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4. OSMIUM

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CONTENTS

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INTRODUCTION

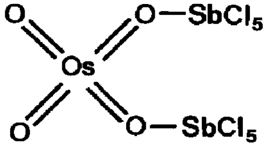
Material from volumes 94 and 95 of Chemical Abstracts forms the basis of this review. Thus the majority of the papers included were published in 1981 but a significant number appeared in 1980. As with the previous two osmium reviews in this series [1,2], the coverage in this review has been selectively directed toward the coordination and cluster chemistry of osmium.

4.1 OSMIUM(VIII)

$[OsO_4]$ was the subject of a number of laser-based spectroscopic investigations this year. Thus, the results of studies involving the IR absorptions of monoisotopic $[OsO_4]$ (by saturation spectroscopy using low-pressure CO_2 and N_2O lasers) [3], the multiple-photon IR excitation of electronic states of $[OsO_4]$ [4] and the effects of laser intensity upon the visible fluoresence resulting from multiple-photon absorption of $[OsO_4]$ [5] were reported. In addition, a low lying T_1 electronic state (origin 27295 cm^{-1}) of $[OsO_4]$ was observed by two-photon gas phase fluoresence excitation spectroscopy [6] and $[OsO_4]$ was proposed as a suitable reference molecule for laser locking in the 28 THz range [7]. A theoretical investigation of the competition between rotation-induced and vibration-induced electric nuclear quadrupole coupling in $[^{189}OsO_4]$ and the use of spin-vibration-rotation interaction to assign hyperfine components of the saturation spectra of the ν_3 band were also presented [8].

Although mixtures of $[OsO_4]/[RuO_4]$ form a continuous solid solution (with a nearly linear liquidus line) mixtures of $[OsO_4]/[Re_2O_7]$ form a degenerate eutectic (on the $[OsO_4]$ side at 41.3 °C) [9]. Dehnicke and Loessberg [10] report the formation of a donor-acceptor complex,

$[OsO_4.2SbCl_5]$, which on the basis of IR evidence has the structure (1).



(1)

Analogous reactions with $[VCl_4]$, $[TiCl_4]$ or $MoCl_5$ all resulted in the formation of $OsCl_4$ and oxohalides of vanadium, titanium or molybdenum [10]. Borohydride reduction of an aqueous solution of $[OsO_4]$ has proved an efficient route to OsO_2 [11]; the kinetics of the reduction of $[OsO_4]$ by thiourea to yield $[Os(tu)_6]^{3+}$ have also been investigated [12]. The reaction of $[OsO_4]$ with cytosine or 5-methylcytosine in the presence of bipy or tmen results in the formation of oxo-osmium(VI) esters (see Section 4.2.3) [13]. A similar reaction occurs between modified dinucleoside monophosphates and $[OsO_4]$; the kinetics of this reaction were determined and its application as a label for certain thymine-cytosine pairs in polynucleotides described [14]. Brief details of the synthesis of a series of osmium(VIII) nitrido complexes, of general form $[OsONL_2]X_3.xH_2O$ (L = bg, mbg, dmbg, ebg, debg; X = [OH] or $[SO_4]/2$; x = 0-2) and $[OsON(au)_2]OH.2H_2O$ have appeared, the complexes being characterised by IR spectroscopy [15]. The use of $[OsO_4]$ as a means of achieving clean *cis*-hydroxylations in substituted cyclopentenes has been utilised in the stereospecific total synthesis of several epipentenomycins [16]. $[OsO_4]$ has also been shown to be an effective homogeneous liquid-phase catalyst for the oxidation of mono-, di-, tri- and tetra- substituted alkenes to glycols by organic selenoxides, R_2SeO, in the presence of dioxygen [17].

The reaction of $[OsO_4]$ with allylamine has been utilised as a new staining technique for electron microscopy of polyesters and segmented copolymers with ester linkages [18].

4.2 OSMIUM(VI)

4.2.1 Fluorides, oxofluorides and nitridohalides

The reduction of [OsF_6] with bromine or chlorine has been investigated [19]; the former reaction led to the isolation of red [Br_2][OsF_6]. The reaction products of [OsF_6] with a variety of other reagents {including EF_3 (E = P, As, Sb or Bi), CS_2, dihydrogen and osmium metal} have also been described [20]. With PF_3, a violent reaction resulted in the formation of PF_5 and osmium metal; the vigour of the reaction was reduced by dilution of the PF_3 with anhydrous HF, allowing isolation of PF_5 and [$Os(PF_3)_2F_4$] (see Section 4.4.3). Although an adduct of stoicheiometry $AsF_3.OsF_5$ formed with AsF_3, no reaction (either at room temperature or 100 °C) was observed with BiF_3. The volatile products of the reaction of [OsF_6] with CS_2 were CF_4 and SF_4; with dihydrogen (at 100 °C) osmium metal and HF resulted. The reactions with dihydrogen or osmium metal, both in anhydrous HF, gave rise to OsF_5; with osmium metal, KF and anhydrous HF, K[OsF_6] was formed preferentially. The oxidation-reduction behaviour of [OsF_6] has been compared with that of [ReF_6] and [IrF_6], and a trend in oxidising strength of [ReF_6] < [OsF_6] < [IrF_6] established [20]. The He I photoelectron spectrum of [OsF_6] has been reported (the first vertical ionisation energy is 12.50 eV) and the spectrum compared with those of other transition metal hexafluorides [21].

High-purity [$OsOF_4$] has been synthesised (in quantitative yield) by the reduction of [$OsOF_5$] with silicon in anhydrous HF, and further investigated by IR spectroscopy and electron diffraction [22]. The photoelectron spectrum of [$OsOF_4$] has been recorded as part of a study upon the electronic structure of MOF_4 compounds (M = W, Mo, Re or Os), as a result of this study, the accepted M=O bond formalism was called into doubt [23].

The single crystal X-ray structure of [$AsPh_4$][$OsNBr_4$] showed the anion to have C_{4v} symmetry with $r(Os-N) = 0.1583$ nm and $\bar{r}(Os-Br) = 0.2457$ nm [24]. Also reported in this publication were the single-crystal polarised electronic absorption spectra of $[AsPh_4][OsNX_4]$ (X = Cl, Br or I) at room temperature and 5 K in the range 10000 to 40000 cm^{-1}.

4.2.2 Oxides

Thermal decomposition of $SrOsO_3$ has been shown to lead, at temperatures above 920 °C, to the formation of a ternary oxide, $SrOsO_4$, with a scheelite structure: at temperatures above 1030 °C, $SrOsO_4$ decomposes to SrO, $[OsO_4]$ and osmium metal [25]. The perovskites $Ba_2M^{II}OsO_6$ (M^{II} = Co or Ni) crystallise with the hexagonal $BaTiO_3$ structure (Fig. 1); IR and FIR data were also presented [26].

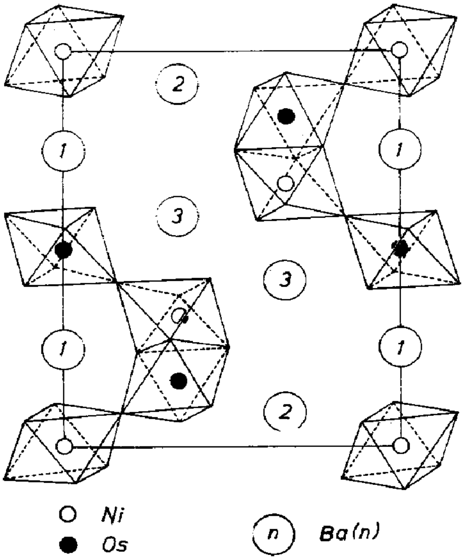


Fig. 1 The structure of Ba_2NiOsO_6 [26].

4.2.3 Complexes

$[OsO_2L_2L'_2]$ complexes continue to attract considerable interest. Thus, the single crystal X-ray structures of $[OsO_2(OH)_2(phen)]$ [27], $[OsO_2(gly)_2]$ [28], $[Os_2O_6(py)_4]$ [27] and $[Os_2O_4(py)_4(C_8H_{12}O_4)]$ [29] have been reported (see

Fig. 2); selected bond lengths are presented in Table 1. Although a mean Os–O bond length is quoted for [$Os_2O_6(py)_4$] in the Table, the Os–O bridge in this

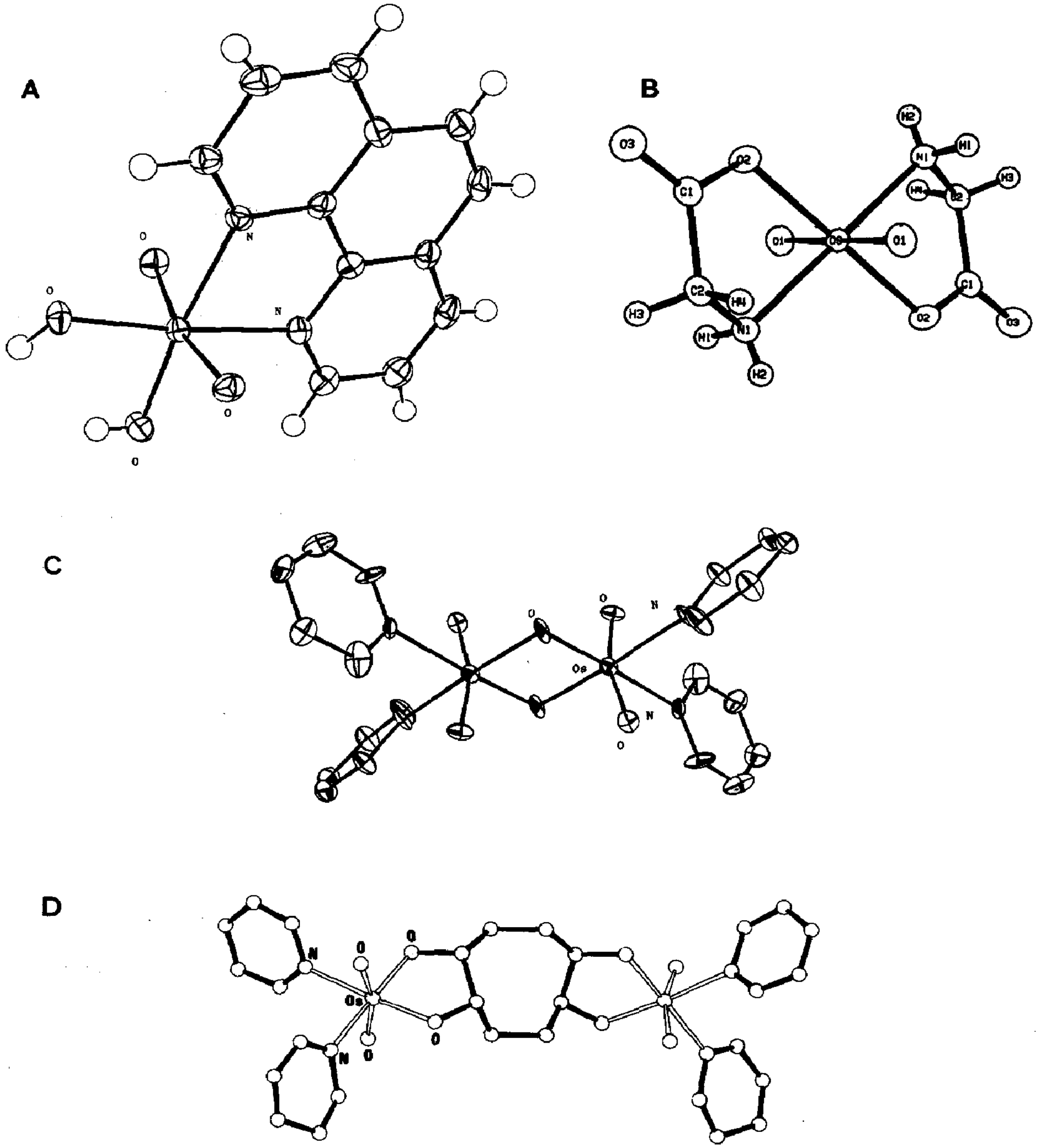


Fig. 2 The molecular structures of (A) [$OsO_2(OH)_2(phen)$] [27], (B) [$OsO_2(gly)_2$] [28], (C) [$Os_2O_6(py)_4$] [27] and (D) [$Os_2O_4(py)_4(C_8H_{12}O_4)$] [29].

TABLE 1

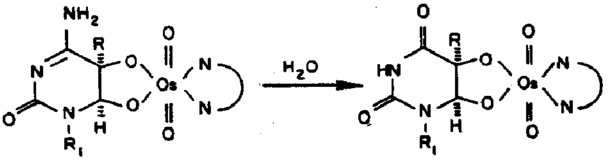
Structural parameters for the $[OsO_2L_2L'_2]$ compounds.

Compound	r(Os=O)/nm	r(OsO)/nm	r(OsN)/nm	Ref.
$[OsO_2(OH)_2(phen)]$	0.1742	0.1983	0.2130	[27]
$[OsO_2(gly)_2]$	0.1731	0.2038	0.2114	[28]
$[Os_2O_6(py)_4]$	0.174	0.193	0.222	[27]
$[Os_2O_4(py)_4(C_8H_{12}O_4)]$	0.172	0.195	0.219	[29]

molecule is slightly asymmetric {*viz*. r(OsO) = 0.198, 0.188 nm} [27].

In addition to $[OsO_2(gly)_2]$, complexes of osmium(VI) with the amino acids DL-alanine, DL-valine, DL-leucine, DL-isoleucine and DL-phenylalanine were prepared [28]. The compounds all exhibit strong IR absorptions at *ca*. 850 cm^{-1} which were assigned to the O=Os=O asymmetric stretch. Slightly lower frequencies (*viz*. 819-832 cm^{-1}) were reported for this stretch in $[OsO_2L_2L'_2]$ (L_2 = bidentate oxygen-donor ligand ; L'_2 = bipy, $(py)_2$ or 4,7-Ph_2-phen); the compounds were also characterised by UV-VIS and NMR spectroscopic techniques [30].

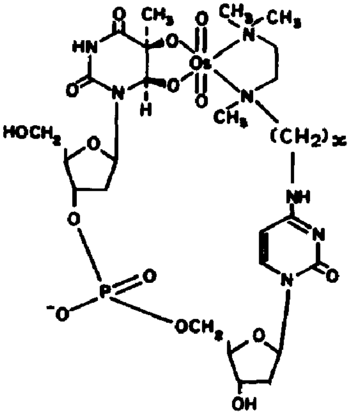
As indicated in Section 4.1, several oxoosmium(VI) esters of the form $[OsO_2L_2L'_2]$ (L_2 = cytosine or 5-methylcytosine; L'_2 = bipy or en) have been prepared [13]. These complexes, once formed, react with water to form the corresponding osmium(VI) uracil or thymine derivatives according to equation (1):



(1)

N⌒N = bipy or tmen; R,R_1 = H, ribosyl or Me

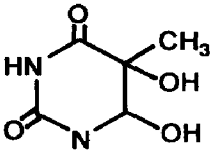
Macrocyclic analogues of the product of equation (1) *viz*. (2) have been



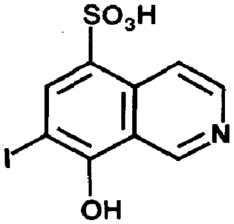
x = 2, 4 or 6

(2)

prepared (by the same group of workers; see Section 4.1) and their ^{1}H NMR spectra obtained [14]. Finally, a report upon the kinetics of the transesterification reactions between oxoosmium(VI) esters, of the general form $[OsO_2L_2L'_2]$ $\{L_2H_2$ = TMP glycol or thymine glycol (3); L'_2 = 2ishq (4), 2py, bipy, tmen or bpds (5)$\}$, and a variety of glycols (*e.g.* ump (6), ethylene glycol or uridine) has appeared [31].



(3)



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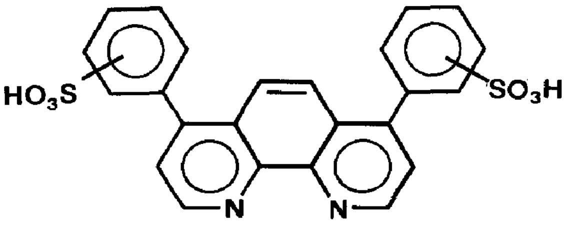

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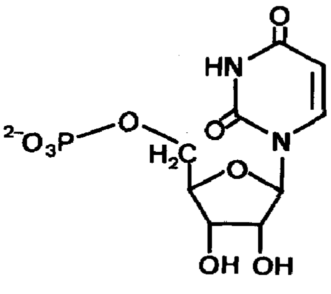


(6)

The Raman and IR spectra of the complex, $Na_6[OsO_2(SO_3)_4].2H_2O$ have been recorded; bands at 842 cm^{-1} (IR) and 858 cm^{-1} (Raman) were assigned to the O=Os=O asymmetric and symmetric stretching frequencies, respectively, and the binding mode of the sulphito groups was identified as monodentate *S*-bonding [32]. The chloride, bromide and iodide salts of $[OsO_2(NH_3)_4]X_2$ have been prepared by the reaction of aqueous $[NH_4]X$ with $K_2[OsO_2(OH)_4]$ at room temperature; the complexes were characterised by elemental analysis, IR spectroscopy and X-ray diffraction [33]. The 1,2-diaminoethane complex *trans*-$[OsO_2(en)_2]^{2+}$ has been shown to be an effective quenching agent for the emission of $\{[Ru(bipy)_3]^{2+}\}^*$ [34].

4.3 OSMIUM(V)

4.3.1 *Halides*

The osmium(V) anion, $[OsF_6]^-$, has been identified as a reduction product of the reaction between liquid bromine and $[OsF_6]$ [19]. Brief details of the characterisation (by mass spectrometry and IR and Raman spectroscopy) of the moisture-sensitive red-brown $[Br_2][OsF_6]$, formed in the above reaction, were presented together with its magnetic moment (μ_{eff} = 3.82 μ_B). The reaction of $[OsF_6]$ with dichlorine did not result in the isolation of a stable product although the presence of highly coloured unstable species was detected.

An improved synthetic route to OsF_5 involving the reduction of $[OsF_6]$ by osmium in anhydrous HF has been demonstrated [20]. Also contained in this report was the synthesis of the adduct $AsF_5.OsF_5$ which may be alternatively formulated as $[AsF_4][OsF_6]$.

An alternative synthetic route to $OsCl_5$ utilising the action of SCl_2 upon $[OsO_4]$ has been described [35]. The $OsCl_5$ so formed exhibited a different IR spectrum - although it possessed identical X-ray powder characteristics - to samples of $[Os_2Cl_{10}]$ prepared by Burns and O'Donnell [36]. The interaction of $OsCl_5$ with $[AsPh_4]Cl$, to yield $[AsPh_4][OsCl_6]$, and the facile reduction of this salt to $[AsPh_4]_2[OsCl_6]$, in dichloromethane, were also described [35].

4.3.2 Oxides

A new $KSbO_3$-type compound, $Nd_4Os_6O_{19}$, has been isolated from the reaction of Nd_2O_3 with osmium metal at 950 °C under oxidising conditions [37]. The single crystal X-ray structure of $Nd_4Os_6O_{19}$ showed the oxide to be isomorphous with $La_4M_6O_{19}$ (M = Ru, Re or Os); as expected, the corner shared Os_2O_{10} dimeric units within the structure contain significant direct Os–Os bonding {r(Os–Os) = 0.2481 nm} [37].

4.4 OSMIUM(IV)

4.4.1 Halides and oxohalides

The zirconium(IV) catalysed hydrolysis of $K_2[OsF_6]$ [38], the formation of green $[AsPh_4]_2[OsCl_6]$ (by the interaction of $[Os_2Cl_{10}]$ with $[AsPh_4]Cl$ in dichloromethane) [35] and the IR and Raman spectra of $[SCl_3]_2[OsCl_6]$ [39a] have been described. The dimeric osmium(IV) oxohalide complexes also continue to attract interest. Thus, the resonance Raman spectrum [39b] and the results of a SCCC MO calculation [40] upon $[Os_2OCl_{10}]^{4-}$ have been reported. An energy level sequence of $2b_{2g}, 2b_{1u}, 6e_g \ll 7e_u \ll 4b_g < 4b_{2u} < 7a_{1g} < 7a_{2u}$ was predicted by the calculation [40]. The resonance Raman spectrum of $[Os_2OCl_{10}]^{4-}$ (measured at 80 K using 418.6 nm exciting radiation) exhibits seven overlapping progressions. Excitation profile measurements confirmed that the axially polarised $e_u^* \leftarrow e_g$ $(1A_{2u} \leftarrow 1A_{1g})$ transition at 24400 cm^{-1} is the resonant electronic transition and that the ν_1 (a_{1g}) symmetric Os–O–Os stretching mode is the progression forming mode. The ν_1 band of $[Os_2OCl_{10}]^{4-}$ occurs at 224.3 cm^{-1}, consistent with significant Os–O–Os double-bond character [39b].

4.4.2 *Oxides and sulphides*

The thermal decomposition of $SrOsO_3$, under conditions of dynamic air flow, has been the subject of investigation by DTA, TGA and X-ray powder diffraction [25,41]. A preparation of OsO_2, by tetrahydroborate reduction of $[OsO_4]$, has been reported [11]. Equation (2) outlines a new synthetic route to OsS_2:

$$[NH_4]_2[OsCl_6] + 2H_2S \xrightarrow[3\ h]{220\ °C} OsS_2 + 2[NH_4]Cl + 4HCl \qquad (2)$$

The OsS_2, which possesses only limited short range order when prepared in this manner, was characterised by TGA, X-ray powder diffraction and magnetic susceptibility measurements [42]. By annealing the OsS_2 at 800 °C for four days, a material with the cubic pyrite structure was obtained (*n.b.* although OsS_2 is formally osmium(IV) it is comprised of low-spin d^6 osmium(II)). The thermodynamics of the oxidation of OsS_2 in acid solution have been investigated [43].

4.4.3 *Complexes*

A preliminary report of a new class of osmium(IV) carboxylate complexes, of general formula $[Os_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2X_4(PR_3)_2]$ (X = halide; R = alkyl or aryl), prepared by the reaction of a suspension of *trans*-$[OsO_2X_2(PR_3)_2]$ with RCOOH at reflux, has appeared [44]. The complexes are highly coloured and diamagnetic. The chloride, $[Os_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2Cl_4(PPh_3)_2].Et_2O$, was examined by single crystal X-ray diffraction, see Fig. 3, which revealed it to possess approximate C_2 symmetry (neglecting the orientation of the phenyl rings); preliminary details of the electrochemical properties of the dimers were also

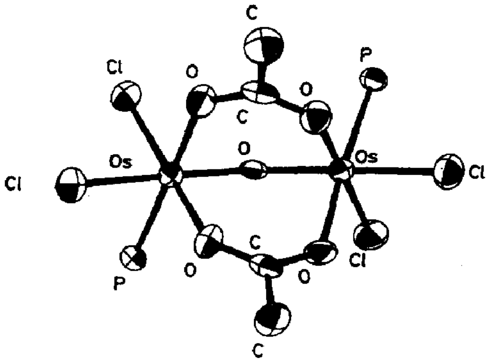
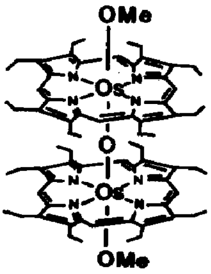


Fig. 3 The molecular structure of $[Os_2(\mu\text{-}O)(\mu\text{-}O_2CMe)_2Cl_4(PPh_3)_2].Et_2O$ [44].

presented. A mixed carboxylate complex, dark blue crystalline six coordinate $[OsCl(O_2CMe)(O_2CCF_3)_2(py)_2]$, has been isolated from the reaction of a solution of $[Os(O_2CMe)_2(py)_2]Cl$ (which has chelating ethanoate groups) and $Ag[OOCCF_3]$ [45]. $[Os(edta)(H_2O)].H_2O$ has been prepared, as black lustrous diamagnetic crystals, by aeration (for twenty hours) of an aqueous solution of $H[OsCl_2(edtaH_2)].2.5H_2O$ [46]. A seven coordinate *N*-ethyl-*N*-(2-methylphenyl)-dithiocarbamato complex of osmium(IV) has been reported [47].

A new sulphito complex, $[Os_2N(SO_3)(NH_3)_8(H_2O)]Cl_3$, prepared by the action of SO_2 upon $[Os_2N(NH_3)_8Cl_2]Cl_3$, has been characterised by IR and Raman spectroscopy which showed it to contain *S*-bonded sulphite [32]. The efficiency of *cis*-$[Os(en)_2H_2]^{2+}$ as a quenching agent for $\{[Ru(bipy)_3]^{2+}\}^*$ has been tested [34]. A linear oxo-bridged structure, has been proposed for $[\{Os(OEP)(OMe)\}_2O]$ (7), formed by the interaction of a dichloromethane/



(7)

methanol solution of [Os(OEP)(CO)] with dioxygen in the presence of 2,3-dimethylindole [48].

An interesting report of the formation of $[Os(PF_3)_2F_4]$, by controlled reduction of $[OsF_6]$ with PF_3 in anhydrous HF, has appeared [20]. The yellow $[Os(PF_3)_2F_4]$ was characterised by elemental analysis, IR (ν(OsF) = 606 cm^{-1}) and UV-VIS absorption spectroscopy, conductance (it is a non-electrolyte in anhydrous HF) and magnetic susceptibility (μ_{eff} = *ca.* 0.3 μB) measurements; it is soluble in thf, 1,4-dioxane, nitromethane and anhydrous HF but reacts with water to eliminate PF_3 [20]. The seven coordinate hydrido arsine complex $[OsH_4(AsPh_3)_3]$ has been prepared by $[BH_4]^-$ reduction of $Na_2[OsCl_6]$ in the presence of $AsPh_3$ [49a]. Its IR spectrum exhibits four peaks attributable to ν(Os-H) (2080, 2060, 2000 and 1850 cm^{-1}; Nujol) but on the NMR timescale the hydrides were equivalent exhibiting only a single resonance (−11.7 ppm; $CDCl_3$) [49a].

4.5 OSMIUM(III)

4.5.1 *Oxides*

Upon heating, orthorhombic $Ca_2Os_2O_7$ undergoes a series of transformations the first of which begins to occur at temperatures above 855 °C when defect orthorhombic $Ca_2Os_2O_{7-x}$ ($x \leq$ *ca.* 0.16) forms. Further heating results in continuous gradual dioxygen loss and eventually the formation of pyrochlores $Ca_2Os_2O_{7-x}$ ($0.42 \leq x \leq 0.62$). At temperatures above 1018 °C complete decomposition to CaO, osmium metal, $[OsO_4]$ and dioxygen occurs [49b]. The details of the decomposition process were determined by the use of DTA, thermogravimetry and X-ray powder diffraction [49b].

4.5.2 *Oxygen donor ligand complexes*

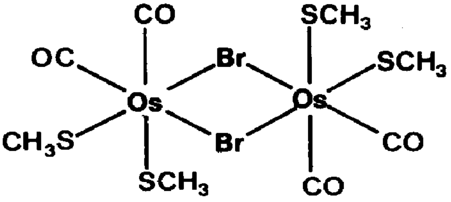
A carboxylate complex $\{Os(O_2CMe)_2Cl\}_n$ has been prepared by the action of ethanoic acid (containing ethanoic anhydride and a small quantity of conc. hydrochloric acid) upon $Na_2[OsCl_6]$ [45]. Although insoluble in common organic solvents, suspensions of $\{Os(O_2CMe)_2Cl\}_n$ react according to Scheme 1 (see page 259) to give a variety of osmium complexes in oxidation states +2 (and +2.5 in the case of $[Os_2(O_2CMe)_4(py)Cl]$), +3 and +4.

In contrast to the reactions of $[OsO_2X_2(PR_3)_2]$ (X = Cl or Br) with carboxylic acids at reflux (the products of which are described in some detail in Section 4.4.3) $[OsO_2X_2(PR_3)_2]$ react with the anions of 2-hydroxypyridine or 2-hydroxy-6-methylpyridine to give rise to magnetically dilute monomeric $[OsX_2(PR_3)_2(mhp)_2]$ or $[OsX_2(PR_3)_2(O\text{-}2\text{-}py)_2]$ (more specific details were not reported) [44].

A series of osmium(III) edta and pdta complexes have been prepared; included were the H^+ and $[NH_4]^+$ salts of $[OsX_2(edtaH_2)]^-$ (X = Cl or Br) and $[OsI(edtaH)]^-$ [46]. The compounds were characterised by elemental analysis, IR and electronic absorption spectroscopy, magnetic susceptibility measurement and analysis of their acid-base behaviour [46].

4.5.3 Sulphur donor ligand complexes

A series of unexceptional dithiocarbamate complexes of the type $[Os(S_2CNR_2)_3]$ (NR_2 = piperidine, morpholine, *N*-methylpiperazine and thiomorpholine) have been prepared and characterised by IR and electronic absorption spectroscopy, and magnetic susceptibility and conductivity measurements; the experimental data are consistent with octahedral coordination about an osmium atom of configuration t_{2g}^5 [50,51]. The reaction of $[Os_3(CO)_{12}]$ with $(CH_3S)_2$ in toluene (at reflux under N_2) gives rise to a high molecular weight polymeric product $\{Os(SCH_3)_2(CO)_2\}_n$ ($\bar{n}$ = 34; see Section 4.6.2) which, as a benzene solution, will react with bromine to give a binuclear derivative, $[Os_2Br_2(SCH_3)_4(CO)_4]$ [52]. After consideration of molecular weight, IR, NMR and XPES data, structure (8) was proposed for the dimer [52].



(8)

An osmium dimer, of empirical formula $[\{(Me_2HCO)_2PS_2\}_2OsS_2P(S)(OCHMe_2)_2]$, with the osmium atoms in an octahedral environment and bridged by a perthiophosphate fragment, has been isolated from the reaction of $[NH_4]_2[OsCl_6]$ and $[NH_4][(Me_2HCO)_2PS_2]$ [53].

4.5.4 *Ammine, amine and diimmine complexes*

$Na_2[S_2O_5]$ and SO_2 act upon hot (75 °C) aqueous $[Os(NH_3)_5Cl]Cl_2$ to give the pink-brown sulphito complex, $[Os(NH_3)_4Cl(SO_3)]$ ($\mu_{eff} = 1.45\ \mu_B$ at 294 K) [32]. Comparison of the IR and Raman absorptions of $[Os(NH_3)_4Cl(SO_3)]$ with those of $[Pd(NH_3)_3(SO_3)]$ and *trans*-$[Rh(NH_3)_4(CN)(SO_3)].2H_2O$ (whose single crystal X-ray structures have been reported) indicated a *trans*- structure with a sulphur bonded sulphito group and with overall C_s symmetry [32].

In an extension to their earlier work upon multidentate amines of iron(III) and ruthenium(III) Poon and coworkers have reported a general synthetic route to complexes of the type $[OsL_2X_2]^+$ (L = en; L_2 = dadn, dadd, tactd or tacpd; X = Cl, Br or I) and their IR and electronic spectral characterisation [54]. The complexes are all monomeric, low-spin and have *trans* halides; their electronic absorption spectra are dominated by intense ligand-to-metal charge transfer bands. The ability of *cis*-$[Os(en)_2Cl_2]^+$ to quench $\{[Ru(bipy)_3]^{2+}\}^*$ has been compared with that of *trans*-$[OsO_2(en)_2]^{2+}$ and *cis*-$[Os(en)_2H_2]^{2+}$; overall *cis*-$[Os(en)_2Cl_2]^+$ is the least efficient quencher of the three cations. An electron transfer quenching mechanism was favoured (though the operation of an energy transfer mechanism could not be totally eliminated) and the observed trend in quenching efficiency was related to the respective redox properties of the complexes [34].

The detailed redox behaviour of $[Os(L\text{-}L)_3]^{3+}$ (L-L = bipy, 4,4'-Me_2bipy, 5,5'-Me_2bipy, phen or 5-Clphen) in aqueous sodium dodecyl sulphate (sds) micellar solution has been investigated by cyclic voltammetry [55].

4.5.5 *Phosphine complexes*

Although the synthesis and spectral characterisation of $[\{OsCl_3(solvent)\}_2(tetraphos)]$, $[OsCl_3L]$ (L = triphos or tp) and $[Os_2X_6(tddx)]$ (X = Cl or Br) have been described by Taqui Khan *et al.* [56], their paper suffers from gross errors and incomplete experimental detail.

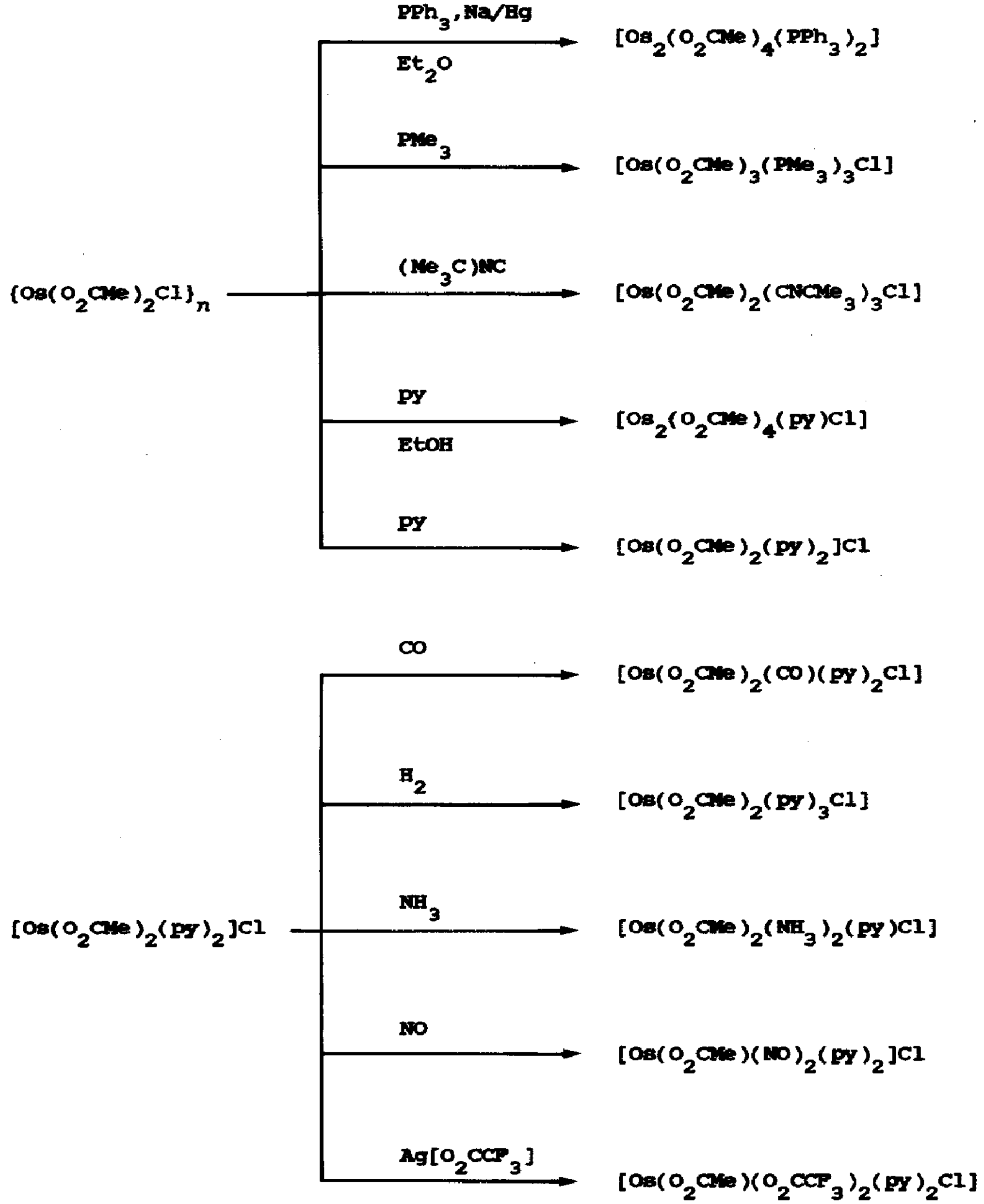
4.6 OSMIUM(II)

4.6.1 *Carboxylate complexes*

The osmium analogue of $[Ru_2(O_2CMe)_4(PPh_3)_2]$ has been prepared by treatment of a diethyl ether suspension of $\{Os(O_2CMe)_2Cl\}_n$ with PPh_3 and sodium amalgam (see Scheme 1) [45].

4.6.2 *Sulphur donor ligand complexes*

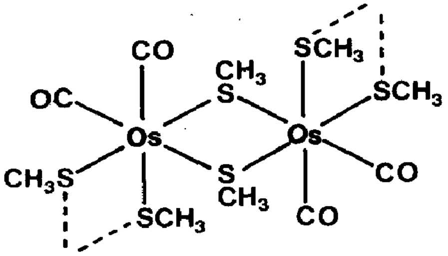
The osmium(II) dithiocarbamate derivatives, $[Os(S_2CNR_2)_2(H_2O)_2].xH_2O$ (x = 0 or 1; R_2 = piperidyl, morphyl, N-methylpiperazyl or thiomorphyl), have been synthesised by mixing osmium(III) chloride and the appropriate sodium dithiocarbamate salt in a 1:3 mole ratio in aqueous methanol [50,51]. The complexes were shown to be diamagnetic non-electrolytes; their IR and electronic absorption spectra were interpreted in terms of a distorted



Scheme 1 The reactions of $\{Os(O_2CMe)_2Cl\}_n$ and $[Os(O_2CMe)_2(py)_2]$ [45].

octahedral coordination.

$[Os_3(CO)_{12}]$ reacts with $(CH_3S)_2$ to give polymeric $\{Os(SCH_3)_2(CO)_2\}_n$ ($\bar{n}$ = 34). The ^1H NMR (in $CDCl_3$, a single broad peak at δ = 2.68 ppm), IR {ν(CO) = 2099, 2015, 1950 and 1915 cm-1 in Nujol} and X-ray photoelectron (Os $4d_{5/2}$ 280.1 eV) spectra of the polymer are consistent with structure (9).



(9)

$\{Os(SCH_3)_2(CO)_2\}_n$ is cleaved by bromine to yield $[Os_2Br_2(SCH_3)_4(CO)_4]$ [52]. Light brown $K_4[Os(SO_3)_3(H_2O)_3]$ has been prepared by the action of $K_2[S_2O_5]$ on aqueous $K_2[OsCl_6]$ [32]. It is diamagnetic and analysis of its IR and Raman spectra indicated the presence of *S*-bonded sulphite groups and a facial configuration of ligands.

4.6.3 Dimethylsulphoxide complexes

Both *cis*- and *trans*-$[Os(dmso)_4Cl_2]$ have been isolated from the reaction of $H_2[OsCl_6]$ with dmso in the presence of $SnCl_2.2H_2O$ [58]. Not only do the products differ in their overall geometry but also in the mode of dmso bonding (as determined by IR and NMR spectroscopy). Thus, whilst the dimethylsulphoxide ligands in *trans*-$[Os(dmso)_4Cl_2]$ are all *S*-bonded, three of those in *cis*-$[Os(dmso)_4Cl_2]$ are *S*- bonded and the remaining one is *O*-bonded [58]. The synthesis of *trans*-$[Os(dmso)_4\{CH_2S(O)CH_3\}_2]$.2dmso has been achieved by the interaction of $OsCl_3.3H_2O$ or $[NH_4]_2[OsCl_6]$ with dmso in the presence of a continuous stream of dihydrogen. The dmso ligands are *S*-bonded and are labile in the presence of dppe, PPh_3 or $AsPh_3$ (the latter two reactions under acidic conditions) to give $[Os(dmso)_2(dppe)\{CH_2S(O)CH_3\}_2]$, $[Os(PPh_3)_6]Cl_2$ or $[Os(dmso)_3(AsPh_3)_2Cl]Cl$ respectively [59].

4.6.4 Diimmine complexes

The $\{[Os(5\text{-}Cl\text{-}phen)_3]^{2+}\}^*$–$[Fe(CN)_6]^{4-}$ system has been shown to exhibit activation controlled static quenching, with values of 1.7 x 10^{10} and 3.2 x 10^{9} M^{-1} s^{-1} for the second order quenching rate constants (at 1.0 x 10^{-3} and 0.10 M ionic strength respectively, both measured at 25 °C) [60]. At high $[Fe(CN)_6]^{4-}$ concentration, a limiting lifetime of 3-4 x 10^{-9} s was established for the system. Values of 8.7 x 10^{7} and 1.6 x 10^{8} s^{-1} (at the same ionic strengths as above) were calculated for the intramolecular electron tranfer rate constant, k_{el}. Intense room temperature charge-transfer emission from solutions of $[Os(terpy)LL']^{n+}$ (L = dppee or dppm; L' = Cl, py, MeCN, CO or dppm; n = 1 or 2) has been observed [61]. The emission was assigned to π^*(terpy) ⟶ d_π(Os) by analogy with that for $[Os(terpy)_2]^{2+}$. Additional support for this assignment is provided by the observation that the emission energy of the luminesence is directly proportional to [$E_{1/2}$(OsIII/II) − $E_{1/2}$(terpy/terpy$^{\cdot-}$)], the difference between the ground state redox potentials of the metal-donor and the ligand-acceptor sites. All the complexes, except the chlorides were shown [61] to be photolabile, *e.g.*:

$$[Os(terpy)(dppee)(CO)]^{2+} \xrightarrow[L]{h\nu} [Os(terpy)(dppee)L]^{2+} + CO \qquad (3)$$

and the relevance of this to the excited-state lifetimes was discussed briefly.

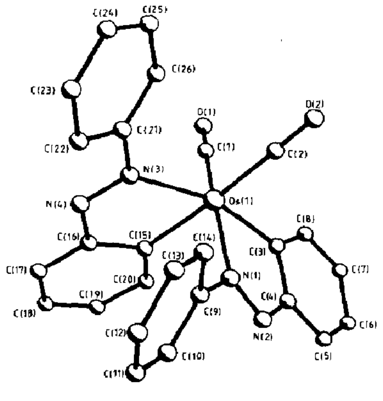
The half-wave potentials of $[OsL_3]^{3+/2+}$ (L = bipy, 5,5'-dmbipy, 4,4'-dmbipy, phen or 5-Clphen) and the rate constant, k_t, for electron transfer between $[OsL_3]^{3+}$ and $[Fe(H_2O)_6]^{2+}$ in aqueous sodium dodecyl sulphate micellar solution have been determined [55].

4.6.5 Porphyrin complexes

The oxidation of [Os(OEP)(CO)] with 2,3-dimethylindole/O_2 in CH_2Cl_2/CH_3OH affords the osmium(IV) complex $[Os_2(OEP)_2(OMe)_2O]$, (7) [48]. A series of disubstituted osmium porphyrin complexes, [Os(OEP)LL'] (both L and L' are taken from 1-Meimid, py, O, N_2, tht, thf, $P(OMe)_3$ or CO) have been synthesised [62]. Of particular interest - as cytochrome c models - were [Os(OEP)(1-Meimid)(tht)] and [Os(OEP)(py)(tht)]. Electron excitation spectra and cyclic voltammograms were obtained for these two complexes; a linear correlation between $E_{1/2}$ and $\tilde{\nu}_{max}$ of the longest wavelength absorption maxima (α bands) for these and several other [Os(OEP)LL'] compounds was reported [62]. Upon irradiation at 365 or 405 nm solutions of $[Os(OEP)\{P(OMe)_3\}_2]$ in CH_2Cl_2, $CHCl_3$ or CCl_4 undergo oxidative substitution to give the osmium(IV) complex $[Os(OEP)Cl_2]$; experimental data were indicative of a radical mechanism [63].

4.6.6 *Azobenzenido complexes*

The azobenzenido complex, $[Os(CO)_2(C_6H_4NNC_6H_5)_2]$ (obtained from the reaction of $[Os_3(CO)_{12}]$ and azobenzene), has been structurally characterised; its molecular structure and some of the interatomic distances are presented in Fig. 4 [64a]. The central osmium atom exhibits a distorted octahedral coordination geometry comprised of two *cis* carbonyl groups and two azobenzenido lignds (for which both of the two Os-N and the two Os-C bonds



$r(OsC_1)$ = 0.1881 nm

$r(OsC_2)$ = 0.1921 nm

$r(OsC_3)$ = 0.2051 nm

$r(OsC_{15})$ = 0.2106 nm

$r(OsN_1)$ = 0.2120 nm

$r(OsN_3)$ = 0.2173 nm

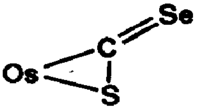
Fig. 4 The molecular structure of $[Os(CO)_2(C_6H_4NNC_6H_5)_2]$ [64a].

have a *cis* configuration). Involvement of the benzenido C atoms in π-bonding to the osmium atom was used to rationalise the magnitude of the $Os-C_2$ bond length relative to that of the $Os-C_1$ bond.

4.6.7 Phosphine and arsine complexes

The synthesis and characterisation of the osmium(II) carbonyl halides, $[OsCl_2(CO)(triphos)]$, $[\{OsCl_2(CO)_2\}_2L_2]$ (L = tetraphos or tp) and $[Os_3Cl_6(tddx)]$ has been described - however, given the number of errors and inconsistensies in this manuscript very little reliance can be placed in the reported data [56]. Convenient syntheses of a range of osmium(II) mixed-ligand triphenylarsine complexes are outlined in Scheme 2; this work [49a] represents a natural extension to earlier studies, by the same authors, upon synthetic routes to osmium(II) triphenylphosphine complexes [49a; refs. 2-4]. The stereochemistries of the complexes were deduced from their IR and ^1H NMR spectra (where obtainable) and by consideration of their reactivity patterns. $[NH_4]_2[OsX_6]$ (X = Cl or Br) has proved a useful starting material in the synthesis of the chloride and bromide complexes $[OsH(CO)X\{As(CH_2Ph)_3\}_3]$; the complexes were characterised by elemental analysis, IR spectroscopy and conductivity measurements [64b].

In an extension of their earlier work upon the reaction of $[OsCl(CS)(CO)(CNR)(PPh_3)_2]^+$ (R = 4-methylphenyl) with $[SH]^-$, Roper and coworkers have investigated nucleophilic attack of the cation by $[SeH]^-$ [65]. Attack occurs at the CS group and gives rise to an η^2-SCSe moiety that is bonded to the osmium *via* the carbon and sulphur atoms, *viz.* $[Os(\eta^2\text{-}CSSe)(CO)(CNR)(PPh_3)_2]$ (10). The conversion of this product to its



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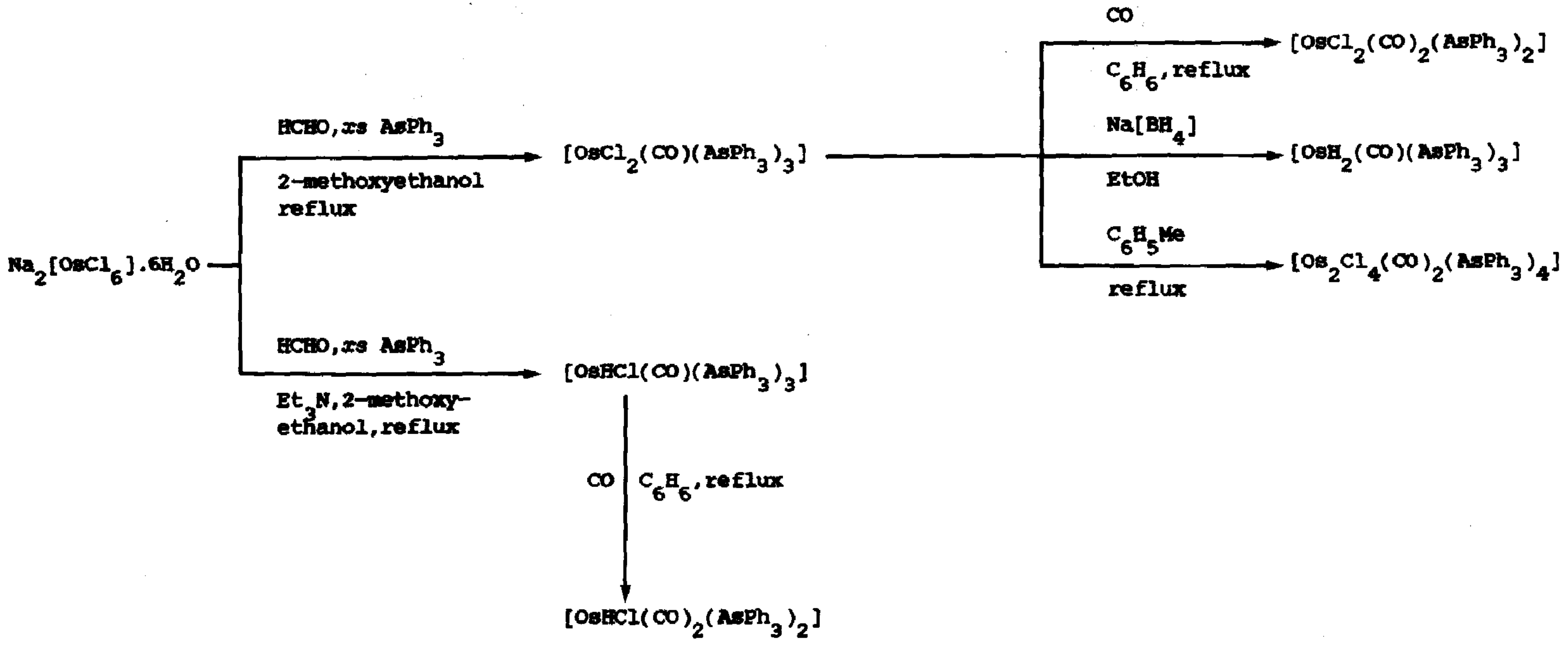


Scheme 2 Some of the reactions of $Na_2[OsCl_6].6H_2O$ with $AsPh_3$ to give osmium(II) arsine products, and their subsequent reactions with CO, $Na[BH_4]$ or heat [49a].

carbon-selenium bound isomer, $[\overline{Os(\eta^2\text{-}CSe}S)(CO)(CNR)(PPh_3)_2]$, is illustrated in Scheme 3. Synthetic routes to the ruthenium analogues and IR data for both the osmium and ruthenium complexes were also presented [65].

4.6.8 Trichlorostannyl complexes

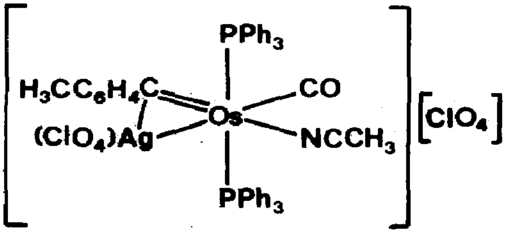
Detailed multinuclear NMR studies upon $[Os(SnCl_3)_5Cl]^{4-}$ have revealed a large $^2J(^{119}Sn\text{-}^{117}Sn)$ spin-spin coupling of the two pairs of *trans* equatorial tin atoms. The magnitude of the coupling constant, 18600 Hz, was rather less than that observed for the ruthenium analogue (21248 Hz) which was the largest reported $^2J(^{119}Sn\text{-}^{117}Sn)$ coupling constant at the time of publication [66].

4.6.9 Cyanide complexes

$K_2Fe[Os(CN)_6]$, in admixture with $K_2Fe[Ru(CN)_6]$, $K_2Fe[Fe(CN)_6]$, $Al_4[Fe(CN)_6]_3$ and $KAl[Fe(CN)_6]$ has been examined for catalytic activity towards ammonia synthesis [67].

4.6.10 Metal-metal bonded complexes

An interesting series of metal-metal bonded compounds of general form $[\overline{Os(CC_6H_4MeM})(CO)(PPh_3)_2Cl]$ (M = CuI, AgCl or AuCl) have been prepared by the action of CuI,AgCl or $(PPh_3)AuCl$ upon $[Os(CC_6H_4Me)(CO)(PPh_3)_2Cl]$. The carbyne complex $[Os(CC_6H_4Me)(CO)(PPh_3)_2Cl]$ also reacts with $Ag[ClO_4]$ (two equivalents) to give (11) and with aqueous $HClO_4$ to give $[Os(CHC_6H_4Me)(PPh_3)_2(CO)Cl(ClO_4)]$;



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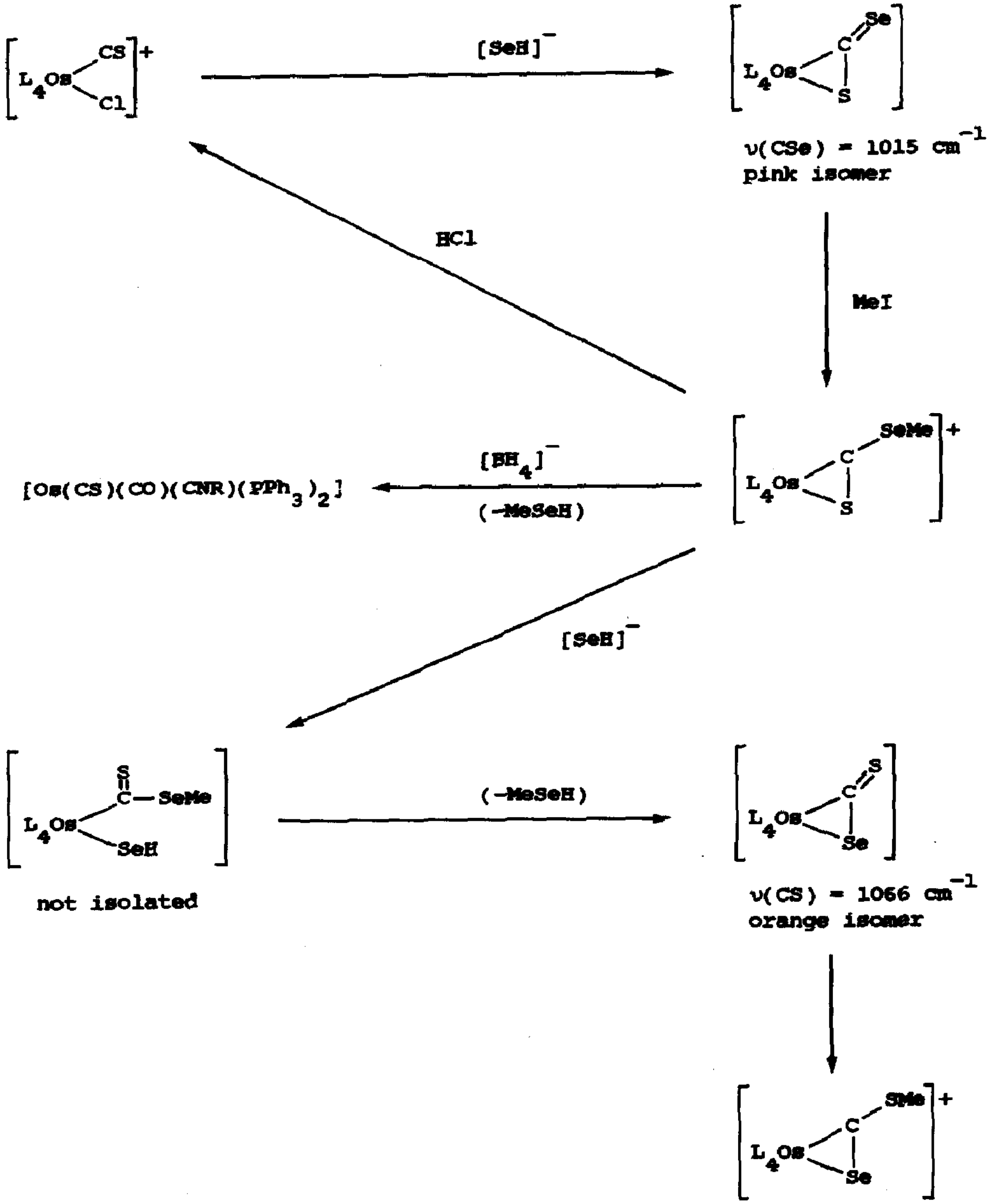


Scheme 3 The formation, and some of the reactions, of the the C–S and C–Se bound isomers of [Os(η^2-CSSe)(CO)(CNC$_6$H$_4$CH$_3$)(PPh$_3$)] [65].

the latter adduct is also formed by the action of aqueous $HClO_4$ upon $[Os(CC_6H_4MeAgCl)(CO)(PPh_3)_2Cl]$ [57]. The single crystal crystal X-ray structure of $[\overline{Os(CC_6H_4MeAg}Cl)(CO)(PPh_3)_2Cl]$ (Fig. 4) was also reported as part of this study [57].

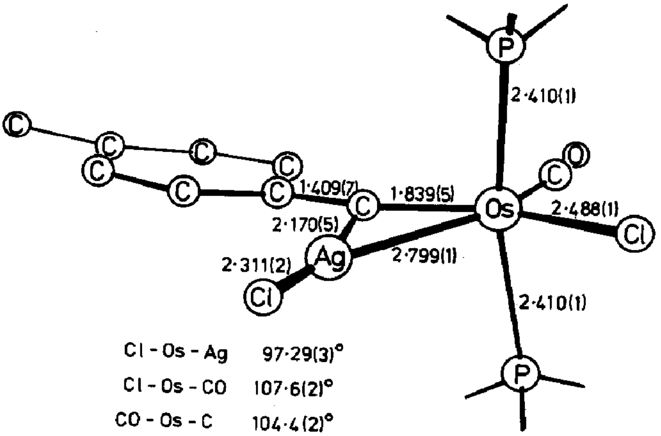


Fig. 5 The molecular structure of $[\overline{Os(CC_6H_4MeAg}Cl)(CO)(PPh_3)_2Cl]$ [57].

4.7 OSMIUM(0)

Two reports concerned with osmium(0) chemistry have appeared. $[Os(PPh_3)_3(CO)(H)Cl]$ undergoes reductive elimination with diazabicycloundecene under CO at 20–80 psi to give $[Os(PPh_3)_2(CO)_3]$ [68], and $[Os_3(CO)_{12}]$ reacts with glyoxalbis(alkylimine) (alkyl = Me_2CH or Me_3C) to give $[Os_2(CO)_6(dab)]$ [69]. $[Os_2(CO)_6(dab)]$ was characterised by FD mass spectrometry, IR and ^1H NMR spectroscopy, and shown to be isostructural with its ruthenium analogue.

4.8 OSMIUM CARBONYL CLUSTERS

The notation which has been used to represent the structures of some of the clusters in this Section is described in detail elsewhere [2;pp. 124-125].

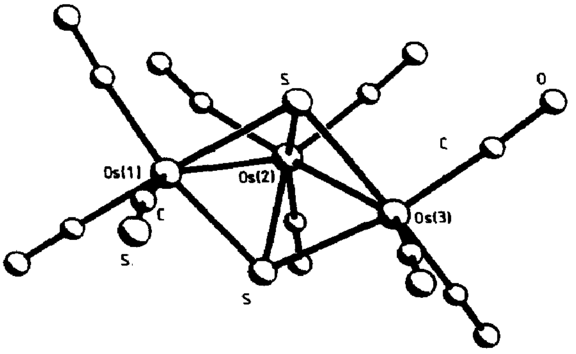
4.8.1 *Trimeric clusters*

The ^{13}C NMR spectra of approximately sixty percent ^{13}CO enriched $[^{187}Os_3(CO)_{12}]$ in C_6D_6 and $C_6H_5CD_3$ solutions at 25 and 150 °C have been reported [70,71]. The spectrum obtained at the lower temperature {two doublets δ = 182.3 and 170.4 ppm; $^1J(^{187}Os^{13}C)$ = 90 ∓2 and 115 ∓2 Hz respectively} was consistent with stereochemical rigidity of the CO groups whereas that obtained at 150 °C {a 1:3:3:1 quadruplet; δ = 176.4 ppm; $^1J(^{187}Os-^{13}C)$ = 33 ∓1 Hz} was consistent with rapid internuclear exchange of all the CO groups over the $\{Os_3\}$ skeleton. A variable temperature (15, 100, 200 and 295 K) laser Raman study of solid $[Os_3(CO)_{12}]$ has been presented; the work emphasised the importance of site symmetry and correlation effects upon the spectral data and confirmed the absence of any phase changes over the temperature range covered [72].

The decomposition of $[Os_3(CO)_{12}]$ has been investigated by thermal gravimetric analysis and IR spectroscopy; the onset of decomposition of the cluster, as a KBr disc, was raised from 160 to 250 °C [73]. Under a stream of dihydrogen, $[Os_3(CO)_{12}]$, dry mixed and dispersed with γ-Al_2O_3, yields detectable quantities of CH_4 at 150 °C: the total yield of CH_4 was 8.49 molecules per cluster molecule [74]. Small amounts of C_2H_4, C_2H_6 and CO_2 were also detected but no evidence was found for C_3 hydrocarbons.

Several other groups have been actively reporting the reactions of $[Os_3(CO)_{12}]$. Thus, $[Os_3(CO)_{12}]$ interacts with CS_2 (under 10 atm of a 1/1 mixture of carbon monoxide and argon) to yield the thiocarbonyl cluster $[Os_3(CO)_8(CS)S_2]$, whose molecular structure is depicted in Fig. 6, and a lesser amount of $[Os_3(CO)_9S_2]$ [75].

The interaction of $[Os_3(CO)_{12}]$ with NMe_3O in the presence of MeCN yields $[Os_3(CO)_{11}(NCMe)]$. The reactions of this cluster with a variety of ligands L



$r(\mathrm{OsOs}) = 0.2780,\ 0.2830$ nm

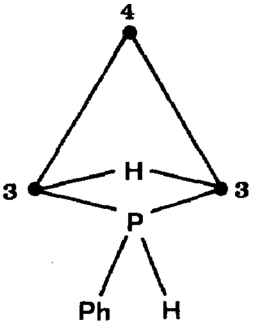
$r(\mathrm{Os...Os}) = 0.3642$ nm

$r(\mathrm{S...S}) = 0.3030$ nm

Fig. 6 The molecular structure of $[Os_3(CO)_8(CS)S_2]$ [75].

(L = carbonyl, triphenylphosphine, CH_3-4-$C_6H_4SO_2CH_2NC$, C_2H_4 or C_5H_5N) to give $[Os_3(CO)_{11}L]$ and with hydrogen halides to yield products of stoicheiometry $[Os_3(CO)_{11}(H)X]$, $[Os_3(CO)_{10}(H)X]$ (X = Cl, Br or I) and $[Os_3(CO)_9(H)I]$ were described. In addition to the detailed spectroscopic characterisation of these cluster products structures were proposed for many of them [76].

The reaction of $[Os_3(CO)_{12}]$ with $Me_2CHN{=}CHNHCHMe_2$, in octane at reflux yields $[HOs_3(CO)_9(\mu_3\text{-}Me_2CHNCHNCHMe_2)]$ which was isolated and spectroscopically (IR and ^1H NMR) characterised [77]. Treatment of $[Os_3(CO)_{12}]$ with PH_2Ph in methylbenzene at reflux has been shown to give rise to the terminally bound phosphine clusters $[Os_3(CO)_{11}(PH_2Ph)]$ and $[Os_3(CO)_{10}(PH_2Ph)_2]$, and the edge-bridged cluster $[HOs_3(CO)_{10}(PHPh)]$ (12) [78]. That $[HOs_3(CO)_{10}(PHPh)]$ is an intermediate in the formation of the face-capped cluster $[H_2Os_3(CO)_9(PPh)]$ (13) is indicated by its pyrolytic conversion to the latter (along with a small amount of $[H_2Os_3(CO)_9(PHC_6H_4)]$)) (14) [78]. Pyrolysis of $[Os_3(CO)_{10}(PH_2Ph)_2]$ gives $[HOs_3(CO)_9(PHPh)(PH_2Ph)]$ (15), and $[H_2Os_3(CO)_9(PPh)]$ reacts with added PH_2Ph to yield $[H_2Os_3(CO)_8(PPh)(PH_2Ph)]$ (16) [78]. The reaction products, some of which were obtained in microscopic yield, were characterised by elemental analysis, IR spectroscopy and mass spectrometry, and where sufficient material was available ^1H and ^{31}P NMR spectroscopy .



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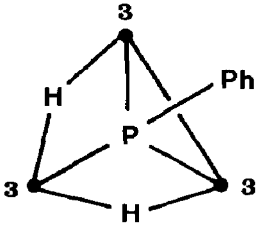

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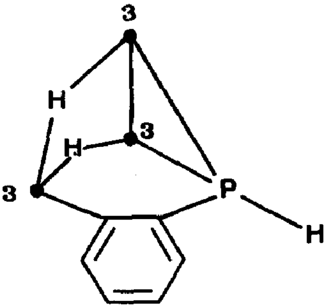

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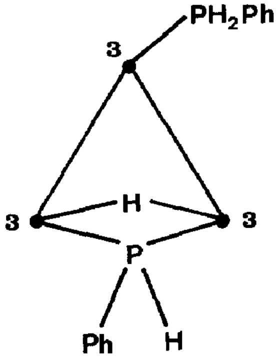

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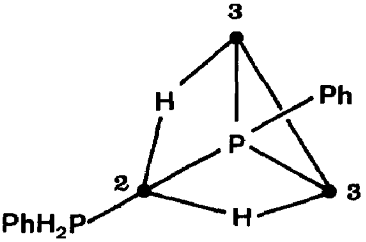
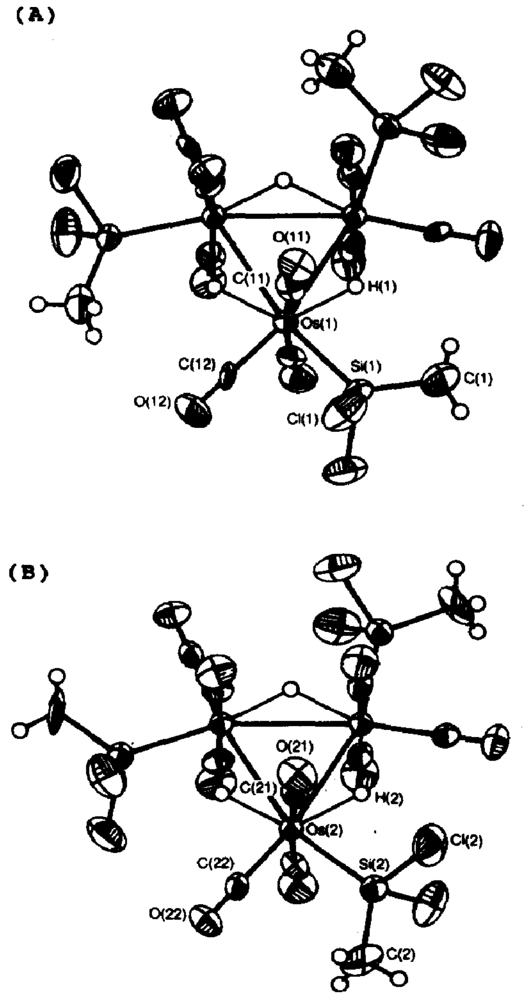


(16)

With an excess of Cl_2XSiH (X = Me or Cl), $[Os_3(CO)_{12}]$ generates $[H_3Os_3(CO)_9(SiXCl_2)_3]$ and *trans*-$[Os(CO)_4(SiXCl_2)_2]$ [79a]. A single crystal X-ray structure of the former compound (X = Me) showed the presence of two conformational isomers which differred in the orientation of the $SiMeCl_2$ group about the OsSi bond (see Fig. 7). The hydrogen atoms (which were not directly located) were presumed to bridge each edge of the $\{Os_3\}$ triangle. In solution, rapid rotation about the Si–Os bond was observed even at −120 °C.

The ^{13}C NMR spectrum of $[HOs_3(CO)_{12}]^+$ (formed by treating $[Os_3(CO)_{12}]$ (containing ^{187}Os in natural abundance) with concentrated H_2SO_4) indicates that the hydride moiety lies in the $\{Os_3\}$ plane and bridges two of the osmium atoms [70].

^1H NMR studies directed at the bridging hydrogen atoms in a



	Molecule A	Molecule B
r(OsOs)/nm	0.3155	0.3125
r(OsSi)/nm	0.2420	0.2400
$r(\mathrm{OsCO})_a$/nm	0.193	0.197
$r(\mathrm{OsCO})_e$/nm	0.189	0.192

Fig. 7 The molecular structures of the two conformers of $[H_3Os_3(CO)_9(SiMeCl_2)_3]$ [79a].

polycrystalline sample of $[H_2Os_3(CO)_{10}]$ showed them to exhibit isotropic chemical shifts similar to those found in solution studies [80]. The proton decoupled ^{13}C NMR spectrum of sixty percent ^{13}CO enriched $[H_2Os_3(CO)_{10}]$ exhibits four resonances (ratio 2:2:2:4), see Fig. 8. The multiplet structure of band B was interpreted as the superposition of a singlet, a doublet and a triplet, the result of the various degrees of ^{13}CO substitution possible at the unique osmium atom. A *cis* $^2J(CC)$ coupling constant of 3.2 Hz was

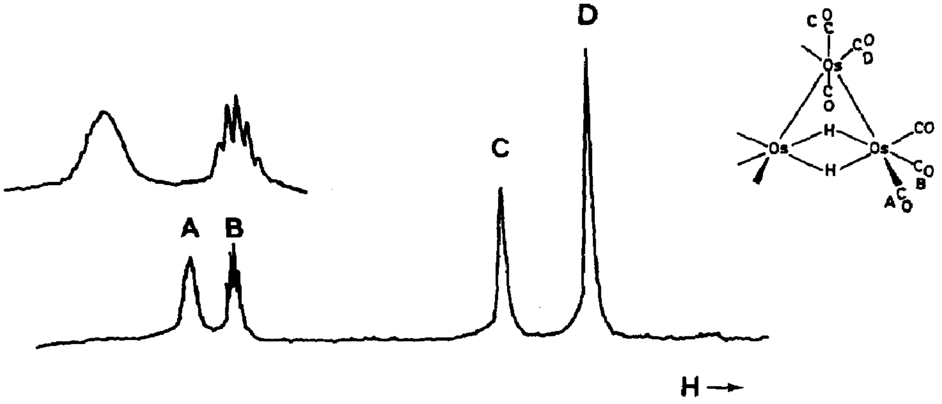
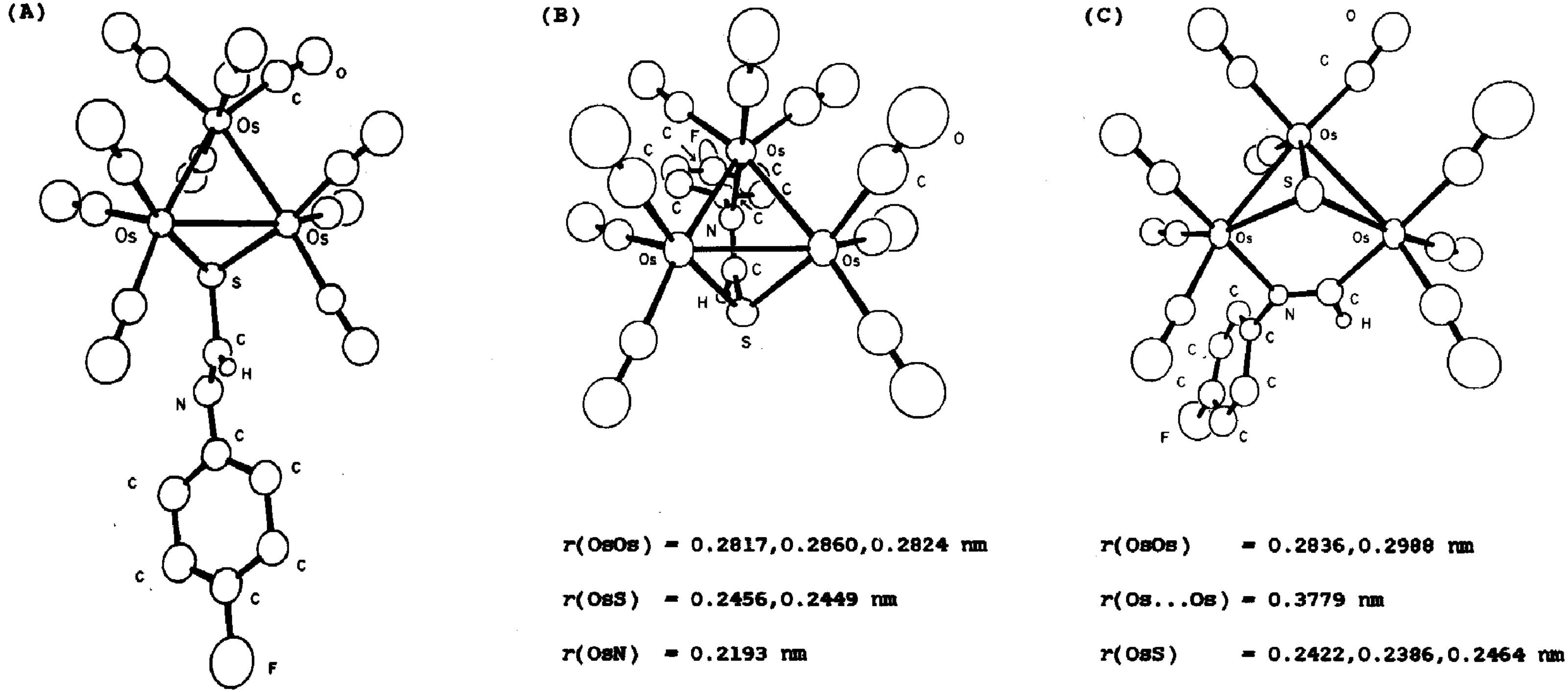


Fig. 8 The proton decoupled room temperature ^{13}C NMR spectrum of ^{13}CO enriched $[H_2Os_3(CO)_{10}]$ [81].

determined from the spectrum. The absence of identical structure on band A was tentatively attributed to further coupling of $(CO)_A$ with $(CO)_C$ [81]. The Raman spectrum of $[H_2Os_3(CO)_{10}]$ (exited using 488.0 nm radiation) exhibits two absorptions at 188 and 145 cm^{-1}, assigned to 'the two A' modes expected from its C_s symmetry' [82a]. However the single crystal structure of $[H_2Os_3(CO)_{10}]$ indicates that the molecule possesses C_{2v} symmetry [82b].

Several reactions of $[H_2Os_3(CO)_{10}]$ have been reported. Thus, it reacts with $F\text{-}4\text{-}C_6H_4NCS$ at 25 °C to give yellow $[HOs_3\{\mu\text{-}\eta^1\text{-}SC(H)N\text{-}4\text{-}C_6H_4F\}(CO)_{10}]$ {Fig. 9 (A)}, which as a hexane solution slowly decarbonylates at room temperature to yield red $[HOs_3\{\mu_3\text{-}\eta^2\text{-}SC(H)N\text{-}4\text{-}C_6H_4F\}(CO)_9]$ {Fig. 9 (B)}. This, in turn, rapidly converts to yellow $[HOs_3(\mu_3\text{-}S)(\mu\text{-}HC{=}N\text{-}4\text{-}C_6H_4F)(CO)_9]$ {Fig. 9 (C)} upon heating to reflux in octane [83]. Overall the desulphurisation of $F\text{-}4\text{-}C_6H_4NCS$ has occurred, a reaction that may have relevance to the purification of fossil fuels.

The reactions of $[H_2Os_3(CO)_{10}]$ or $[H_2Os_3(CO)_9(PMe_2Ph)]$ with CS_2 [84], $Me\text{-}4\text{-}C_6H_4NCO$ [85] or MeNCO [86] have been studied in some detail, Scheme 4. Mechanisms for the formation of some of the complexes were also presented. In addition to detailed physical and spectroscopic characterisation of the



(B)

r(OsOs) = 0.2817,0.2860,0.2824 nm

r(OsS) = 0.2456,0.2449 nm

r(OsN) = 0.2193 nm

(C)

r(OsOs) = 0.2836,0.2988 nm

r(Os...Os) = 0.3779 nm

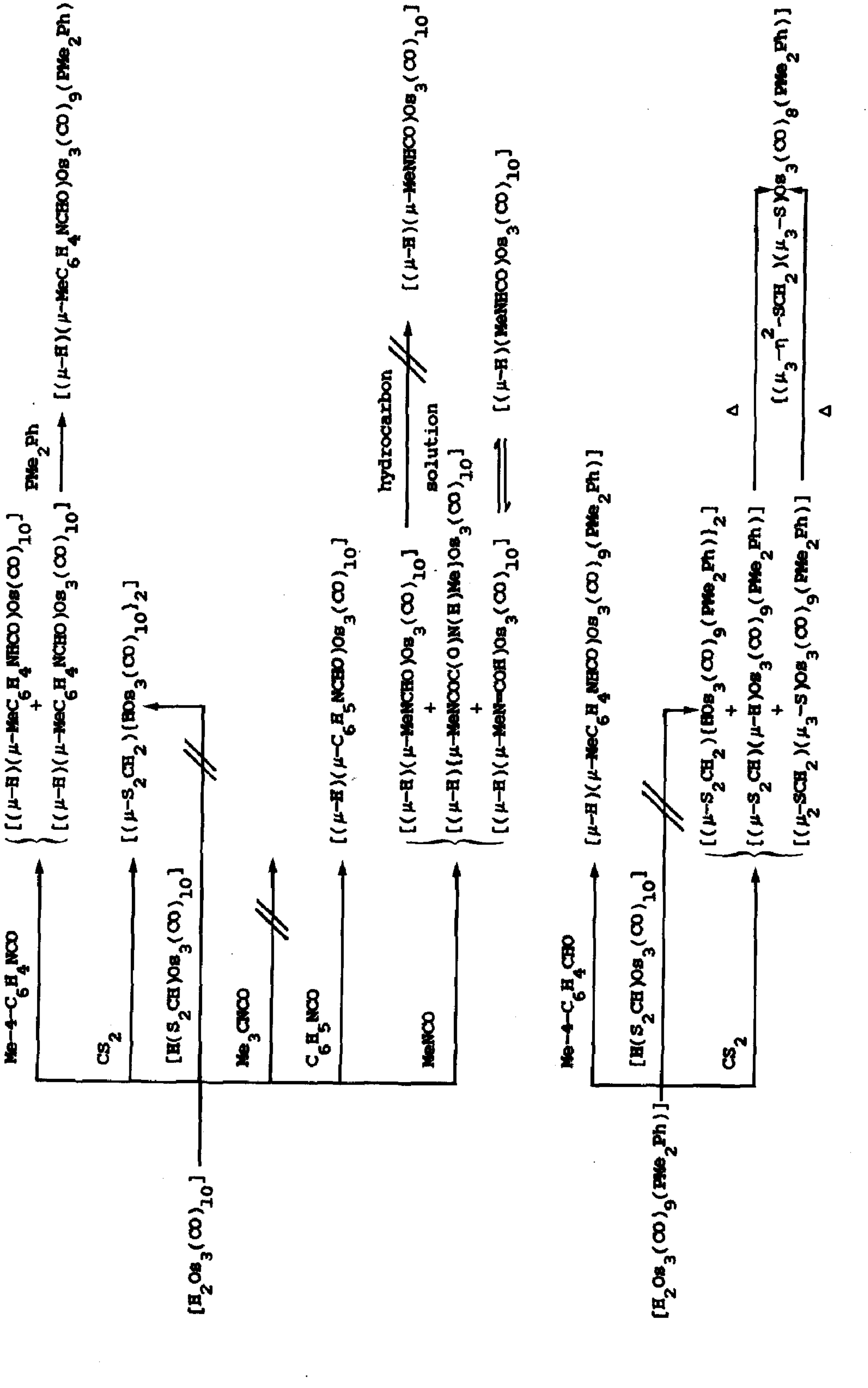
r(OsS) = 0.2422,0.2386,0.2464 nm

(A)

r(OsOs) = 0.2861,0.2870,0.2868 nm

r(OsS) = 0.2420,0.2431 nm

Fig. 9 The molecular structures of (A) $[HOs_3(\mu-\eta^1-SC(H)N-4-C_6H_4F)(CO)_{10}]$, (B) $[HOs_3(\mu_3-\eta^2-SC(H)=N-4-C_6H_4F)(CO)_9]$ and (C) $[HOs_3(\mu_3-S)(\mu-HC=N-4-C_6H_4F)(CO)_9]$ [83].



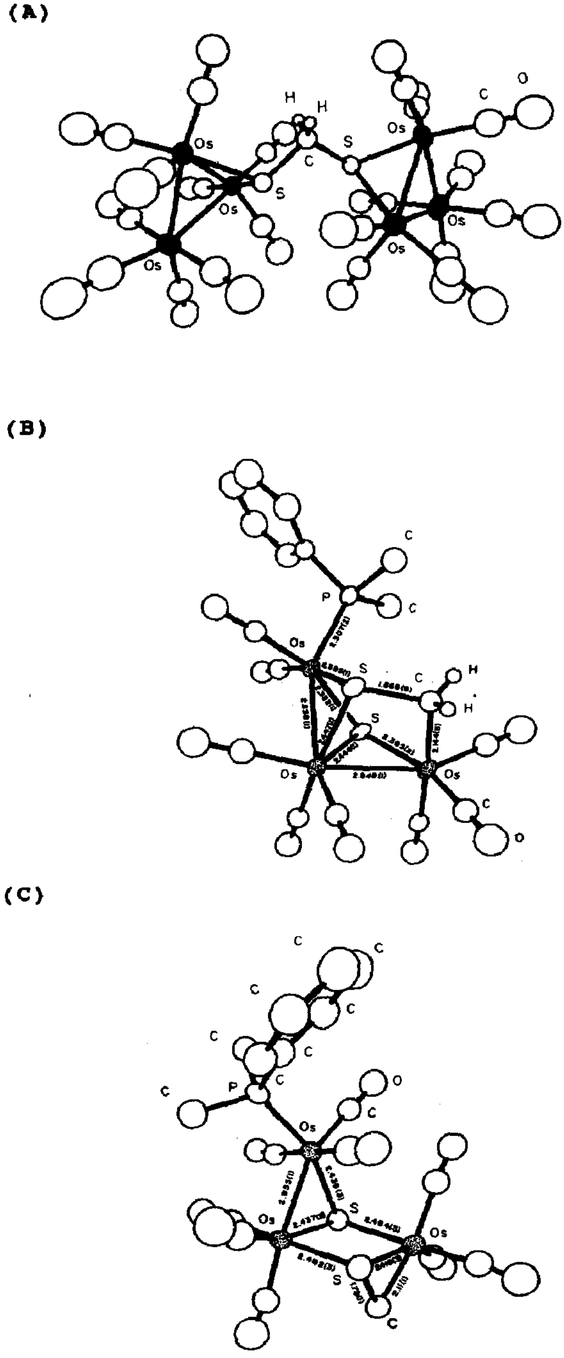
Scheme 4 Some of the reactions of $[H_2Os_3(CO)_{10}]$ and $[H_2Os_3(CO)_9(PMe_2Ph)]$ [84–86].

clusters, the single crystal X-ray structures of $[(\mu\text{-}S_2CH_2)\{HOs_3(CO)_{10}\}_2]$, $[(\mu\text{-}\eta^2\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_9(PMe_2Ph)]$ and $[(\mu_3\text{-}\eta^2\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_8(PMe_2Ph)]$ (Fig. 10) and those of $[(\mu\text{-}H)(\mu\text{-}Me\text{-}4\text{-}C_6H_4NCHO)Os_3(CO)_{10}]$, $[(\mu\text{-}H)(\mu\text{-}Me\text{-}4\text{-}C_6H_4NCHO)Os_3(CO)_9(PMe_2Ph)]$,$[(\mu\text{-}H)(\mu\text{-}Me\text{-}4\text{-}C_6H_4NHCO)Os_3(CO)_9(PMe_2Ph)$ and $[(\mu\text{-}H)\{\mu\text{-}MeN{=}COC(O)N(H)Me\}Os_3(CO)_{10}]$ (Fig. 11), have been determined. Although the hydride ligand was only directly located in $[(\mu\text{-}H)(\mu\text{-}MeN{=}COC(O)N(H)Me)Os_3(CO)_{10}]$, a $\{Os(\mu\text{-}H)(\mu\text{-}Y)Os\}$ structure appears to be generally adopted. A similar structural arrangement appears to be adopted by $[(\mu\text{-}H)(\mu\text{-}NHN{=}CPh_2)Os_3(CO)_{10}]$ [87] and $[(\mu\text{-}H)(\mu\text{-}N{=}NC_6H_4\text{-}4\text{-}Me)Os_3(CO)_{10}]$ [88], whose molecular structures are depicted in Fig. 12. $[(\mu\text{-}H)(\mu\text{-}NHN{=}CPh_2)Os_3(CO)_{10}]$ was synthesised by the action of $Ph_2C{=}N{=}N$ upon $[H_2Os_3(CO)_{10}]$ or by dehydrogenation of $Ph_2CHNHNH_2$ with $[Os_3(CO)_{10}L_2]$ (where L is MeCN or C_8H_{14}). $[(\mu\text{-}H)(\mu\text{-}N{=}NC_6H_4\text{-}4\text{-}Me)Os_3(CO)_{10}]$ was prepared according to equation (4):

$$[H_2Os_3(CO)_{10}] + [Me\text{-}4\text{-}C_6H_4N_2][BF_4] \xrightarrow[\text{(ii) dry } NH_3(g)]{\text{(i) } \Delta/CH_2Cl_2} [(\mu\text{-}H)(\mu\text{-}N{=}NC_6H_4\text{-}4\text{-}Me)Os_3(CO)_{10}] + [NH_4][BF_4] \qquad (4)$$

$[Os_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)]$ undergoes oxidative cleavage with HCl to give $[HOs_3(CO)_8(PMe_2Ph)(\mu_3\text{-}S)(\mu_3\text{-}\eta^2\text{-}SCH_2)Cl]$ which upon structural characterisation was shown (see Fig. 13) to possess triply bridging S and H_2CS moieties and only one metal-metal bond [89]. The hydride ligand, which was not directly located, was proposed to bridge the $Os_1\text{-}Os_3$ bond.

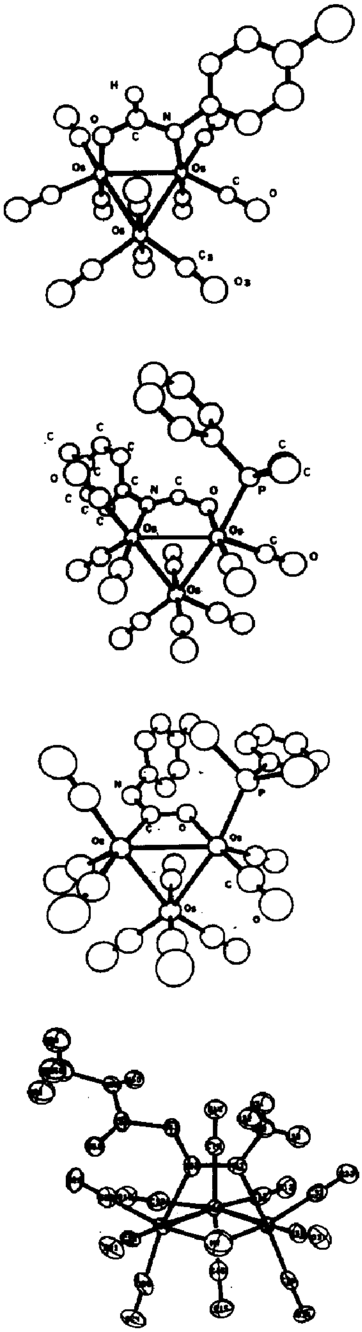
Finally, in an investigation aimed primarily at the preparation of triosmium clusters exhibiting the bonding mode (17) Deeming reported the reactions of $[Os_3(CO)_{10}(C_8H_{14})_2]$ with $PhCH_2N{=}CHNHCH_2Ph$ or $C_5H_4NNHCH_2Ph$ Scheme



$r(\mathrm{OsOs})$ = 0.2854–0.2876 nm

$r(\mathrm{OsOs})_{\mathrm{br}}$ = 0.2863,0.2873 nm

Fig. 10 The molecular structures of (A) $[(\mu\text{-}S_2CH_2)\{HOs_3(CO)_{10}\}_2]$, (B) $[(\mu\text{-}\eta^2\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_9(PMe_2Ph)]$ and (C) $[(\mu_3\text{-}\eta^2\text{-}SCH_2)(\mu_3\text{-}S)Os_3(CO)_8(PMe_2Ph)]$ [84].



(A)

$r(\mathrm{OsOs}) = 0.2888, 0.2903$ nm

$r(\mathrm{OsOs})_{br} = 0.2909$ nm

(B)

$r(\mathrm{OsOs}) = 0.2897, 0.2911$ nm

$r(\mathrm{OsOs})_{br} = 0.2940$ nm

(C)

$r(\mathrm{OsOs}) = 0.2859, 0.2893$ nm

$r(\mathrm{OsOs})_{br} = 0.2945$ nm

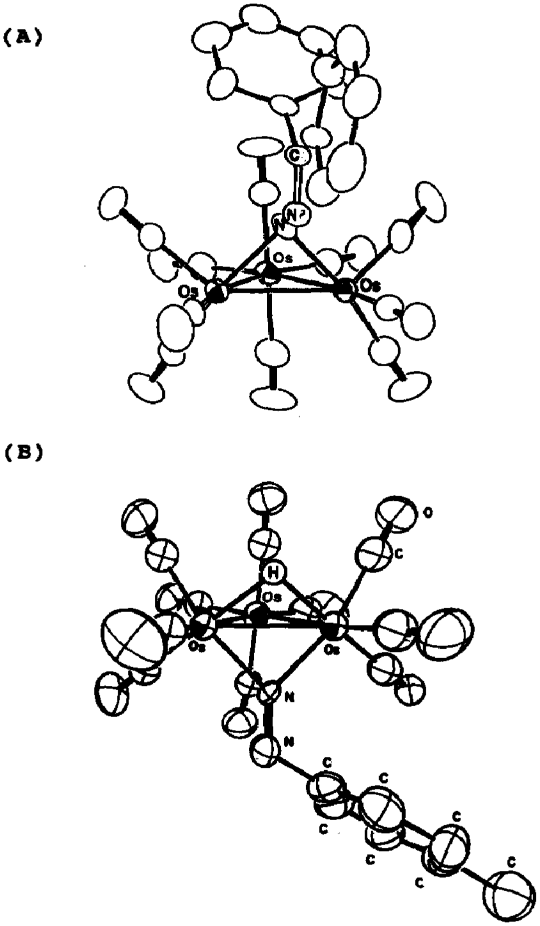
(D)

$r(\mathrm{OsOs}) = 0.2882, 0.2881$ nm

$r(\mathrm{OsOs})_{br} = 0.2923$ nm

$r(\mathrm{OsH}) = 0.194, 0.177$ nm

Fig. 11 The molecular structures of (A) $[(\mu\text{-H})(\mu\text{-Me-4-C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_{10}]$, (B) $[(\mu\text{-H})(\mu\text{-Me-4-C}_6\text{H}_4\text{NCHO})\text{Os}_3(\text{CO})_9(\text{PMe}_2\text{Ph})]$, (C) $[(\mu\text{-H})(\mu\text{-Me-4-C}_6\text{H}_4\text{NHCO})\text{Os}_3(\text{CO})_9(\text{PMe}_2\text{Ph})]$ and (D) $[(\mu\text{-H})\{\mu\text{-MeN=COC(O)N(H)CH}_3\}\text{Os}_3(\text{CO})_{10}]$ [85,86].



(A)

r(OsOs) = 0.28468,0.28421 nm

$r(\mathrm{OsOs})_{\mathrm{br}}$ = 0.27863 nm

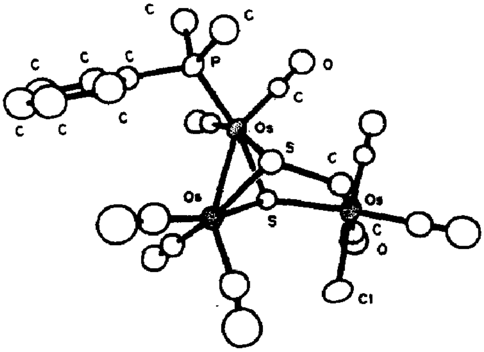
(B)

r(OsOs) = 0.2834,0.2855 nm

$r(\mathrm{OsOs})_{\mathrm{br}}$ = 0.2823 nm

r(OsH) = 0.197,0.201 nm

Fig. 12 The molecular structure of (A) $[(\mu\text{-H})(\mu\text{-NHN=CPh}_2)\mathrm{Os}_3(\mathrm{CO})_{10}]$ [87] and (B) $[(\mu\text{-H})(\mu\text{-N=N C}_6\mathrm{H}_4\text{-4-Me})\mathrm{Os}_3(\mathrm{CO})_{10}]$ [88]



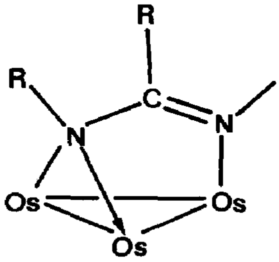
r(OsOs) = 0.2834 nm

r(Os...Os) = 0.4037, 0.4005 nm

r(OsP) = 0.2350 nm

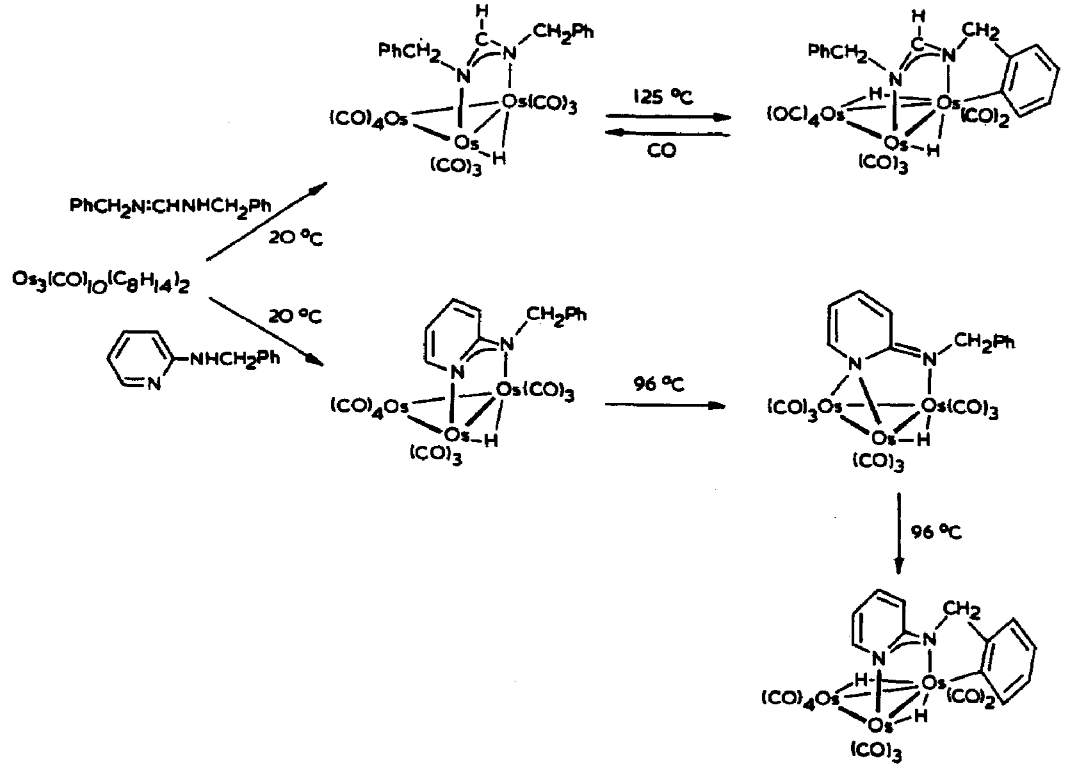
r(OsCl) = 0.2423 nm

Fig. 13 The molecular structure of $[\mathrm{HOs}_3(\mathrm{CO})_8(\mathrm{PMe}_2\mathrm{Ph})(\mu_3\text{-S})(\mu_3\text{-}\eta^2\text{-SCH}_2)\mathrm{Cl}]$ [89].



(17)

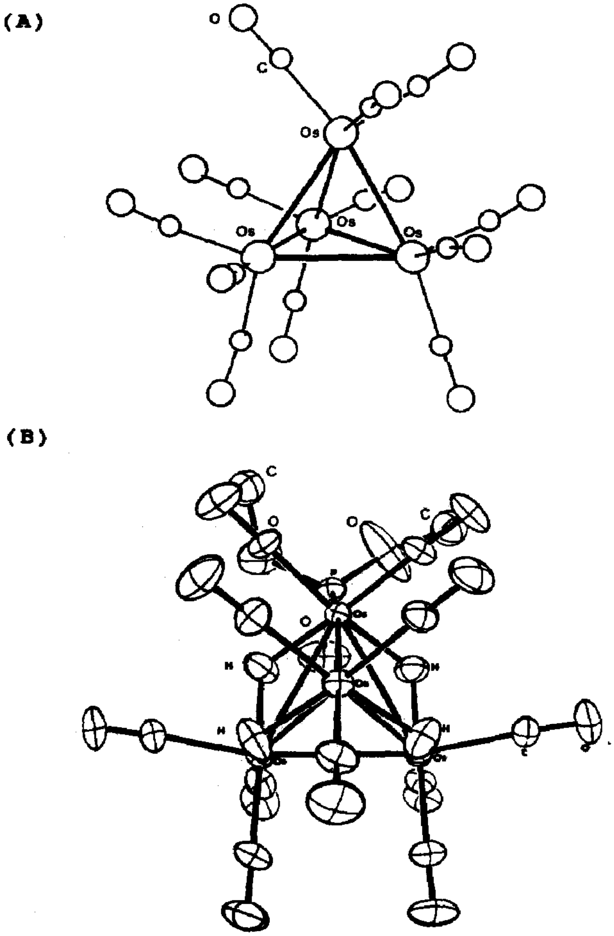
5 [77]. All the products were spectroscopically (IR and ^{1}H NMR) characterised.



Scheme 5 Some of the reactions of [$Os_3(CO)_{10}(C_8H_{14})_2$] with $PhCH_2N{=}CHNHCH_2Ph$ or $C_5H_4NNHCH_2Ph$ [77].

4.8.2 Tetrameric clusters

An X-ray structural analysis of [$H_4Os_4(CO)_{12}$] has established that the osmium atoms define a distorted tetrahedron with four long (hydrogen bridged) and two short metal-metal distances, see Fig. 14 [90]. Also contained in this Figure are the results of a combined single crystal X-ray and neutron diffraction study upon [$H_4Os_4(CO)_{11}\{P(OMe)_3\}$] [91]. The four edge-bridging hydrogen atoms contained within the approximatly D_{2d} structure of [$H_4Os_4(CO)_{11}\{P(OMe)_3\}$] were all directly located.



$\bar{r}(OsOs)_{long}$ = 0.2964 nm

$\bar{r}(OsOs)_{short}$ = 0.2817 nm

$\bar{r}(OsOs)_{long}$ = 0.2966 nm

$\bar{r}(OsOs)_{short}$ = 0.2814 nm

Fig. 14 The molecular structures of (A) [$H_4Os_4(CO)_{12}$] [90] and (B) [$H_4Os_4(CO)_{11}\{P(OMe)_3\}$] [91].

The solid state ${}^{1}H$ NMR spectrum of $[H_4Os_4(CO)_{12}]$ has also been reported; the bridging hydrogens were found to exhibit isotropic chemical shifts similar to those found in solution studies [80].

4.8.3 Pentameric clusters

Heptane solutions of $[Os_6(CO)_{18}]$ react with CO (160 °C; 90 atm; *ca.*1 hr) to give $[Os_5(CO)_{19}]$ in *ca.* 80% yield [92]. The conditions required for the formation of this pentaosmium cluster are critical and longer reaction times or higher temperatures or pressures result in a variety of osmium containing products ranging from mononuclear to heptanuclear. The molecular structure of $[Os_5(CO)_{19}]$ is depicted in Fig. 15. The five osmium atoms define two isosceles triangles which share a common vertex {*r*(OsOs) 0.2848–0.2950 nm}, this structure being colloquially refferred to as a 'bow-tie' arrangement. The two triangles are skewed with respect to each other (dihedral angle 21.2°) and the carbonyl ligands are all terminal.

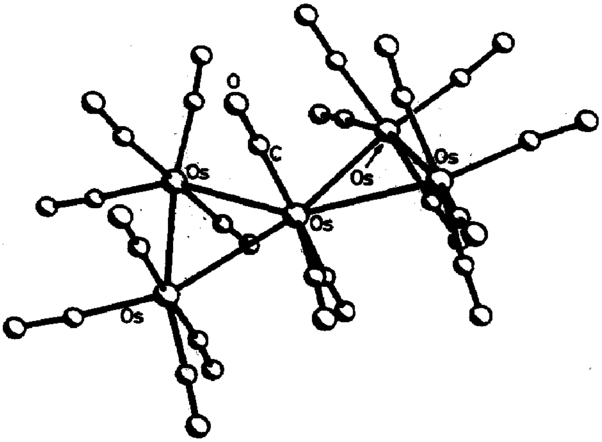


Fig. 15 The molecular structure of $[Os_5(CO)_{19}]$ [92].

$[HOs_5(CO)_{13}(PhNC_6H_4N)]$ undergoes a reversible reaction with CO to give $[HOs_5(CO)_{14}(PhNC_6H_4N)]$ [93]. Similar products are formed, but irreversibly, with other donor ligands such as PEt_3 or $CNCMe_3$ [93]. The molecular structure of $[HOs_5(CO)_{13}(PEt_3)(PhNC_6H_4N)]$ {r(OsOs) = 0.2767–0.2926 nm} is depicted in Fig. 16. Unlike the structure of the closely related cluster $[HOs_5(CO)_{13}(PhNC_6H_4N)]$ [2; pp 183–184], the Os–Os bond lengths in $[HOs_5(CO)_{13}(PEt_3)(PhNC_6H_4N)]$ all fall in the range expected for normal single Os–Os bonds; there are also differences in the arrangements of the carbonyl/PEt_3 ligands and the $PhNC_6H_4N$ moiety.

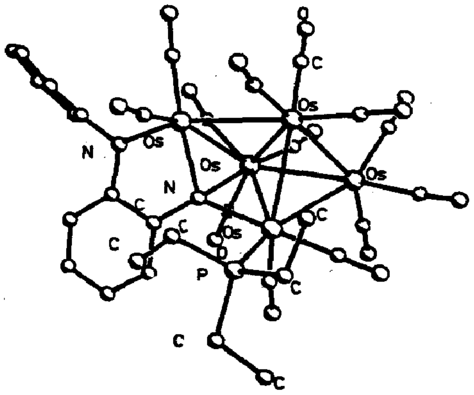
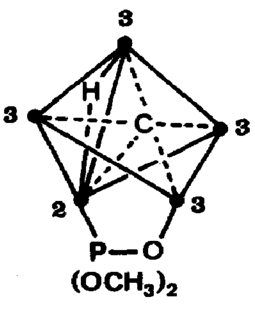
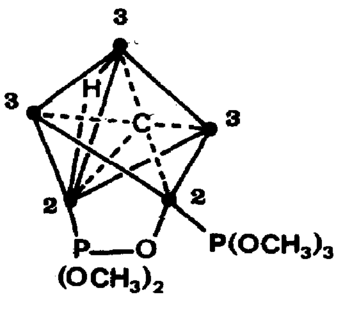


Fig. 16 The molecular structure of $[HOs_5(CO)_{13}(PEt_3)(PhNC_6H_4N)]$ [93].

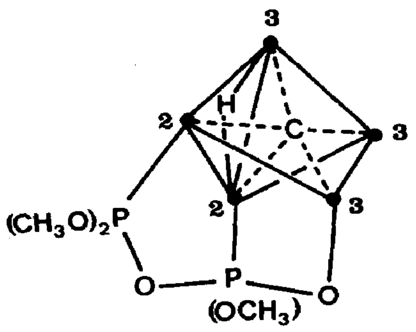
Four pentanuclear osmium clusters, $[HOs_5C(CO)_{14}\{OP(OMe)_2\}]$ (18), $[HOs_5C(CO)_{13}\{OP(OMe)_2\}\{P(OMe)_3\}]$ (19), $[HOs_5C(CO)_{13}\{OP(OMe)OP(OMe)_2\}]$ (20) and $[Os_5(CO)_{15}\{P(OMe)\}]$ (21), have been identified, *inter alia*, as products of the



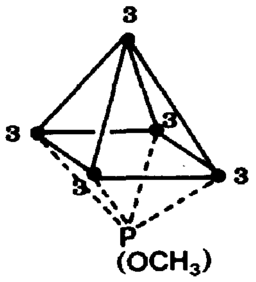
(18)



(19)

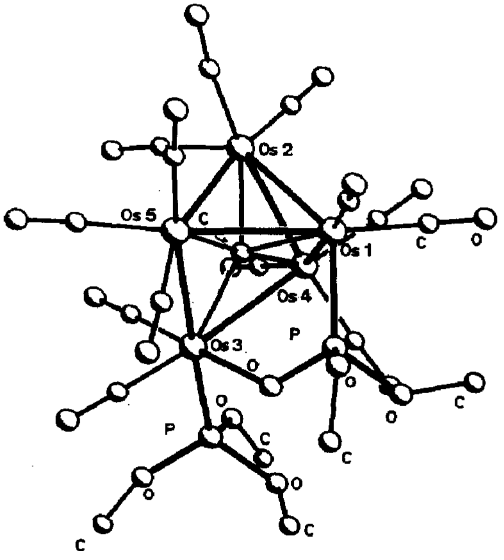


(20)



(21)

pyrolysis (210 °C; 16h) of [Os$_3$(CO)$_{11}${P(OMe)$_3$}] [94]. All the products were spectroscopically characterised; (19) was, in addition, the subject of a single crystal X-ray diffraction study (see Fig. 17) [94]. The carbonyl and P(OMe)$_3$ ligands are all terminally bound two-electron donors; the OP(OMe)$_2$ unit bridges two osmium atoms and acts as a three-electron donor.



r(OsOs) = 0.2867–0.2903 nm

Fig. 17 The molecular structure of [HOs$_5$C(CO)$_{13}${OP(OMe)$_2$}{P(OMe)$_3$}] [94].

4.8.4 Hexameric clusters

Although $[Os_6(CO)_{20}]$ is only a minor product of the reaction of $[Os_6(CO)_{18}]$ with CO under the conditions described in Section 4.8.3, *solid* $[Os_6(CO)_{18}]$ reacts with CO to give $[Os_6(CO)_{20}]$ in almost quantitative yield [92]. A detailed reaction pathway describing the carbonylation of $[Os_6(CO)_{18}]$ was presented [92].

4.8.5 High nuclearity clusters

The carbido dianion, $[Os_{10}C(CO)_{24}]^{2-}$, reacts with X_2 (X = Cl, Br or I) according to equation (5). The final high nuclearity cluster product of the reaction, $[Os_{10}C(CO)_{24}X_2]$, reforms $[Os_{10}C(CO)_{24}]^{2-}$ by the addition of nucleophiles, *viz.* X^-, PR_3 or C_5H_5N [95]. The molecular structures of $[Os_{10}C(CO)_{24}I]^-$ and $[Os_{10}C(CO)_{24}I_2]$ (Fig. 18) indicate that attack by I^+, in this case, occurs at the capping $\{Os(CO)_3\}$ units.

$$\begin{tikzcd}
{[Os_{10}C(CO)_{24}]^{2-}} \arrow[r, "2X_2"] & {[Os_{10}C(CO)_{24}X]^- + [I_3]^-} \arrow[r, "2X_2"] & {[Os_{10}C(CO)_{24}X_2] + [I_3]^-} \arrow[d, "xs\ X_2"] \\
 & & {[Os_2(CO)_6X_4]}
\end{tikzcd} \tag{5}$$

The vibrational frequencies of solid $[H_2Os_{10}C(CO)_{24}]$, its deuterium and ^{13}C, analogues and $[NMe_4]_2[Os_{10}C(CO)_{24}]$ have been recorded both at room- and liquid nitrogen temperatures [96]. Analysis of the spectra indicated that the pseudo-cubic symmetry of $[Os_{10}C(CO)_{24}]^{2-}$ was removed on protonation. The possibility of protonation occurring at the central $\{Os_6\}$ core was discussed [96].

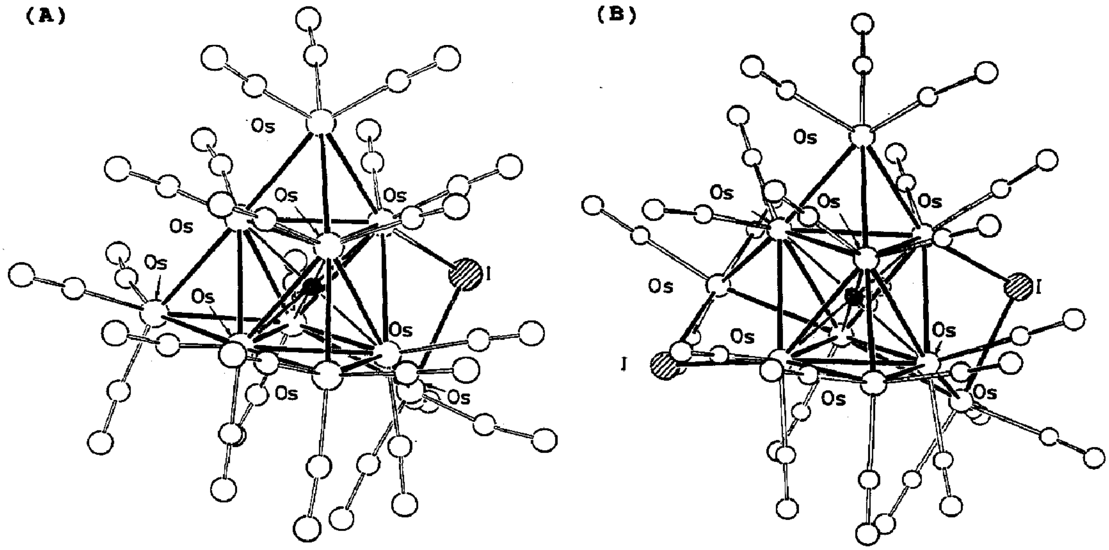


Fig. 18 The molecular structures of (A) $[Os_{10}C(CO)_{24}I]^-$ and (B) $[Os_{10}C(CO)_{24}I_2]$ [95].

4.8.6 Catalysis by cluster compounds

The hydrogenation of CO using $[Os_3(CO)_{12}]$ as a catalyst or catalyst precursor has received further attention this year. Thus, the activity of methylbenzene solutions of $[Os_3(CO)_{12}]$ towards CO/H_2 is enhanced by the presence of $P(OMe)_3$. However, isotopic labelling experiments have clearly demonstrated that the enhancement is due to an $[Os_3(CO)_{12}]$-catalysed side-reaction between H_2 and $P(OMe)_3$ (which rearranges to $(MeO)_2MePO$ under the reaction conditions), and that the enhanced methane yield is derived mainly from the phosphite methyl groups [97]. Homogeneous $[Os_3(CO)_{12}]/CO/H_2/BX_3$ systems (X = Cl or Br), in which BX_3 acts as a solvent, catalyst promoter and reactant and $[Os_3(CO)_{12}]$ acts as a catalyst precursor, have also received attention [98,99].

Continuing their studies upon cluster models for intermediates in the metal-catalysed formation of CH_4 from CO, Steinmetz and Geoffroy have described the action of acid upon $[Os_3(CO)_{11}(CHO)]^-$ (formed by the action of $[BH(OCHMe_2)_3]^-$ upon $[Os_3(CO)_{12}]$). This results in the formation of the methylene-bridged cluster $[Os_3(CO)_{11}(CH_2)]$ which, when heated under dihydrogen, evolves methane. Overall, the stepwise reduction of CO to CH_4 on a cluster face was demonstrated [79b].

The selectivity of the hydrogenation of the carbonyl group within α,β-unsaturated aldehydes using an osmium catalyst is improved if it is modified with ZnO, Al_2O_3 or B_2O_3 [101].

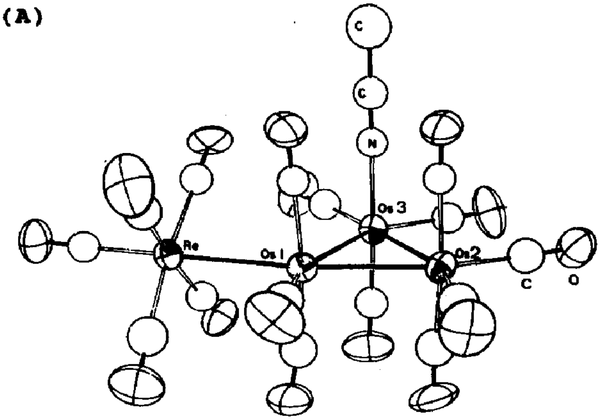
4.9 MIXED METAL CLUSTERS

The ^{13}C NMR spectra of $[Ru_2Os(CO)_{12}]$ and $[RuOs_2(CO)_{12}]$ are indicative of internuclear scrambling at 30 °C for $[Ru_2Os(CO)_{12}]$ (δ = 191.5 ppm) and 145 °C for $[RuOs_2(CO)_{12}]$ (δ = 183.9 ppm). Upon cooling to 30 °C, a new spectrum is obtained for $[RuOs_2(CO)_{12}]$ which consists of two signals at δ 186.4 and 170.3 ppm (relative intensity 10:2) [71].

Burkhardt and Geoffroy have explored the general applicability of photochemical methods for the synthesis of mixed-metal clusters [102]. In particular, they report the synthesis and characterisation of $[(Ph_3P)_2N][Os_3Co(CO)_{13}]$, $[H_2Os_3Fe(CO)_{13}]$ and $[H_2Os_3Ru(CO)_{13}]$ and discuss the mechanism of their formation. The photolysis (366 nm) of 2,2,4-trimethylpentane solutions of $[H_2FeOs_3(CO)_{13}]$ in the presence of triphenylphosphine (Φ = 0.057) or dihydrogen leads to the formation of $[H_2FeOs_3(CO)_{13-x}(PPh_3)_x]$ (x = 1 or 2) and $[H_4FeOs_3(CO)_{12}]$ respectively [103]. $[H_4FeOs_3(CO)_{12}]$ is itself photosensitive in the presence of H_2 giving rise, on photolysis, to a complex mixture of products that were not identified.

The single-crystal X-ray structures of a variety of mixed-metal clusters have been reported, see Figs 19-22. $[(\mu\text{-}H)Os_3Re(CO)_{15}(NCMe)]$ (Fig. 19 (A)) was prepared in quantitative yield by heating $[(\mu\text{-}H)_2Os_3Re_2(CO)_{20}]$ in MeCN (*n.b.* the former cluster has previously been incorrectly formulated as

(A)



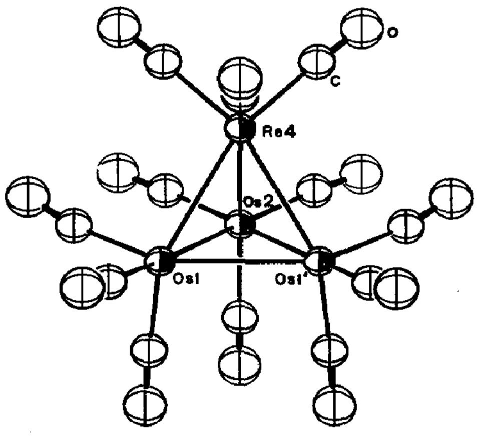
$r(\mathrm{OsRe}) = 0.2959$ nm

$r(\mathrm{Os_1Os_2}) = 0.2861$ nm

$r(\mathrm{Os_2Os_3}) = 0.2885$ nm

$r(\mathrm{Os_1Os_3}) = 0.3032$ nm

(B)



$r(\mathrm{Os_1Os_2}) = r(\mathrm{Os_{1'}Os_2}) = 0.2838$ nm

$r(\mathrm{Os_1Os_{1'}}) = 0.2964$ nm

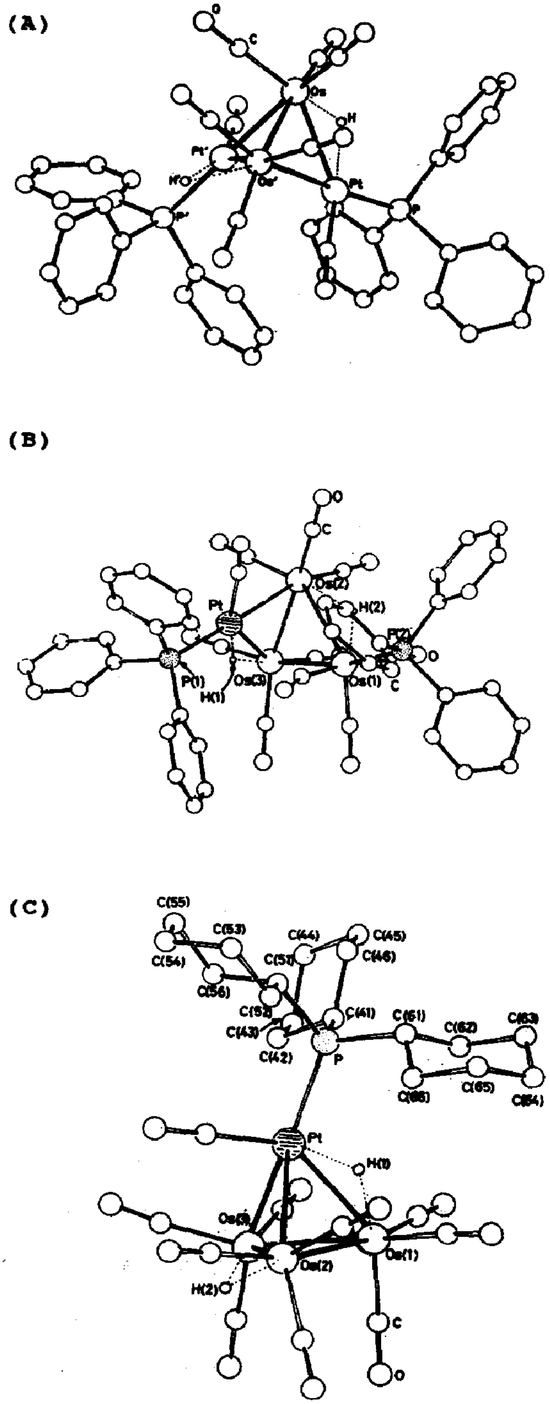
$r(\mathrm{Os_1Re_4}) = r(\mathrm{Os_{1'}Re_4}) = 0.3017$ nm

$r(\mathrm{Os_2Re_4}) = 0.2989$ nm

Fig. 19 The molecular structures of (A) $[\mathrm{HOs_3Re(CO)_{15}(NCMe)}]$ and (B) $[\mathrm{H_5Os_3Re(CO)_{12}}]$ [104,105].

$[\mathrm{HOs_3Re(CO)_{15}}]$) [104,105]. Ethanenitrile solutions of $[(\mu\text{-H})\mathrm{Os_3Re(CO)_{15}(NCMe)}]$ when heated to reflux with trimethylamine *N*-oxide under H_2, yield $[(\mu\text{-H})_5\mathrm{Os_3Re(CO)_{12}}]$ (Fig. 19 (B)). Churchill has proposed that the five hydride ligands in $[(\mu\text{-H})_5\mathrm{Os_3Re(CO)_{12}}]$ bridge five of the six edges of the tetrahedron (*n.b.* the distinction between the osmium and rhenium atoms was achieved by consideration of the relative metal-metal bond lengths) [104].

$[(\mu\text{-H})_2\mathrm{Os_2Pt_2(CO)_8(PPh_3)_2}]$, Fig. 20 (A), is one of a series of three



(A)

r(OsPt) = 0.2862,0.2708 nm

r(OsOs) = 0.2781 nm

r(Pt...Pt) = 0.3206 nm

(B)

r(OsPt) = 0.2717, 0.2848 nm

r(Os...Pt) = 0.3530 nm

r(OsOs) = 0.2914, 0.3043 nm

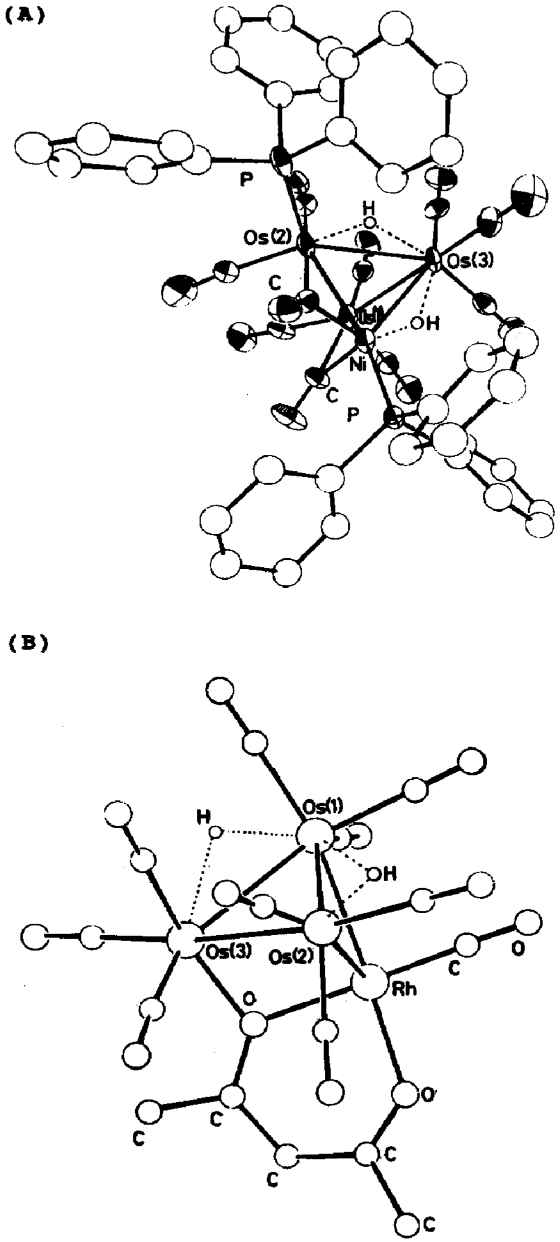
r(Os_2Os_3) = 0.2773 nm

(C)

r(OsPt) = 0.2791–0.2863 nm

r(OsOs) = 0.2741–0.2789 nm

Fig. 20 The molecular structures of (A) $[(\mu\text{-}H)_2Os_2Pt_2(CO)_8(PPh_3)_2]$ [106]
(B) $[(\mu\text{-}H)_2Os_3Pt(CO)_{10}(PPh_3)_2]$ [107] and
(C) $[(\mu\text{-}H)_2Os_3Pt(CO)_{10}\{P(C_6H_{11})_3\}]$ [108].



$r(\mathrm{OsOs}) = 0.2861$–$0.2984$ nm

$r(\mathrm{OsNi}) = 0.2605$–$0.2733$ nm

$r(\mathrm{OsOs}) = 0.2809, 0.2968$ nm

$r(\mathrm{Os_1Os_2}) = 0.2831$ nm

$r(\mathrm{OsRh}) = 0.2743, 0.2690$ nm

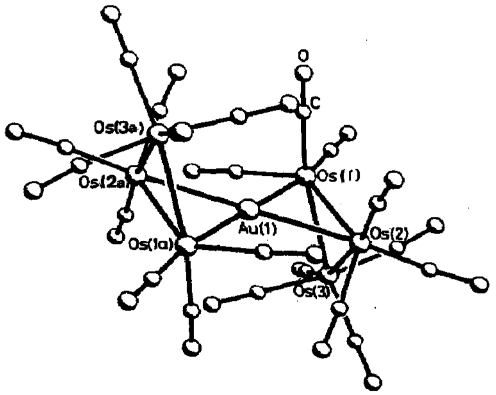
$r(\mathrm{Os...Rh}) = 0.3292$ nm

Fig. 21 The molecular structures of (A) $[(\mu\text{-H})_2Os_3Ni(CO)_{10}(PPh_3)_2]$ and (B) $[(\mu\text{-H})_2Os_3Rh(CO)_{10}(acac)]$ [109].

phosphine substituted mixed-metal osmium/platinum clusters of general formula, $[(\mu\text{-H})_2Os_2Pt_2(CO)_8(PR_3)_2]$ (R = Ph, C_6H_{11} or Me), which have been prepared by the interaction of [$H_2Os(CO)_4$] and [$Pt(C_2H_4)_2(PR_3)$]; it exhibits a butterfly arrangement of osmium and platinum atoms [106]. [$(\mu\text{-}H)_2Os_3Pt(CO)_{10}(PPh_3)_2$] (prepared by the reaction of [$(\mu\text{-}H)_2Os_3Pt(CO)_{10}(PPh_3)$] with PPh_3) also exhibits a butterfly arrangement of metal atoms, see Fig 20 (B). Reaction of [$(\mu\text{-}H)_2Os_3Pt_2(CO)_{10}(PPh_3)_2$] with but-2-yne yields a mixture of cluster products from which [$OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)$] was isolated and characterised [107]. [$(\mu\text{-}H)_2Os_3Pt(CO)_{10}\{P(C_6H_{11})_3\}$] (Fig. 20 (C)) was prepared by the interaction of [$Pt(C_2H_4)_2\{P(C_6H_{11})_3\}$] and [$H_2Os_3(CO)_{10}$] (a route that appears to have general synthetic applicablity to [$H_2Os_3Pt(CO)_{10}(PR_3)$] clusters) [108]. In addition to structural data, this report contains a detailed discussion of the variable temperature ^1H and ^{31}P NMR spectra of [$(\mu\text{-}H)_2Os_3Pt(CO)_{10}\{P(C_6H_{11})_3\}$].

The molecular structures of [$(\mu\text{-}H)_2Os_3Ni(CO)_{10}(PPh_3)_2$] and [$(\mu\text{-}H)_2Os_3Rh(CO)_{10}(acac)$] are depicted in Fig. 21. The clusters were prepared by the now well established route of interacting a low oxidation state metal complex with [$H_2Os_3(CO)_{10}$] [109].

Dark green [$N(PPh_3)_2$][$H_2Os_6Au(CO)_{20}$] has been prepared by the reaction of [$HOs_3Au(CO)_{10}(PR_3)$] (R = Ph or Et) with a two fold excess of [$N(PPh_3)_2$]Cl in CH_2Cl_2 at reflux [110]. Structural characterisation revealed the anion to possess two centrosymmetrically related {Os_3} triangles linked *via* a gold(I) atom, see Fig. 22. The short Os-Os bonds are each bridged by the gold atom



r(AuOs) = 0.2806,0.2802 nm

r(Os_1Os_2) = 0.2698 nm

r(Os_1Os_3) = 0.2830 nm

r(Os_2Os_3) = 0.2826 nm

Fig. 22 The molecular structure of [$H_2Os_6Au(CO)_{20}$]$^-$ [110].

and a hydride (not directly located). The gold atom is in a square planar environment and the dihedral angle between the $\{Os_1Os_2Os_3\}$ and $\{Os_1Os_2Au\}$ planes is 113.8°. Infrared and ^1H NMR data were also reported.

4.10 OSMIUM NITROSYLS

Sinitsyn has reviewed (in Russian) the *trans* effect in nitrosyl complexes of osmium; the usefulness of this 15 page article will undoubtedly be limited by the language barrier [111]. The same author has also reported the syntheses of *trans*-$[Os(NO)(NH_3)_4(OH)]X_2$ (X = Cl, Br or I), $[Os(NO)(NH_3)_4X]X_2$ (X = Cl, Br, I or NO_3) and $[Os(NO)(NH_3)_4(H_2O)]Cl_3.H_2O$ together with their characterisation by IR and electronic absorption spectroscopy, conductivity measurements and thermal stability studies [112]. The action of NOX (X = Cl, Br or I) or N_2O_3 upon osmium(III) chloride in the presence of EPh_3 (E = P or As) has been utilised in the preparations of $[Os(NO)X_3(EPh_3)_2]$, $[Os(NO)(NO_2)(PPh_3)_3]$ and $[Os(NO)Cl(AsPh_3)_3]$ [113]. Finally, the electrochemical reduction of $[Os(NO)(dppe)_2]^+$, which proceeds *via* two one-electron steps, has been compared with the behaviour of its ruthenium analogue [114].

4.11 OSMIUM PHOSPHIDO COMPOUNDS

Black air stable $ThOs_4P_{12}$, and its iron and ruthenium analogues, have been synthesised by direct reaction of the elements at 1150 K (in an evacuated silica ampoule); the compounds all crystallise with the filled skutterudite ($LaFe_4P_{12}$) structure [115].

4.12 SURFACE MODIFICATION

The surfaces of γ-Al_2O_3, TiO_2, SiO_2 or ZnO have been modified by reaction with $[Os_3(CO)_{12}]$ in octane at reflux; spectroscopic evidence indicates the presence of surface bound hydridoosmium clusters after this process [116]. The surfaces were subjected to temperatures between 100 and 400 °C under He, H_2 or CO at atmospheric pressure, this caused degradation of the cluster metal-metal bonds and the formation of atomically dispersed osmium. These conclusions were supported by a study of the $[Os_3(CO)_{12}]/Al_2O_3$ system by Raman spectroscopy [82]. Surface modification of Al_2O_3 by $[H_2Os_3(CO)_{10}]$, $[Os_3(CO)_{10}(C_6H_8)]$, $[Os_3(CO)_9(PPh_3)(C_6H_8)]$ or $H_2[OsCl6]$ [82,116,117] and of ZrO2 or TiO_2 by $[Os_3(CO)_{10}(C_6H_8)]$ [117] together with brief details of the catalytic activity of the modified surfaces have also been reported .

surfaces, have also been reported.

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