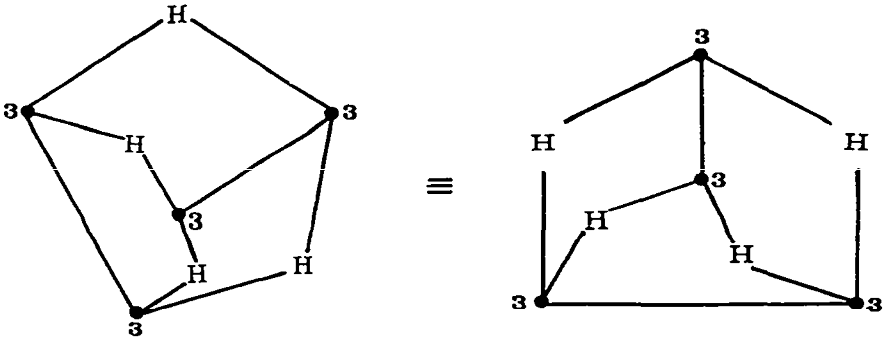


(47)

$[H_2Os_3(CO)_9(PMe_2Ph)]$ with $CS_2$. (46) contains only one Os-Os bond; upon heating, this complex loses a mole of CO (*i.e.* a two-electron donor) to form $[Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)(\mu_3\text{-}S{=}CH_2)]$ (47), which contains *two* Os-Os bonds [99].

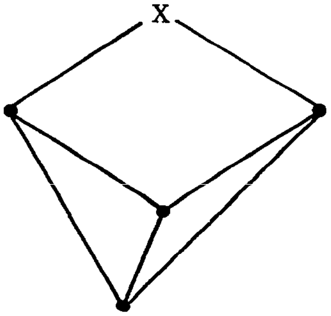
### *3.9.2 Tetrameric clusters*

The $pK_a$ of $[H_4Os_4(CO)_{12}]$ is 12.0 [61] and a UVPES (He-I and He-II) study of it indicates that its bonding should be visualised as indicated in (48) [84],



(48)

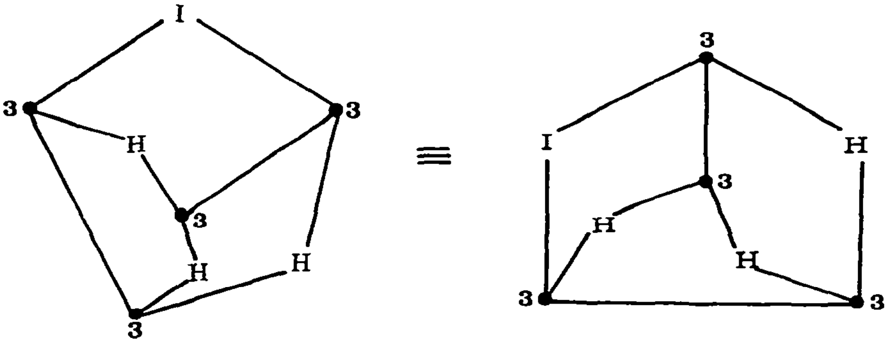
with four two-electron three-centre bonds and only two direct metal-metal bonds (see the discussion for [$H_2Os_3(CO)_{10}$] in Section 3.9.1). This view of the structure helps draw an analogy between what have traditionally been considered different classes of cluster, the tetrahedral cluster (as exemplified by [$H_4Os_4(CO)_{12}$]) and the 'butterfly' structure (49). An excellent example of this



(49)

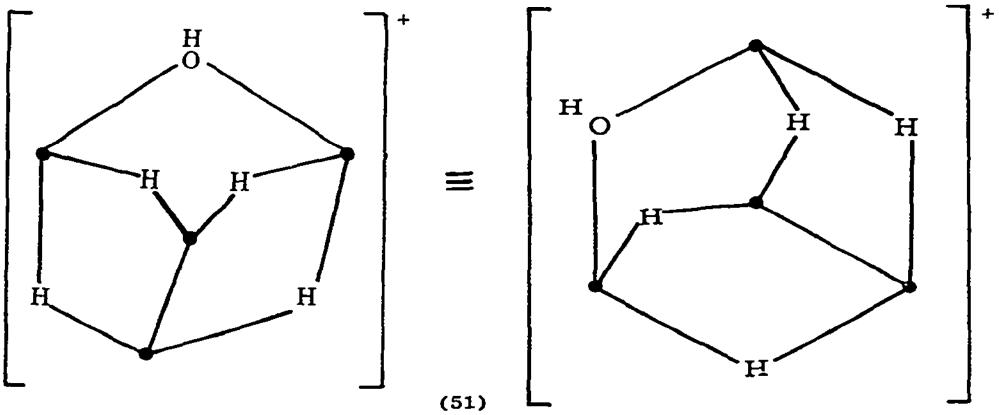
latter class of compound has been provided this year, in a combined X-ray and neutron diffraction study of [$H_3Os_4(CO)_{12}I$], in which all of the hydrides were directly located [100]. The structure of [$H_3Os_4(CO)_{12}I$] can thus be represented as in (50), the left-hand representation emphasising its relationship to (49) and the right-hand representation emphasising its relationship to a tetrahedral structure. Comparison between (48) and (50) reveal that the complexes may be thought of, from a bonding point-of-view, in an identical manner. Structure (50) has two additional electrons in the Os-I-Os bridge, which force the metal centres further apart than in the equivalent Os-H-Os bridge in (48). This effect may be thought of as steps in a reaction profile of cluster breakdown, promoted by the addition of a two-electron donor, an excellent example of which was discussed in the final paragraph of Section 3.9.1.

The molecular structure of [$H_4Os_4(CO)_{11}(CNMe)$] (prepared by the hydrogenation



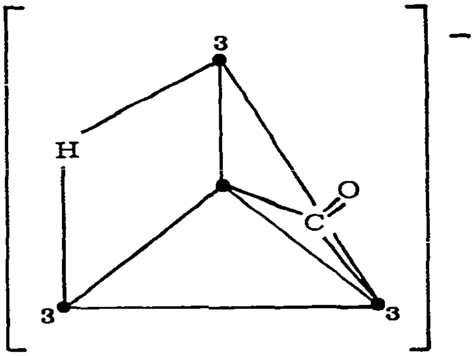
(50)

of $[HOs_3(CO)_{10}(CNHMe)]$) has been reported. The hydride ligands were directly located: the skeleton is as (48), with each osmium carrying three terminal ligands (the CNMe and one CO were disordered) [101]. Treatment of $[H_4Os_4(CO)_{12}]$ with $[NO]X$ {X = $[NO_3]$, $[PF_6]$, $[BF_4]$ or Cl} in MeCN or $CH_2Cl_2$ yields $[H_4Os_4(CO)_{12}(OH)]^+$ (51), which was also isolated as a salt of $[Os(CO)_3(NO_3)_3]^-$

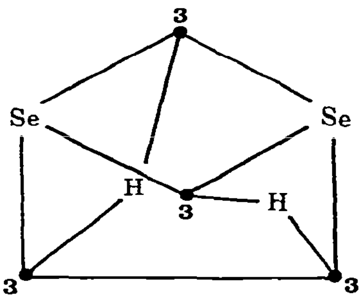


(51)

(see Section 3.7.6), in the reaction between $[H_4Os_4(CO)_{12}]$ and $N_2O_4$: $[H_3Os_4(CO)_{12}(OH)]$ was formed as a by-product and is readily converted to (51) by treatment with acid. The source of water in the synthetic steps is unclear [60]. The reaction of $[HOs_3(CO)_{11}]^-$ with $[Fe_2(CO)_9]$ in boiling thf leads to the isolation of $[HOs_4(CO)_{13}]^-$ (52) as its $[N(PPh_3)_2]^+$ salt, which can also be prepared in low yield by the pyrolysis of $[N(PPh_3)_2][HOs_3(CO)_{11}]$. The complex was crystallographically characterised but the hydride was not directly located [102]. Finally, $[H_2Os_4(CO)_{12}Se_2]$ (53), isolated from the reaction between $[Os_3(CO)_{12}]$ and selenium (see also Section 3.9.1), has also been structurally characterised: $[H_2Os_4(CO)_{12}E_2]$ (E = S or Te) were prepared similarly [95].



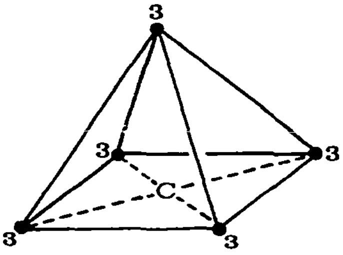
(52)



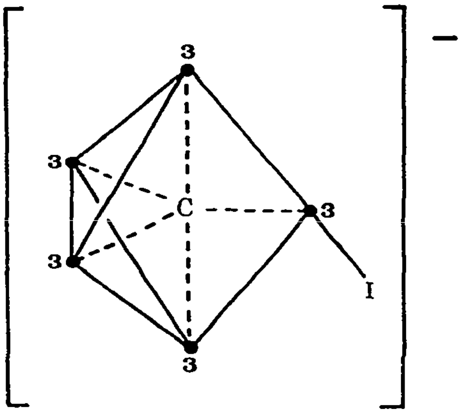
(53)

### *3.9.3 Pentameric clusters*

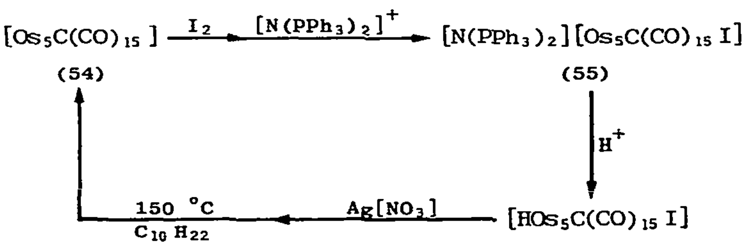
Some exciting new chemistry centred on the $Os_5$ skeleton is being developed. The structure of $[Os_5C(CO)_{15}]$ (54) has been determined, and the molecule been shown to enter the reaction cycle illustrated in Scheme IV. (55) was also crystallographically characterised [103]. The reactions of $[H_2Os_5(CO)_{15}]$ (56)



(54)

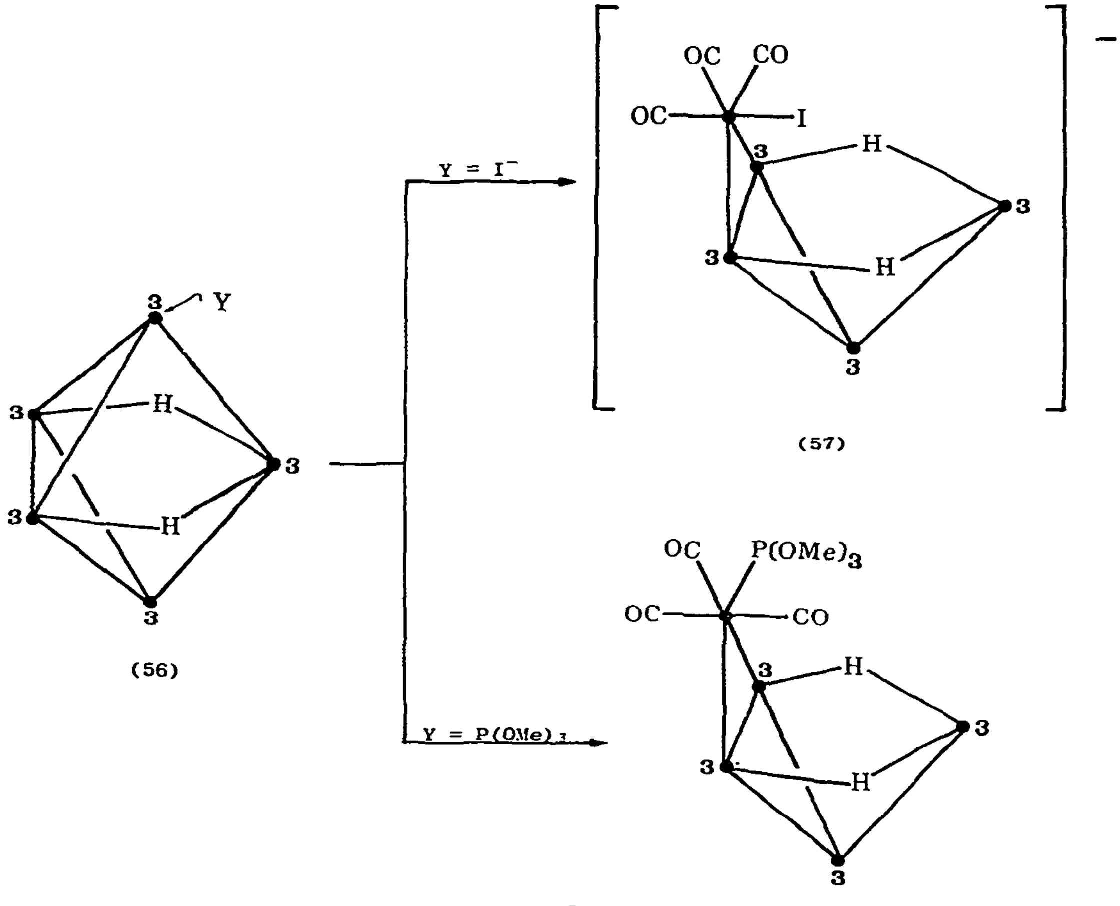


(55)



SCHEME IV: Some reactions based on $[Os_5C(CO)_{15}]$ [103].

with various nucleophiles have been investigated. With $[OH]^-$ or LiMe, deprotonation to give $[HOs_5(CO)_{15}]^-$ or $[Os_5(CO)_{15}]^{2-}$ occurs, whereas treatment with $I^-$, $P(OMe)_3$ or CO yields $[H_2Os_5(CO)_{15}I]^-$ (57), $[H_2Os_5(CO)_{15}\{P(OMe)_3\}]$ (58) or $[H_2Os_5(CO)_{16}]$ respectively, as indicated in Scheme V; the structures of (57) (as a $[NBu_4]^+$ salt) and (58) have been determined [104]. Here, again, a two-electron donor has caused metal-metal bond cleavage.

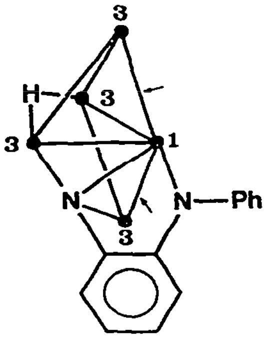


SCHEME V: Nucleophilic attack upon (56) [104].

Treatment of $[H_2Os_3(CO)_{10}]$ in boiling octane with azobenzene yields the complex $[HOs_5(CO)_{13}\{PhNC_6H_4N\}]$ (59), which contains two extremely short Os-Os bonds, marked with → in (59), at 0.2606 and 0.2601 nm {*cf.* $\bar{r}$(OsOs) in $[Os_3(CO)_{12}]$ is 0.2877 nm} [105].

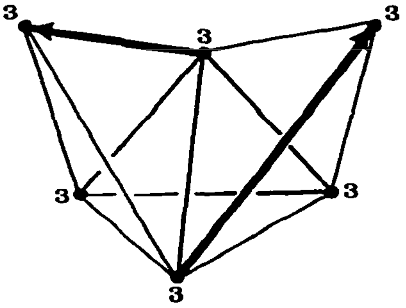
### 3.9.4 *Hexameric clusters*

The electronic structure of $[Os_6(CO)_{18}]$ has been described in terms of a



(59)

molecular orbital model, based on the assumption that the $Os_6$ core resembles a recognisable fragment of the bulk metal [106]. The full conclusions of this work, however, are not immediately accessible. Of much greater immediate impact is a very helpful discussion of the bonding in $[Os_6(CO)_{18}]$ in terms of the postulated presence of heteropolar homonuclear metal-metal bonds, as illustrated in (60) [107]. This makes a lot of sense, both in terms of the observed

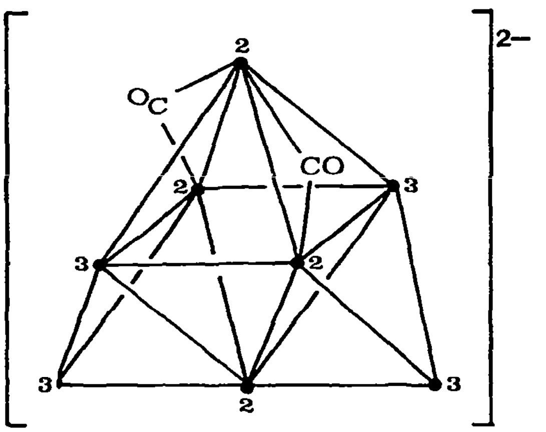


(60)

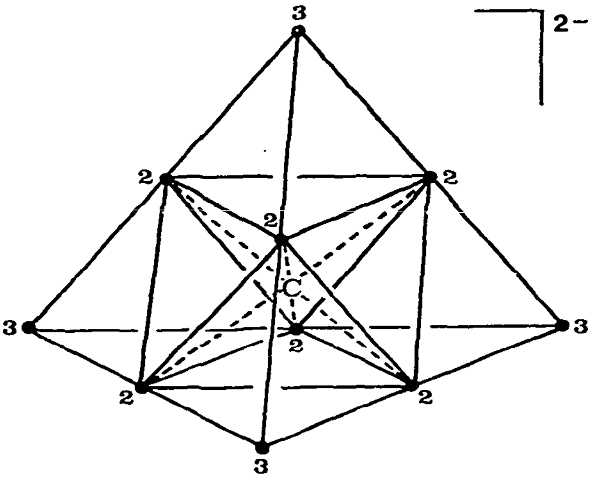
structure and, more importantly, the observed reactivity of these polynuclear clusters; these concepts are well worth further consideration and development.

### 3.9.5 *High nuclearity clusters*

Treatment of $[Os_8(CO)_{23}]$ in thf with $I_2$ leads to the isolation of $[Os_8(CO)_{22}]^{2-}$ (61) as a dark red salt of $[N(PPh_3)_2]^+$ [108]. Pyrolysis of $[Os_3(CO)_{12}]$ or $[Os_3(CO)_{11}(py)]$ leads to the isolation of $[Os_{10}C(CO)_{24}]^{2-}$ (62), also as a $[N(PPh_3)_2]^+$ salt [109]. Both (61) and (62) have been structurally characterised; the structure of (62) represents a fragment of a cubic close-packed array.



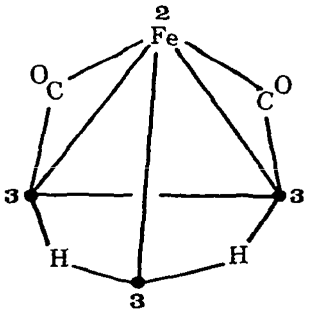
(61)



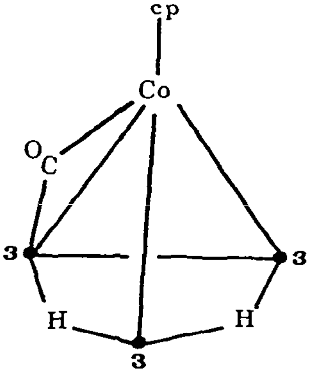
(62)

### *3.9.6 Mixed-metal clusters*

Mixed-metal clusters involving osmium and ruthenium were discussed in Section 2.13.4. $[N(PPh_3)_2][HFeOs_3(CO)_{13}]$ was isolated as a by-product in the preparation of $[N(PPh_3)_2][HOs_4(CO)_{13}]$ (see Section 3.9.2) [102]. Treatment of $[H_2Os_3(CO)_{10}]$ with $[Fe(CO)_4]^{2-}$, followed by acidification, yields $[H_2FeOs_3(CO)_{13}]$ (63); the initial reaction step involves nucleophilic attack by $[Fe(CO)_4]^{2-}$ on the cluster. The reaction between $[H_2Os_3(CO)_{12}]$ and $[Fe_2(CO)_9]$ also yields (63), but it was postulated to occur by a very strange mechanism, involving formulation (28) of $[H_2Os_3(CO)_{10}]$ donating its Os=Os double bond electrons to $Fe(CO)_4$, rather like an $[Fe(CO)_4(alkene)]$ complex [110]. Finally, reaction between $[H_2Os_3(CO)_{10}]$ and $[(cp)Co(CO)_2]$ gives $[(cp)CoOs_3(CO)_{10}H_2]$ (64) [110].



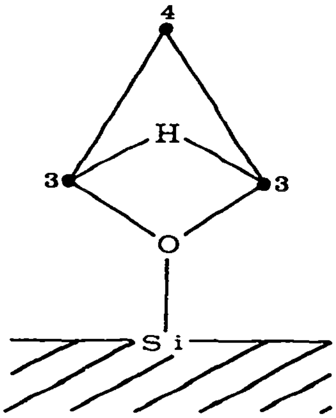
(63)



(64)

### *3.9.7 Surface modification*

$[Os_3(CO)_{12}]$, $[H_2Os_3(CO)_{10}]$ and $[Os_6(CO)_{18}]$ physisorb onto hydroxylated silica at room temperature. At 150 °C, oxidative addition of surface Si-OH groups to the Os-Os bond of $[Os_3(CO)_{12}]$ occurs to form the surface-anchored complex (65).



(65)

Similar results were obtained with $Al_2O_3$. A model complex, $[HOs_3(CO)_{10}(OSiPh_3)]$, was prepared by reaction of $[Os_3(CO)_{12}]$ with $Ph_3SiOH$. (65) has been prepared also by the direct reaction of silica with $[Os_3(CO)_{10}(NCMe)_2]$ at 25 °C. (65) was characterised by both IR and EXAFS measurements. Heating (65) at 200 °C results in cluster decomposition, to yield oligomeric osmium(II) derivatives, such as $\{Os(CO)_2(O{-}Si\equiv)_2\}_n$ or $\{Os(CO)_3(O{-}Si\equiv)_2\}_2$ [111,112].

## 3.10 OSMIUM NITROSYLS AND THIONITROSYLS

The kinetics of the hydrolysis of $[Os(NO)X_5]^{2-}$ (X = Cl, Br or I) have been studied [113]. $[Os(CN)_6]^{4-}$ reacts with nitric acid to produce, as the final product of the process, $[Os(NO)(CN)_3(H_2O)_2]$. Intermediates $K_2[Os(NO)(CN)_5]$ and $Ag[Os(NO)(CN)_4(H_2O)]$ were also isolated [114]. $OsCl_3$ reacts with $N_3S_3Cl_3$ in thf, in the presence of $AsPh_3$ or $PPh_3$, to yield $[Os(NS)Cl_3(AsPh_3)_2]$ or $[Os(NS)Cl_3(PPh_3)_2]$, respectively [115].

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