

6. Osmium

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INTRODUCTION

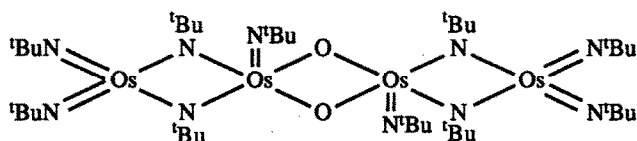
This review is the first to cover the chemistry of osmium in the new series of annual reviews and is concerned with the literature for the year 1990; some references from late 1989 are also included. The coverage corresponds to that of volumes 112 and 113 of *Chemical Abstracts*; in addition major journals for the year 1990 have been searched manually. In keeping with the new policy, the coverage of the literature is not comprehensive. Chemistry which is primarily organometallic in nature is not discussed in this review. The majority of complexes containing carbonyl ligands have been omitted on this basis, unless there are especial features of interest

associated with the other ligands which are present. No coverage of the extensive literature concerned with polynuclear cluster compounds is attempted. In general, the review is concerned with compounds and reactions which are likely to be of interest to the coordination chemist, and within these bounds omissions are somewhat idiosyncratic. We apologise to anyone whose favourite compounds have been omitted!

We should like to acknowledge the Cambridge Crystallographic Data Base for providing the coordinates of the complexes shown in the structural figures.

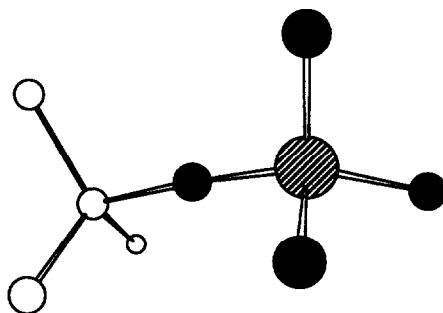
6.1 OSMIUM (VIII)

Many examples of the applications of osmium(VIII) oxide in organic synthesis and as a stain for biological materials have been reported. These will not be explicitly listed here, although structurally novel derivatives obtained in these reactions are discussed in appropriate sections dealing with lower oxidation states. An excellent review upon the general topic of oxidation of organic substrates by osmium (and ruthenium) oxo complexes has appeared [1]. An effective method for the colorimetric determination of osmium(VIII) oxide (and hence of osmium) by spectrophotometric detection at 480 nm of the coloured complex formed with thiourea, $\text{SC}(\text{NH}_2)_2$, in sulphuric acid solution has been reported [2]. Another method for the determination of osmium by the reduction of osmium(VIII) oxide with ferrocene has also been described [3]. It has also been observed that osmium(VIII) oxide shows a strong and characteristic emission which makes determination of osmium by Inductively Coupled Plasma (I.C.P.) atomic emission spectroscopy particularly attractive. The technique is particularly sensitive for acidic solutions and is very considerably superior to I.C.P. analysis of osmium in lower oxidation states. The sensitivity decreases in alkaline solution [4]. A detailed spectroscopic study of vibrationally excited osmium(VIII) oxide has been published [5]. The reaction of osmium(VIII) oxide with neat $^t\text{BuNH}(\text{SiMe}_3)$ has been investigated. The products include 20% of homoleptic osmium(VIII) *tert*-butylimido complex $\text{Os}(\text{=N}^t\text{Bu})_4$ and 10% of the tetranuclear osmium(VI) complex (1) [6].

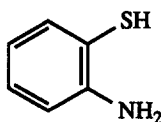


(1)

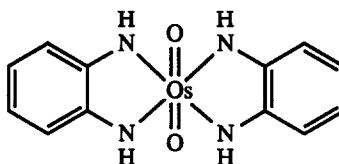
A spectroscopic study of OsO_3F_2 has been described; in general, the results are in accord with previous studies [7]. The imido complex $\text{OsO}_3(\text{=N}^t\text{Bu})$, (2), has been structurally characterised [8].



(2)



(3)



(4)

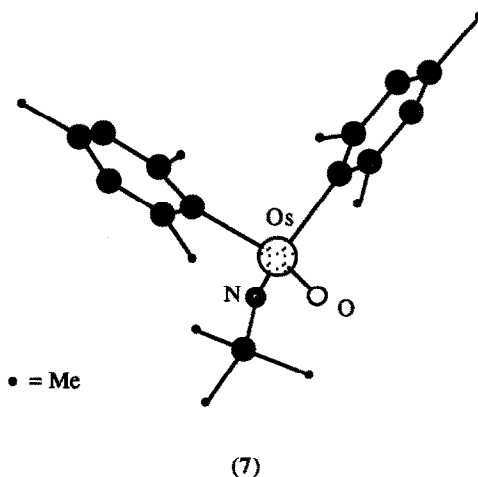
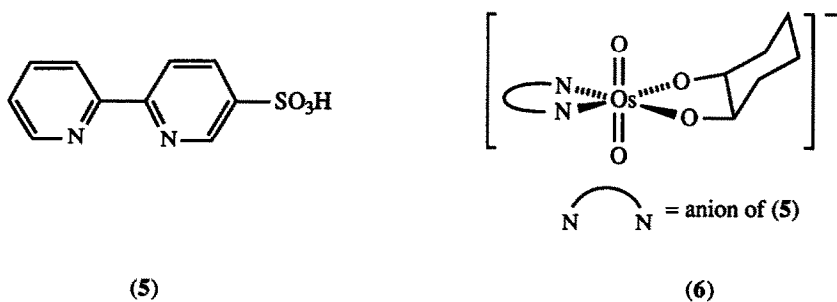
The reaction of OsO_4 with H_2L , (3), in thf and in the presence of molecular sieves gives red plates of the diamagnetic osmium(VI) complex OsL_3 (see also Section 6.2). Under similar conditions, OsO_4 reacts with 1,2-diaminobenzene to give the diamagnetic osmium(VIII) complex (4) [9].

6.2 OSMIUM (VI)

6.2.1 Oxo-complexes

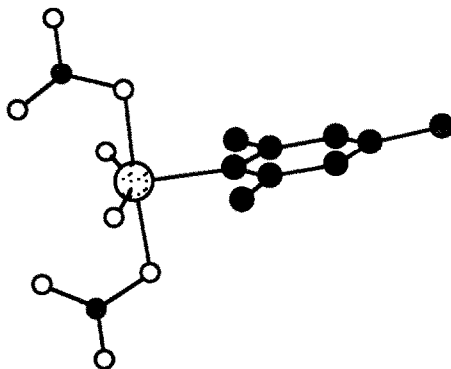
A review concerned with the oxidation of organic substrates by oxoosmium complexes has been published [1].

A detailed ^1H NMR spectroscopic study of a dioxoosmium(VI) complex containing bidentate 2,2'-bipyridine-5-sulfonate and 1,2-benzenediolate ligands has been reported [10]. The reaction of $[\text{PPh}_4]\text{L}$, where $\text{HL} = (5)$, with OsO_4 and cyclohexene gives a 94% yield of the $[\text{PPh}_4]^+$ salt of the dioxo-complex (6); ^1H NMR spectroscopic data are presented. Anion (6) is characterised by an infrared absorption for $\nu(\text{Os}=\text{O})$ at 828 cm^{-1} [11].



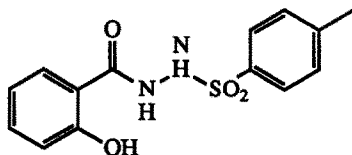
A series of preparative routes to oxoosmium(VI) species has been reported. The complexes involve diolate, trimethylsilylmethyl, methyl, ethyl, and pyridyl groups attached to the osmium centre. Dimethylbis(pyridyl)dioxoosmium has been the subject of an X-ray crystallographic study [12]. The reaction of *trans*-[OsO₂Cl₄]²⁻ with Na[OSiMe₃] gives the expected complex anion *trans*-[OsO₂(OSiMe₃)₄]²⁻. Reaction of this with Me₃SiCH₂MgCl or Mg(CH₂SiMe₃)₂ gives the osmium(VI) organometallic complex OsO(CH₂SiMe₃)₄, which may also be obtained directly from the interaction of Me₃SiCH₂MgCl with *trans*-[OsO₂Cl₄]²⁻ [13]. A series of reactions of the organometallic dioxoosmium(VI) species R₂OsO₂ (R = 2,4,6-trimethylphenyl) have been reported. Treatment with 4-*tert*-butylpyridine (L) gives the complex [OsO₂L₂R₂] in which the two oxo substituents are *trans* and the two R and L groups are mutually *cis*. A similar complex is obtained from the reaction with 2,2'-bipyridine. In contrast to these results, phosphines react to give OsO₂R₂(PR'₃)₂ (R'₃ = Me₃, Me₂Ph or MePh₂) in which the two oxo substituents and the two phosphines are *cis* and the mesityl groups are *trans*. Reaction with 2,6-dimethylphenyl isonitrile gives the five-coordinate complex OsO₂R₂(ArNC) in which the aryl groups are *trans* and the two oxo and the isonitrile ligands occupy the equatorial plane of a trigonal bipyramid. The starting complex R₂OsO₂ is obtained, together with OsO(=N^tBu)R₂, (complex (7) for R = 2,4,6-Me₃C₆H₂)

from the reaction of $\text{OsO}_3(=\text{N}^t\text{Bu})$ with MgR_2 . A corresponding reaction with the tolyl analogues was unsuccessful. A novel reaction of OsO_2R_2 with a mixture of nitric oxide and dioxygen has been reported, and the product crystallographically characterised as a diazonium salt $[\text{RN}_2][\text{cis-OsO}_2(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)(\text{ONO}_2)_2]$, $[\text{RN}_2][\text{(8)}]$. The mechanisms of these and related reactions have been discussed [8].



(8)

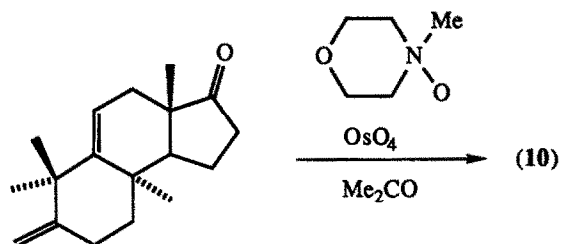
A method for the spectroscopic determination of osmium(VI) (and hence osmium) by the extraction of $\{\text{OsO}_2\}^{2+}$ from $[\text{OsO}_2(\text{OH})_4]^{2-}$ solutions by the ligand (9) has been reported [14]. Upon binding to dioxoosmium(VI) both the phenol and the hydrazido groups are deprotonated. The unusual bidentate *O-O*-donor ligand $\{\text{IO}_5(\text{OH})\}$ is present in the complex $\text{Na}_6[\text{OsO}_2\{\text{IO}_5(\text{OH})\}_2] \cdot 18\text{H}_2\text{O}$ which is the solid species precipitated from the reaction of $\text{K}_2[\text{OsO}_2(\text{OH})_4]$ with $\text{Na}[\text{IO}_4]$ in methanol. The ^{127}I NMR spectrum of this complex has been reported, as has the preparation of the related tellurato complex $\text{Na}_6[\text{OsO}_2\{\text{TeO}_4(\text{OH})_2\}_2] \cdot 8\text{H}_2\text{O}$ which is obtained from the reaction of $\text{K}_2[\text{OsO}_2(\text{OH})_4]$ with H_6TeO_6 in alkaline solution [15].



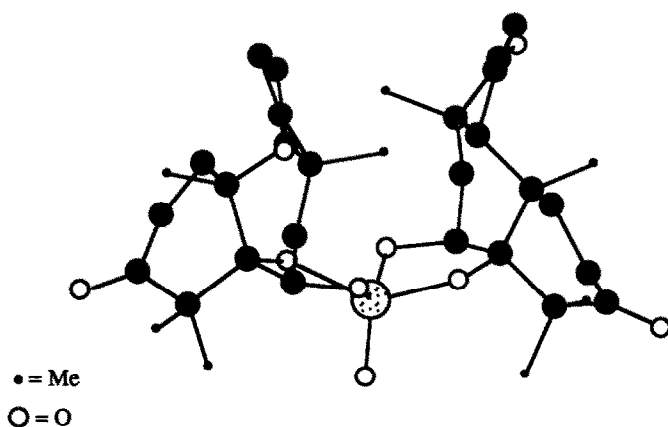
(9)

The reaction of a sterically-hindered chiral alkene with OsO_4 , Scheme (i), gives the oxoosmium(VI) complex (10). A mechanism for the reaction has been proposed and involves the

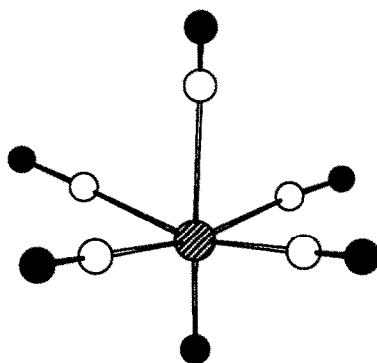
stepwise incorporation of the two organic ligands. Hydrolysis of (10) gives the diol or the original alkene [16].



Scheme (i)



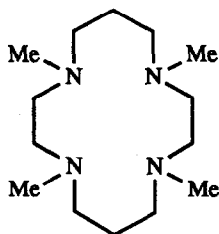
(10)



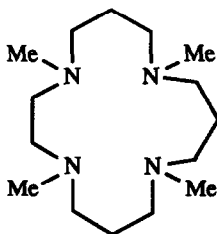
(11)

The reaction of $[\text{Os}(\equiv\text{N})\text{Cl}_4]^-$ with cyanide in methanolic thf yields the yellow six-coordinate complex *trans*- $[\text{Os}(\equiv\text{N})(\text{OH})(\text{CN})_4]^{2-}$ in which the four cyano ligands occupy the equatorial plane. Upon recrystallisation from methanol in the presence of cyanide the new anion $[\text{Os}(\equiv\text{N})(\text{CN})_5]^{2-}$ (**11**) is formed [17]. The reaction of either *trans*- $[\text{Os}(\equiv\text{N})(\text{OH})(\text{CN})_4]^{2-}$ or $[\text{Os}(\equiv\text{N})(\text{CN})_5]^{2-}$ with $\text{CF}_3\text{CO}_2\text{H}$ generates the new anion *trans*- $[\text{Os}(\equiv\text{N})(\text{OCOCF}_3)(\text{CN})_4]^-$, whilst treatment with $(\text{CF}_3\text{CO})_2\text{O}$ yields *trans*- $[\text{Os}(\equiv\text{NCOCF}_3)(\text{OCOCF}_3)(\text{CN})_4]^-$ [17]. Substitution of the hydroxide groups in *trans*- $[\text{OsO}_2(\text{OH})_4]^{2-}$ by CN^- , $\text{C}_2\text{O}_4^{2-}$, MeO^- , NCO^- , NCS^- , SeCN^- , py, or bpy has been described [18].

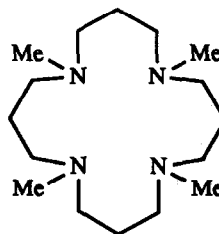
The photochemical oxidation of various organic substrates with osmium(VI) has been investigated. Osmium complexes involved include *trans*- $[\text{OsO}_2(\text{CN})_4]^{2-}$ [19]. The reaction of Na_2OsCl_6 with the macrocycle (**12**), **L**, in the presence of tin followed by treatment with water and hydrogen peroxide gives $[\text{OsO}_2\text{L}]^{2+}$. Similar reactions with ligands (**13**) to (**15**) have also been carried out. The dication $[\text{OsO}_2\text{L}]^{2+}$ is reduced electrochemically to the corresponding monocation. Reactions of $[\text{OsO}_2\text{L}]^{2+}$, where **L** = (**12**) or (**15**), with PPh_3/MeCN give $[\text{OsL}(\text{MeCN})_2]^{2+}$ [20]. Rate constants for the electron transfer quenching of *trans*- $[\text{OsO}_2\text{L}]^{2+}$, where **L** = (**12**) or (**15**), have been determined. The 3E_g states of the dications are powerful one electron oxidants [21]. A discussion of the photochemistry and photophysics of the complexes *trans*- $[\text{OsO}_2\text{L}]^{2+}$ for **L** = (**12**) to (**15**) has been presented [22].



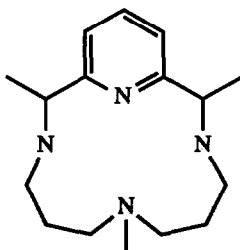
(12)



(13)

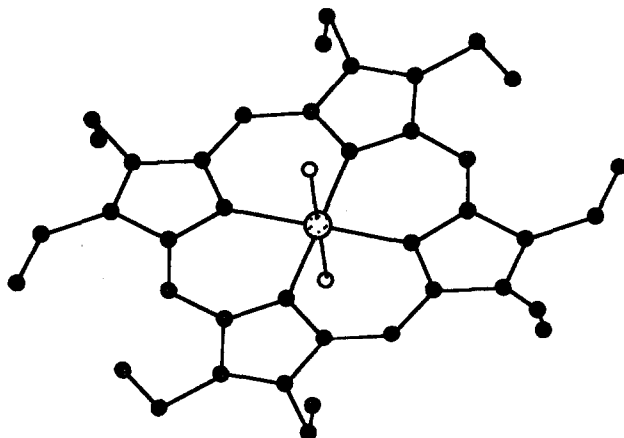


(14)



(15)

The molecular structure of the complex (2,3,7,8,12,13,17,18-octaethylporphyrinato) dioxoosmium(VI), (16), has been determined. The porphyrin ring is essentially planar and the osmium atom is in the plane of the four nitrogen atom donors; pertinent distances are Os-N(av.) = 2.052 (6) Å and Os-O(av.) = 1.745 (5) Å [23].



(16)

The reaction of *trans*-[OsO₂(OMe)₄]²⁻ with carbon monoxide in methanol gives the diosmium complex [(MeO₂C)₂OsO₂(μ-OMe)₂OsO₂(O₂CMe)₂]²⁻. Each osmium atom retains two axial oxo-ligands. This feature and the presence of two bridging methoxy-ligands and terminal acetate groups have been confirmed crystallographically [24].

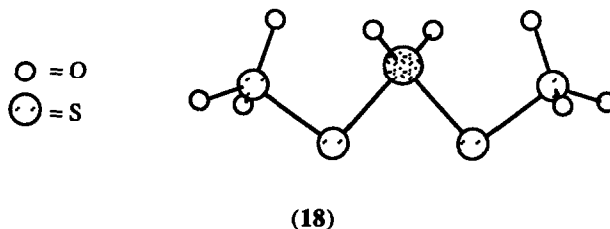


(17)

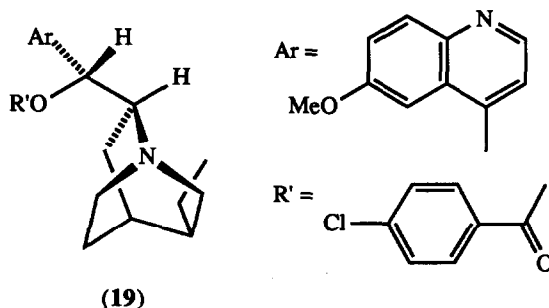
A novel five-coordinate osmium(VI) oxo complex has been prepared and is stabilised by diaminato ligands. The new red complex contains the cation [OsO(HNCMe₂CMe₂NH)(HNCMe₂CMe₂NH)]⁺ and the perchlorate salt has been characterised by X-ray crystallography; the cation is shown in structure (17). The Os-O bond length is 1.72 (2) Å. In the infrared spectrum, the oxo group is characterised by an absorption, ν_{Os=O}, at 920 cm⁻¹ [25]. Complex (17) can be formed from *trans*-[OsO₂L₂]²⁺ where L = H₂NCMe₂CMe₂NH₂ by treatment with base or from K[OsO₃(N^tBu)] by treatment with L in methanol. An osmium(VIII)

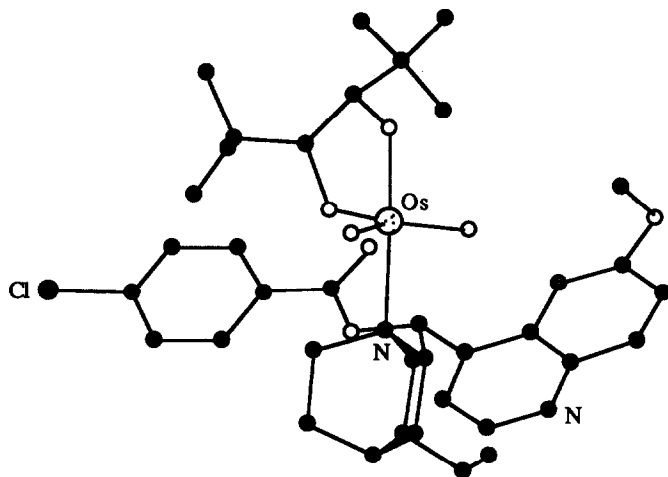
complex, (4), related to (17) was described in Section 6.1 [9]. The reaction of OsO_4 with H_2L , (3), in the presence of molecular sieves gives the diamagnetic osmium(VI) complex OsL_3 which has a distorted octahedral coordination shell about the metal atom. An electrochemical study of OsL_3 shows that the complex exhibits two reversible oxidation and two reversible reduction processes [9].

The synthesis and structural characterisation of $[\text{Bu}_4\text{N}][\text{OsO}_2(\text{SSO}_3)_2]$, the dianion of which is shown in (18), have been described. Anion (18) possesses C_2 symmetry; pertinent parameters are $\angle \text{S-Os-O} = 108.5 (1)^\circ$, $\angle \text{O-Os-O} = 127.2 (2)^\circ$, $\angle \text{S-Os-S} = 89.2 (1)^\circ$, $\text{Os-O} = 1.692 (3) \text{ \AA}$, $\text{Os-S} = 2.218 (1) \text{ \AA}$. The complex is diamagnetic and electrochemical studies show $E_{1/2} = -1.10 \text{ V}$ with respect to the Fc/Fc^+ couple [26].

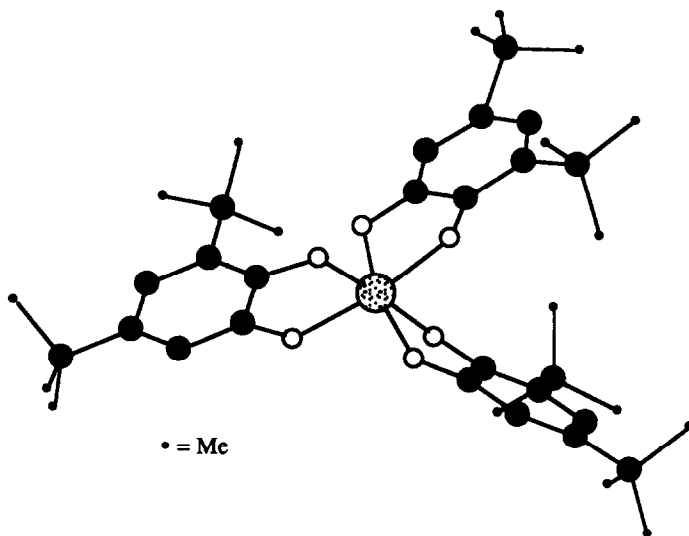


The reactions of OsO_4 with olefins in the presence of chiral auxiliaries have been investigated. Equimolar amounts of OsO_4 , *trans*- $^t\text{BuHC}=\text{CH}^t\text{Bu}$, and the chiral organic compound (19) react to give dioxo-((3*S*,4*S*)-2,2,5,5-tetramethyl-3,4-hexanediolato-*O,O'*)-((4-(6-methoxy)quinolyl)-(6-(3-ethyl)quinuclidinyl)methyl *p*-chlorobenzoate-*N*)osmium(VI), (20). A similar reaction leads to dioxo-((3*R*,4*R*)-2,5-dimethyl-3,4-hexanediolato-*O,O'*)-((4-(6-methoxy)quinolyl)-(6-(3β-ethyl)quinuclidinyl)methyl *p*-chlorobenzoate-*N*)osmium(VI). Each of the products has been characterised by single crystal X-ray analysis and in each, the osmium atom is in an approximately trigonal bipyramidal coordination site. There are differences in the stereochemistry of the ethyl substituent in the two complexes [27].





(20)



(21)

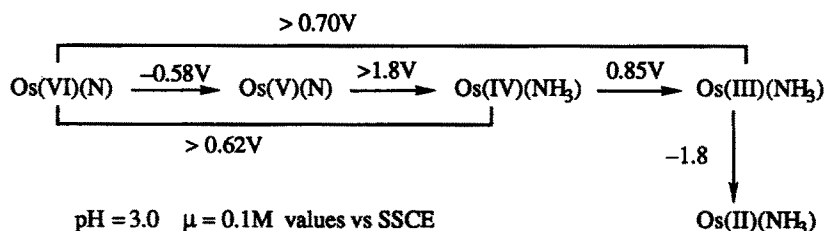
6.2.2 Complexes with oxygen donor ligands other than oxo-complexes

Osmium tetroxide reacts with H_2L where $H_2L = 1,2-(OH)_2-3,5-tBu_2C_6H_2$ to give OsL_3 . An analogous ruthenium complex has also been synthesised. The infrared spectral properties of the osmium and ruthenium complexes are similar but differ from those of an iron analogue which

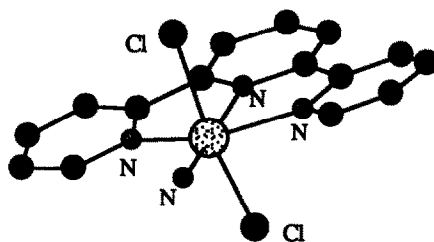
exhibits a semiquinone structure. The structure of *trans-tris*(3,5-di-⁴butylquinone)osmium (21) has been determined; Os-O bond lengths fall in the range 1.947(7) to 1.984 (7) Å. Both the osmium and ruthenium complexes are diamagnetic. Complex (21) racemises and isomerises by a twist mechanism; the mechanism is discussed [28].

6.2.3 Complexes with nitrogen donor ligands

The tetrabutylammonium salt of $[\text{Os}(\text{N})\text{X}_4]^-$ ($\text{X} = \text{Cl}$ or Br) reacts with terpy under reflux conditions in acetone to yield the complexes $[\text{Os}(\text{N})(\text{terpy})\text{X}_2]\text{X}$. For $\text{X} = \text{Cl}$, the crystal structure of the purple product has been determined; the cation is shown in structure (22) and exhibits a short nitrido Os-N bond of 1.663 (5) Å. The Os-N_{terpy} distances are 2.073 (4), 2.162 (4), and 2.086 (4) Å. Electrochemical or chemical reduction of the osmium(VI) complex (22) in acidic aqueous solution gives the osmium(II) complex $\text{Os}(\text{NH}_3)(\text{terpy})\text{Cl}_2$. The interconversion is reversible. Electrochemical studies are described in detail and some results are summarised in Scheme (ii) [29].



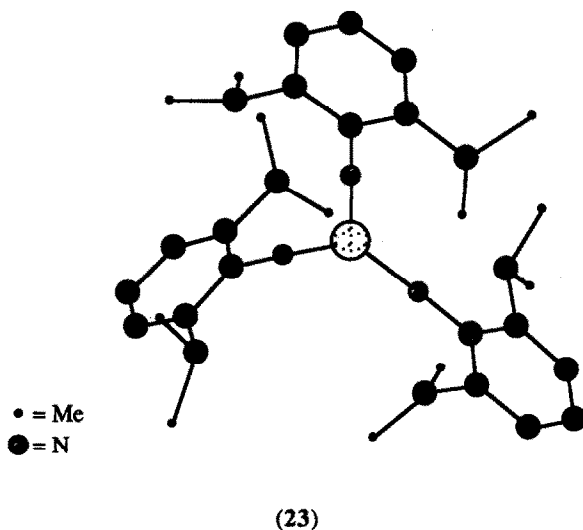
Scheme (ii)



(22)

Osmium tetroxide reacts with $(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{NCO}$ (ArNCO) to produce $\text{Os}(\text{NAr})_3$ (23). This is an example of a formally 20 electron complex with a planar disposition of donor atoms about the osmium atom. Structural data show Os-N distances of 1.736 (5) Å (twice) and 1.738 (7) Å and $\angle\text{N-Os-N} = 119.8 (3)^\circ$ and $120.1 (2)^\circ$ (twice). This complex suggests that the

observation of a linear imido-ligand does *not* necessarily mean that the lone pair of electrons from the nitrogen donor atom is donated to the central metal atom. Complex (23) is soluble and is stable in organic solvents; it does not react with water but does react with PPhMe_2 to give *trans*- $\text{Os}(\text{NAr})_2(\text{PPhMe}_2)_2$ the structure of which has been confirmed crystallographically [30].



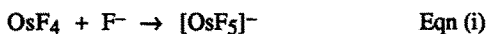
6.2.4 Complexes with hydride ligands

As part of a study of multihydride complexes of rhenium, osmium, and iridium, the preparation and spectroscopic characterisation of $\text{OsH}_6(\text{PR}_3)_2$, $\text{OsH}_4(\text{PR}_3)(\eta^2\text{-dppm})$, and $\text{OsH}_4(\text{PR}_3)_2(\eta^1\text{-dppm})$ ($\text{R} = \text{C}_6\text{H}_{11}$) have been reported. The hydride $\text{OsH}_6(\text{PR}_3)_2$ forms when $\text{OsO}_2\text{Cl}_2(\text{PR}_3)_2$ is treated with LiAlH_4 ; the precursor is prepared from OsO_4 , HCl and PR_3 . See Section 6.3 for the osmium(IV) complexes $\text{OsH}_4(\text{PR}_3)(\eta^2\text{-dppm})$, and $\text{OsH}_4(\text{PR}_3)_2(\eta^1\text{-dppm})$ [31].

6.3 OSMIUM (IV)

6.3.1 Complexes with halide ligands

The enthalpy change for the addition of fluoride ion to osmium(IV) fluoride, Eqn (i), has been determined to be $364 \pm 27 \text{ kJ mol}^{-1}$ [32]. The ^{19}F NMR spectroscopic shifts and spin-spin couplings for $[\text{OsF}_6]^{2-}$, $[\text{OsF}_5\text{Cl}]^{2-}$, *cis*- $[\text{OsF}_4\text{Cl}_2]^{2-}$, *fac*- $[\text{OsF}_3\text{Cl}_3]^{2-}$ and *trans*- $[\text{OsF}_2\text{Cl}_4]^{2-}$ have been measured and the results have been analysed in terms of electronic wavefunctions [33].



Osmium(IV) hexachloride dianion has been the subject of a solid state ^{35}Cl NQR spectroscopic study [34, 35]. The Cl K β -emission fluorescence spectra of $[\text{NH}_4]_2[\text{OsCl}_6]$ [36] and $\text{K}_2[\text{OsCl}_6]$ [37] have been measured. A UV spectroscopic study of $[\text{NH}_4]_2[\text{OsCl}_6]$ in the presence of other metal ions has been carried out. Beer-Lambert behaviour has been observed [38]. The electron density distribution in $\text{K}_2[\text{OsCl}_6]$ has been determined [39].

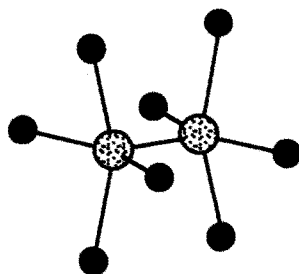
A vibrational spectroscopic study of $[\text{OsCl}_n\text{Br}_{6-n}]^{2-}$ ($n = 0-6$) has been carried out; for $n = 2$ and 4, the geometrical isomers have been studied at 80K. The bromide ligand exerts a stronger *trans*-influence than the chloride ligand [40]. An investigation of $\text{K}_2[\text{OsCl}_n\text{Br}_{6-n}]$ has looked at damage by halogen recoil atoms [41].

A report of some reactions of $[\text{Bu}_4\text{N}]_2[\text{OsBr}_6]$ have detailed the formation of the blue complex anions $[\text{Os}_2\text{Br}_{10}]^{2-}$ and $[\text{Os}_2\text{Br}_9]^{2-}$. These have been isolated as the $[\text{PPh}_4]^+$ salts; infrared spectroscopic data are given in Table 1. Borohydride reduction of $[\text{Os}_2\text{Br}_9]^{2-}$ yields the osmium(III) complex anion $[\text{Os}_2\text{Br}_9]^{3-}$; this has been isolated as the $[\text{Bu}_4\text{N}]^+$ salt as an air sensitive, blue-black material and infrared spectral data are listed in Table 1. Electrochemical reduction of $[\text{Os}_2\text{Br}_{10}]^{2-}$ leads to $[\text{Os}_2\text{Br}_{10}]^{3-}$, $[\text{Os}_2\text{Br}_{10}]^{4-}$ and $[\text{Os}_2\text{Br}_{10}]^{5-}$ although the latter decomposes rapidly to $[\text{Os}_2\text{Br}_9]^{4-}$ and bromide ion [42].

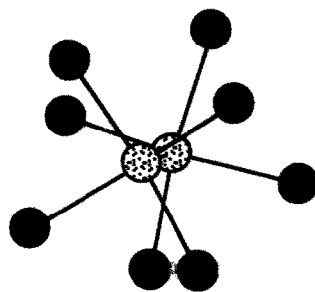
Table 1 *Infrared characteristics of some binuclear osmium(IV) and osmium(III) polybromide complexes.*

Complex	$\nu(\text{Os-Br})$ terminal / cm^{-1}	$\nu(\text{Os-Br})$ bridge / cm^{-1}
$[\text{Os}_2\text{Br}_{10}]^{2-}$	235, 222, 198	170
$[\text{Os}_2\text{Br}_9]^{2-}$	230 br	183
$[\text{Os}_2\text{Br}_9]^{3-}$	223, 203	181

The molecular structure of $[\text{MePh}_3\text{P}]_2[\text{Os}_2\text{Cl}_8]$ has been determined. In the anion, (24), the two OsCl_4 -units are mutually eclipsed; the Os-Os distance is 2.209 (1) Å [43]. When treated with hydrogen iodide in CH_2Cl_2 , $[\text{nBu}_4\text{N}]_2[\text{Os}_2\text{Cl}_8]$ is converted to the green-brown complex $[\text{nBu}_4\text{N}]_2[\text{Os}_2\text{I}_8]$. The structure of this salt has also been established crystallographically and the anion, (25), exhibits mutually staggered OsI_4 -units [43]. The structure of (25) has been independently determined for the $[(\text{Ph}_3\text{P})_2\text{N}]^+$ salt and again, it has been shown to possess staggered OsI_4 -units [44]. Attention is drawn to the trend in the Os-Os distance as a function of halide in $[\text{Os}_2\text{X}_8]^{2-}$: 2.182, 2.196, 2.217 Å for X = Cl, Br, I respectively [43]. The preparation of $[\text{Os}_4\text{I}_{14}]^{2-}$ has also been reported [43, 45]. The structure [45] of this dianion consists of two staggered Os_2I_8 -units connected by shared iodine atoms.



(24)

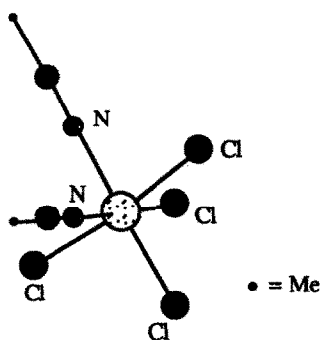


(25)

Tribromo(methoxy)*bis*(triphenylphosphine)osmium(IV) has been prepared from $[\text{nBu}_4\text{N}]_2[\text{OsBr}_6]$ and has been characterised by a single crystal X-ray diffraction study [46]. The phosphine ligands lie mutually *trans* with $\text{Os-P} = 2.413$ (3) and 2.424 (3) Å. For the bromide ligands, distances are $\text{Os-Br}_{(\text{trans to OMe})} = 2.471$ (2) Å and $\text{Os-Br}_{(\text{trans to Br})} = 2.492$ (2) and 2.494 (2) Å and the angle $\angle \text{Br-Os-Br} = 100.9^\circ$; $\text{Os-O}_{\text{OMe}} = 2.200$ (7) Å.

Members of a series of complexes with the general formula OsL_2X_4 ($\text{L} = \text{PEt}_3, \text{PPh}_3, \text{PPhEt}_2, \text{PPh}_2\text{Et}, \text{AsEt}_3, \text{AsPh}_3, \text{SbPh}_3, \text{SeMe}_2, \text{py}$; $\text{X} = \text{Cl}, \text{Br}$) have been synthesised; for example, $\text{Os}(\text{SbPh}_3)_2\text{Cl}_4$ is prepared from $\text{Os}(\text{SbPh}_3)_3\text{Cl}_3$ by treatment with chlorine [47]. Derivative osmium(III) complexes are described in Section 6.4.1.

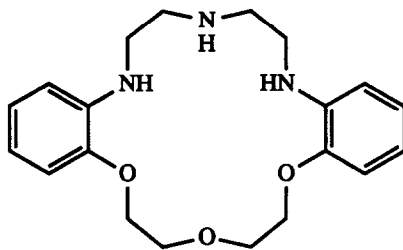
The complex *bis*(acetonitrile)tetrachloroosmium, (26), has been prepared and structurally characterised; it crystallises as an acetonitrile solvate [48].



(26)

6.3.2 Complexes with nitrogen and oxygen donor ligands

The extraction of osmium(IV) with the macrocyclic ligand (27) has been investigated. This has been developed into a method for the determination of Os(IV) in the 10^{-4} to $10^{-2} \mu\text{g cm}^{-3}$ range [49].



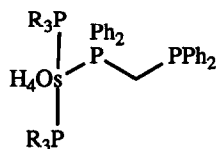
(27)

Some novel osmium(IV) porphyrin complexes have been prepared and characterised spectroscopically and electrochemically. For $H_2L = OEPH_2$, p -X-TPPH₂ (X = MeO, H, Me, Cl) and *meso*porphyrin IX dimethyl ester, the dioxo-complex OsO_2L has been used as a precursor to $Os(OR)_2L$ (R = Me, Et, ⁱPr). Other complexes synthesised are $Os(OPh)_2(OEP)$, $Os(OPh)_2(TPP)$, $Os(SPh)_2(OEP)$, $Os(SPh)_2(TPP)$, and $OsBr_2(TPP)$. The latter has been prepared from $OsO_2(TPP)$ and bromine. UV-vis spectroscopic data are reported, in addition to well resolved paramagnetically shifted ¹H NMR spectral results. Reversible electrochemical oxidation occurs to give osmium(V) species for all but the $Os(SPh)_2L$ complexes [50].

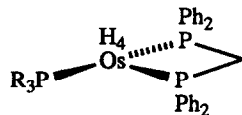
When $[NH_4]_2[OsCl_6]$ is treated with ammonia in a sealed tube for three days at 150°C, the dinuclear complex $[Os_2N(NH_3)_8Cl_2]Cl_3 \cdot 2H_2O$ is formed. The related osmium(IV) complex $[Os_2N(NH_3)_7Cl_3]Cl_2$ has been prepared in a similar manner. Both complexes aquate with concomitant loss of chloride ion to give $[Os_2N(NH_3)_7(OH_2)_3]^{5+}$ and $Os_2N(NH_3)_8(OH_2)_2$. Values of pK_a have been measured [51].

6.3.3 Complexes with hydride ligands

The osmium(VI) complex $OsH_6\{P(c-C_6H_{11})_3\}_2$ was described in Section 6.2.4. It reacts with dppm to give $OsH_4(PR_3)_2(\eta^1\text{-dppm})$, (28), and $OsH_4(PR_3)(\eta^2\text{-dppm})$, (29), (R = *c*-C₆H₁₁). These complexes have been characterised by ³¹P and ¹H NMR spectroscopy [31]. The donor atoms in the tetrahydrido complex $OsH_4(PMe_2Ph)_3$ provide a pentagonal bipyramidal coordination sphere around the metal atom. Chemical trapping of PMe_2Ph and H_2 from this complex has evidenced concurrent photodissociation of the latter species in a variety of solvents. The final products of the photochemical process are $Os_2H_4(PMe_2Ph)_6$ and $Os_2H_4(PMe_2Ph)_5$. Both have been structurally characterised by X-ray diffraction. In $Os_2H_4(PMe_2Ph)_6$, the Os-Os distance is 2.818 (1) Å; there are two bridging hydrido ligands and one terminal hydride ligand per osmium atom. In $Os_2H_4(PMe_2Ph)_5$, the Os-Os distance is 2.551 (1) Å. This bond is supported by three bridging hydride ligands; one osmium atom possesses one terminal hydride and two phosphine ligands whilst the second osmium atom has attached to it three phosphine ligands [52].

R = *c*-hexyl

(28)

R = *c*-hexyl

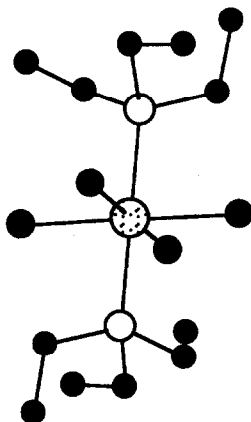
(29)

6.4 OSMIUM(III)

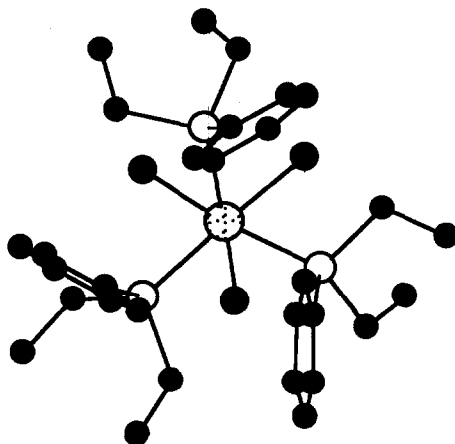
6.4.1 Complexes with halide and pseudo-halide ligands

The salt $K_2[Os(NO)X_5]$ ($X = F, Cl, Br$ or I) has been studied by infrared and Raman spectroscopy [53]. Photoinduced electron transfer in the couple $[Os(CN)_6]^{3-/4-}$ has been described [54].

In Section 6.3.1, osmium(IV) complexes of type OsL_2X_4 ($L =$ phosphine, arsine, stibine, $seMe_2$, py , and $X = Cl$ or Br) were described [47]. Some of these have been used as precursors to a series of osmium(III) complexes. For example, $Os(PEt_3)_2Cl_4$ is reduced by borohydride in ethanol to give $[Os(PEt_3)_2Cl_4]^-$. The structure of $[PPh_4][Os(PEt_3)_2Cl_4]$ has been confirmed by X-ray diffraction; the anion is (30) [47]. The reaction of OsO_4 with L and HX ($L = AsEt_3$ or PR_3 where $R_3 = Me_3, Et_3, Et_2Ph, EtPh_2$; $X = Cl, Br$) gives the complexes *mer*- OsL_3X_3 . Oxidation of these compounds by HNO_3/HBF_4 gives $[mer-OsL_3X_3][BF_4]$. Similarly, *fac*- and *mer*- $[Os(py)_3X_3]^+$ have been synthesised. An X-ray diffraction study of *fac*- $Os(PEt_2Ph)_3Cl_3$ (31) has been carried out [55].



(30)



(31)

A series of related papers covers some mixed ligand osmium(III) complexes. Infrared and Raman spectroscopic data have been discussed for $[\text{Os}(\text{NO})(\text{NH}_3)_3\text{X}(\text{H}_2\text{O})]\text{Y}_2$ where $\text{X} = \text{Cl}$, $\text{Y} = \text{Cl}$, Br , I , or $\text{X} = \text{Y} = \text{Br}$ or I and for $[\text{Os}(\text{NO})(\text{NH}_3)_4(\text{H}_2\text{O})]\text{Cl}_3 \cdot \text{H}_2\text{O}$. The results suggest the presence of intramolecular hydrogen bonds between water molecules and halide ions [56]. The complexes $[\text{Os}(\text{NO})(\text{NH}_3)_4\text{X}]\text{X}_2$ for $\text{X} = \text{Br}$, I or NO_3 react with ammonium chloride with an exchange of the non-coordinated X^- for chloride ion; structural data are presented for $[\text{Os}(\text{NO})(\text{NH}_3)_4\text{Cl}]\text{Cl}_2$, $[\text{Os}(\text{NO})(\text{NH}_3)_4\text{Br}]\text{Br}_2$, $[\text{Os}(\text{NO})(\text{NH}_3)_4\text{Br}]\text{Cl}_2$, $[\text{Os}(\text{NO})(\text{NH}_3)_4\text{I}]\text{Cl}_2$ and $[\text{Os}(\text{NO})(\text{NH}_3)_4(\text{NO}_3)]\text{Cl}_2$ [57]. The fusion of $[\text{NH}_4][\text{HF}_2]$ with $[\text{Os}(\text{NO})(\text{NH}_3)_4(\text{OH})]^{2+}$ yields $[\text{Os}(\text{NO})(\text{NH}_3)_4\text{F}]^{2+}$ isolated as I^- , Cl^- and $[\text{SiF}_6]^{2-}$ salts. Similar reactions between $[\text{Os}(\text{NO})\text{F}_5]^{2-}$ or $[\text{Os}(\text{NO})\text{Cl}_5]^{2-}$ and $[\text{NH}_4][\text{HF}_2]$ have also been studied [58].

A series of diosmium bromides including the osmium(III) complex anion $[\text{Os}_2\text{Br}_9]^{3-}$ was described in Section 6.3.1 and Table 1 [42]. Diosmium(III) bromide complexes with an $\text{Os} \equiv \text{Os}$ bond are rare and methods for converting suitable chloride to bromide complexes have been developed. $\text{Os}_2(\text{O}_2\text{CR})_4\text{Cl}_2$ ($\text{R} = \text{Et}$) reacts with HBr at -78°C to yield the red-brown compound $\text{Os}_2(\text{O}_2\text{CR})_4\text{Br}_2$. An analogous reaction with $\text{R} = \text{Pr}$ is also successful. $\text{Os}_2\text{L}_4\text{Cl}_2$ where $\text{HL} = 2$ -hydroxypyridine can also be converted to the corresponding dibromide complex [59].

Hydride complexes of osmium(II) and osmium(III) are described in Sections 6.5.5 and 6.4.2.

6.4.2 Complexes with nitrogen donor ligands

The reduction of $[\text{Os}(\text{NH}_3)_5(\text{CF}_3\text{SO}_3)][\text{CF}_3\text{SO}_3]_2$ with zinc/mercury in methanol or water yields $[\text{Os}(\text{NH}_3)_5\text{H}_2][\text{CF}_3\text{SO}_3]_2$; in the ^1H NMR spectrum, a resonance at $\delta -8.473$ supports the osmium-hydrogen direct interaction. Oxidation of the new complex with ferrocinium ion gives a route to $[\text{Os}(\text{NH}_3)_5\text{H}_2]^{3+}$. This is found to be a hydrogenation agent for the conversion of acetone to propan-2-ol [60].

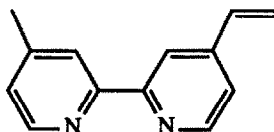
A theoretical study of the complex anions $[\text{OsCl}_5(\text{NX})]^{2-}$ ($\text{X} = \text{O}$ or S) at the CNDO/2-U level has been carried out and the electronic structures of the anions have been analysed. It is concluded that the Os-NS interaction is stronger than the Os-NO interaction and that the NS ligand is a better acceptor than NO; consistent with this is the finding that the Os-Cl bond *trans* to the Os-NS group is weaker than that *trans* to the Os-NO [61].

The ammonium salt of $[\text{OsCl}_6]^{2-}$ reacts with $\text{ArN}=\text{N}-\text{N}(\text{H})\text{Ar}$ ($\text{Ar} = 4\text{-MeC}_6\text{H}_4$, Ph , $4\text{-ClC}_6\text{H}_4$) to produce the air-stable, green osmium(III) complexes $\text{Os}(\text{ArNNNAr})_3$. Magnetic properties have been reported; values of μ_{eff} lie in the range 1.82-1.86 BM. This corresponds to the presence of low spin osmium(III) [62].

As expected, osmium(II) and osmium(III) complexes with bpy ligands have been the centre of some attention. $[\text{Os}(\text{bpy})_3]^{3+}$ has been prepared by the oxidation of $[\text{Os}(\text{bpy})_3]^{2+}$ in triflic acid by bromine in acetonitrile. The complex cation $[\text{Os}(\text{bpy})_3]^{3+}$ oxidises SO_3^{2-} to give SO_4^{2-} and $[\text{Os}(\text{bpy})_3]^{2+}$. The kinetics of the reaction have been investigated and the rate equation is given in Eqn (ii) where $k_1 = (1.63 \pm 0.03) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ and K_a is the acid dissociation constant for HSO_3^- . The k_1 value is larger than that previously reported and is now consistent with the cross relationship of Marcus Theory. Mechanistic and kinetic data are discussed in detail [63].

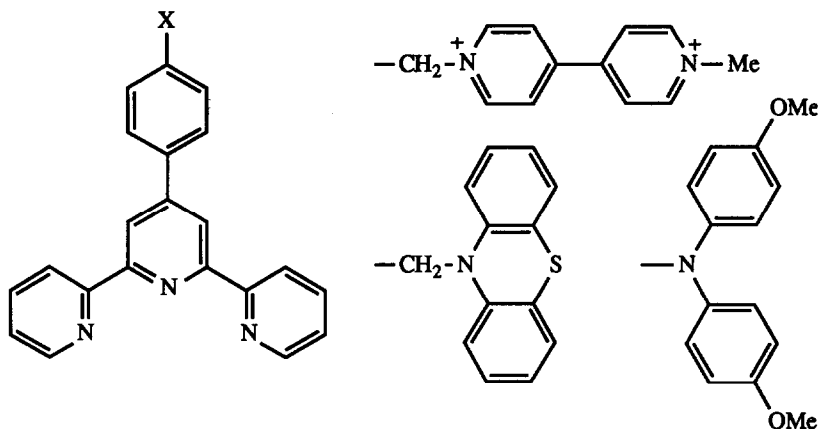
$$-\frac{d[\text{Os(III)}]}{dt} = \frac{2k_1 [\text{Os(III)}] [\text{S(IV)}]}{1 + [\text{H}^+] / K_a} \quad \text{Eqn (ii)}$$

Electrochemical studies have shown that the $[\text{Os}(\text{bpy})_3]^{4+}/3+$ couple is accessible in neat $\text{CF}_3\text{SO}_3\text{H}$ with $\text{Na}(\text{CF}_3\text{SO}_3)$ as supporting electrolyte; E° is 2.59V vs. NHE [64]. The results of electrochemical investigations of the $[\text{Os}(\text{bpy})_3]^{3+}/2+$ couple in relation to binding to calf thymus DNA have been presented [65]. Electron transfer between ruthenium and/or osmium(III)/(II) complexes at monolayer polymer/polymer interfaces has been evaluated for thermodynamically disfavoured cross-reactions. The systems chosen involve bpy, vpy (vpy = vinylpyridine) and vbpy (vinylbipyridine) ligands and are $[\text{Os}(\text{bpy})_2(\text{vpy})\text{Cl}]^{2+}/[\text{Os}(\text{bpy})_2(\text{vpy})_2]^{2+}$, $[\text{Os}(\text{bpy})_2(\text{vpy})_2]^{3+}/[\text{Ru}(\text{vbpy})_3]^{2+}$, $[\text{Os}(\text{bpy})_2(\text{vpy})_2]^{3+}/[\text{Ru}(\text{bpy})_2(\text{vpy})_2]^{2+}$ [66]. The salt $[\text{OsL}_3][\text{PF}_6]_2$, where $\text{L} = (32)$, has been prepared from $[\text{NH}_4]_2[\text{OsCl}_6]$. The electropolymerisation of $[\text{RuL}'_2\text{L}]^{2+}$ ($\text{L}' = \text{bpy}$, 4,4'-dimethyl-2,2'-bipyridine, 4,4',5,5'-tetramethyl-2,2'-bipyridine) and of $[\text{Os}(\text{bpy})_2\text{L}]^{2+}$ has been effected. The properties of the polymer systems upon photolysis have been reported [67].



(32)

X = Me, OMe, Br or:



(33)

The reaction of OsCl_3 with ligands of the family (33), L, yields OsLCl_3 . This complex further reacts to give $[\text{OsLL}']^{2+}$ where L' is from the same ligand family. These mixed polypyridine complexes can also be accessed by the reaction $[\text{OsO}_2(\text{OH})_4]^{2-}$ with L in aqueous HNO_3 (giving the green $[\text{OsO}_2\text{L}(\text{OH})][\text{NO}_3]$) followed by electrochemical reduction in the presence of L' (giving $[\text{OsLL}']^{2+}$) [68].

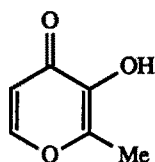
Further nitrogen donor ligands are included in Section 6.4.4.

6.4.3 Complexes with oxygen donor ligands

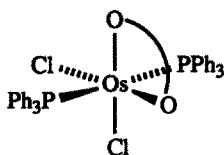
When the osmium(IV) precursor $\text{Na}_2[\text{OsCl}_6]$ reacts with triphenylphosphine and HCl in $\text{MeOCH}_2\text{CH}_2\text{OH}$ followed by treatment with methanol, the osmium(III) complex $\text{OsCl}_3(\text{PPh}_3)_2(\text{MeOH})$ results. The methanol can be displaced by a variety of oxygen donor ligands ($\text{HL} = \text{RC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{R}'$ where $\text{R} = \text{R}' = \text{Me}, \text{CF}_3, \text{Ph}$; $\text{R} = \text{Me}$ and $\text{R}' = \text{CF}_3$; $\text{R} = \text{Me}$ and $\text{R}' = \text{Ph}$, or $\text{HL} = \text{tropolone}$ or maltol, (34)) to give the complexes $\text{OsCl}_2(\text{PPh}_3)_2\text{L}$ (35) [69]. In an independent piece of work [70], it has been reported that the reaction of $\text{OsCl}_2(\text{PPh}_3)_3$ with $\text{RC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{R}'$ where $\text{R} = \text{R}' = \text{Me}, \text{CF}_3$ or $\text{R} = \text{Me}$ and $\text{R}' = \text{CF}_3$ leads to the osmium(III) complexes (36) although for $\text{HL} = \text{CF}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CF}_3$ two isomers are obtained [70].

The osmium(II) complex $\text{Os}(\text{bpy})_2\text{Cl}_2$ reacts with 1,2-(OH)₂-3,5-^tBu₂-C₆H₂, H₂L, in aqueous ethanol in the presence of NaOH to give $\text{Os}(\text{bpy})_2\text{L}$. Oxidation of this complex in the presence of $[\text{nBu}_4\text{N}][\text{ClO}_4]$ in $\text{CH}_2\text{Cl}_2/\text{MeOH}$ yields the black cationic osmium(III) complex (isolated as the perchlorate salt) $[\text{Os}(\text{bpy})_2\text{L}]^+$ (37). Pertinent geometrical parameters in (37) are Os-O = 2.040 (5), 2.004 (5) Å, Os-N = 2.041 (6)-2.066 (5) Å, C_{ring}-O = 1.344 (8), 1.345 (8) Å.

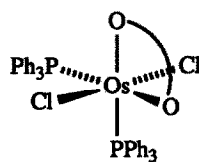
Infrared spectroscopic data are presented as well as EPR spectroscopic results which are consistent with a low spin d^5 configuration for the osmium(III) centre [71].



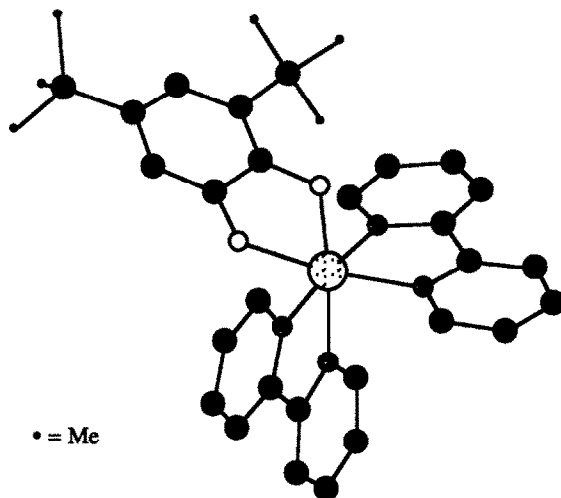
(34)



(35)



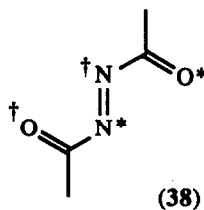
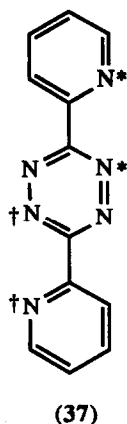
(36)



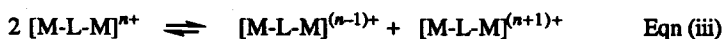
(37)

6.4.4 Complexes with mixed donor ligands

Two metal centres, M, (M = ruthenium and/or osmium) have been connected by either ligand (38) = L or ligand (39) = H_2L' in the complexes $[(bpy)_2M(L)M(bpy)_2]^{4+/5+/6+}$ and $[(bpy)_2M(L')M(bpy)_2]^{2+/3+/4+}$ and the electrochemical stability constants have been measured for the mixed-valent intermediates in the redox series indicated. The results have allowed the stability of the intermediates with respect to disproportionation to be rationalised; the equilibrium constant (Eqn (iii)) K_C depends on the π -donor or π -acceptor character of the metal centres and on the occupancy of the donor atom orbitals [72].

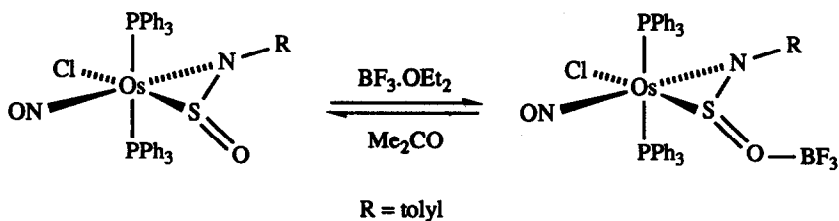


†.....† and *.....* are the pairs of donor atoms

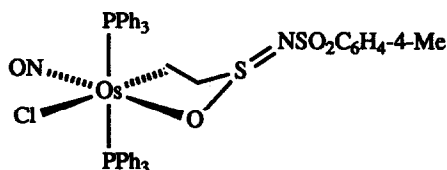


$$K_c = \frac{([M-L-M]^{n+})^2}{([M-L-M]^{(n-1)+}) ([M-L-M]^{(n+1)+})}$$

A series of papers by Herberhold *et al.* describes complexes involving the tosyliminooxosulphurane ligand and related ligands [73-75]. The equilibrium shown in Scheme (iii) has been studied [74]. $\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ reacts with 4-MeC₆H₄SO₂NSO to give complex (40) via the coupling of the alkene and incoming tosyliminooxosulphurane. Similar reactions have been reported with the allene and alkynes [75]; see also Section 6.6.



Scheme (iii)

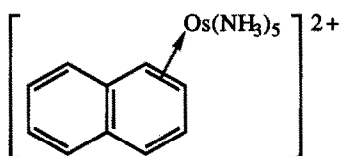


The synthesis from $[\text{OsCl}_6]^{2-}$ of the osmium(III) complex $\text{Os}(\text{S}_2\text{PC}_6\text{H}_2\text{-2,4,5-Me}_3)_3$ has been reported [76].

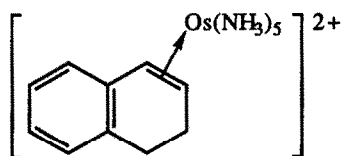
6.5 OSMIUM(II)

6.5.1 Complexes with nitrogen donor ligands

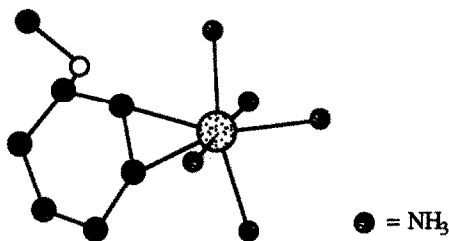
Treating the complex dication $[\text{Os}(\text{NH}_3)_5(\text{CF}_3\text{SO}_2)]^{2+}$ with naphthalene in dimethoxyethane and dimethylacetamide and in the presence of magnesium gives the complex dication (41). The catalysed reduction of (41) with dihydrogen gives a high yield of (42). The reduction of $[\text{Os}(\text{NH}_3)_5(\text{CF}_3\text{SO}_2)]^{2+}$ with zinc/mercury in the presence of PhOMe in methanol gives $[(\eta^2\text{-C}_6\text{H}_5\text{OMe})\text{Os}(\text{NH}_3)_5]^{2+}$, (43). The structure of this complex has been determined by X-ray crystallography and its reactivity has been investigated [77].



(41)



(42)

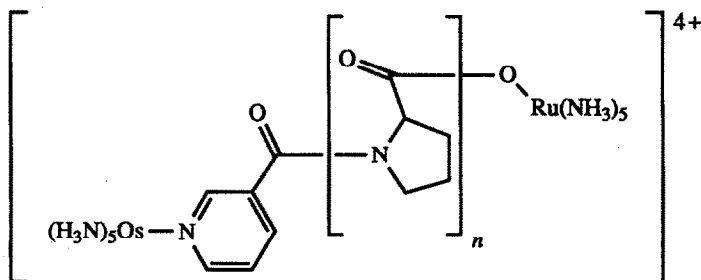


(43)

Complexes of the type $(\text{H}_3\text{N})_5\text{OsNC-Ar-CNOs}(\text{NH}_3)_5$ featuring a range of aromatic dinitriles have been reported and infrared spectroscopic data discussed [78]. The vibrational spectra of *trans*- $[\text{Os}(\text{NO})(\text{NH}_3)_4\text{L}]^{n+}$ ($\text{L} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OH}, \text{NO}_3, \text{H}_2\text{O}, \text{NH}_3$) have been interpreted [79].

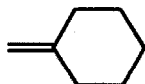
Electron transfer rates have been measured in a series of isonicotinyl-derivatised polyproline heterodinuclear complexes (44) [80]. Related studies have involved osmium-cobalt and osmium-ruthenium complexes with polypeptide spacer ligands. The synthesis of $[(\text{H}_3\text{N})_5\text{Os}(\text{Pro})_n\text{Co}(\text{NH}_3)_5]^{5+}$ ($n = 0\text{-}4$) has been described and long range intramolecular electron

transfer reactions have been investigated by the formation of the Os(II)(Pro)_nRu(III) precursors. The rates of electron transfer depend upon *n*. For *n* = 0, the rate is very fast; for *n* = 1, 2 and 3, the rates are 3.1×10^6 , 3.7×10^4 and $3.2 \times 10^2 \text{ s}^{-1}$ respectively. For *n* = 4, the rate constant is 50 s^{-1} at 298 K. The results of the study indicate that electron transfer across polypeptides can be rapid even when the metal-metal separation is greater than 20 Å [81].

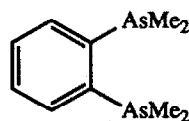


(44) *n* = 1-4

The five-coordinate complex OsH(Cl)(CO)(PMe^tBu)₂ reacts with HON=CRR' (R = R' = Me; R = H, R' = Me; (R,R') = (45)) to give the six-coordinate oxime complex OsH(Cl)(CO)(PMe^tBu)₂(N(OH)=CRR'). The oxime is easily displaced, for example by carbon monoxide, borohydride and alkynes [82].



(45)



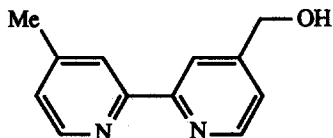
(46)

Aspects of the chemistry of [Os(bpy)₃]²⁺ have been reported in a number of papers. The results of a photochemical study of the osmium(II) complexes [Os(bpy)₃]²⁺, [Os(bpy)(dppe)]²⁺, [Os(bpy)₂(PPh₂Me)₂]²⁺ and [Os(phen)₂(das)]²⁺ (das = (46)) provide experimental evidence for the participation of a higher lying MLCT state in these polypyridyl complexes [83]. There has been an investigation by luminescence quenching and flash photolysis of the outer sphere electron transfer kinetics of the platinum(IV) complexes [Pt(NH₃)_nX_{6-n}]⁽ⁿ⁻²⁾⁺ (*n* = 0-6, X = Cl, Br) with [Os(bpy)₃]²⁺ and [OsL₃]²⁺ (where L = 4,4'-dimethyl-2,2'-bipyridine) at 293K [84]. A high resolution spectroscopic study of [Os(bpy)₃]²⁺ has been reported [85]. Hydrodynamic modulation voltammetry has been used in the detection of [Os(bpy)₃]²⁺ [86]. Cyclic voltammetry of [Os(bpy)₃]²⁺ in acetonitrile at high temperatures shows well-behaved reversible processes [87]. The electrocatalytic oxidation of cysteine at [Os(bpy)₃]²⁺/Nafion coated glassy carbon electrodes has been studied [88]. Highly resolved emission spectra of [Os(bpy)₃]²⁺ doped into [Ru(bpy)₃][ClO₄]₂ have been analysed in detail. The three lowest lying states are at 14201±1,

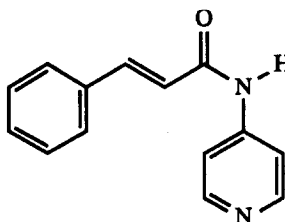
14261±1, and 14415±3 cm⁻¹. Each shows a blue shift (*ca.* 32 cm⁻¹) upon ligand deuteration. There are only small vibrational changes in the excited states with respect to the ground state [89]. Two independent studies cover work on clay modified electrodes with adsorbed [Os(bpy)₃]²⁺ [90, 91].

A family of osmium(II) complexes [cis-L₂OsCl₂].xH₂O has been synthesised from [OsCl₆]²⁻ where L = 4,4'-X₂-5,5'-Y₂bpy with X = NEt₂, OMe, Me, H, Cl, and Y = H, or X = H and Y = Me, or X = Y = Me. In the case of L = 4,4'-(NEt₂)₂bpy, the product is the osmium(III) complex [cis-L₂OsCl₂].Cl.5H₂O. The osmium(II) complexes are converted to [cis-L₂Os(CO)Cl]⁺ by bubbling carbon monoxide through solutions of the complexes in glycol under reflux. Further related products are also reported [92].

Soluble polymers containing osmium(II) diimine complexes have been prepared. Two equivalents of [Os(bpy)₂L][PF₆]₂ where L = (47) were reacted with an equivalent of the copolymer poly(*m,p*-chloromethylstyrene-*stat*-styrene, [PS-CH₂Cl]₃₀) in dmsO. The green-black solid which analyses as [PS-Os(II)₃₀][PF₆]₆₀ was produced, the ¹H NMR spectrum of which exhibits signals which are similar to those of the parent osmium(II) complex. The oxidation of [PS-Os(II)₃₀][PF₆]₆₀ is reported in addition to photochemistry [93]. The electrochemical copolymerisation of osmium, ruthenium and zinc complexes has been studied; the metal complexes involved are [Os(bpy)L₂]²⁺/[Ru(bpy)L₂]²⁺, [Os(vbpy)₃]²⁺/[Zn(vbpy)₃]²⁺ and [Os(bpy)₂(vpy)₂]²⁺/[Ru(bpy)₂(vpy)₂]²⁺ where L = (48), vbpy = (32) and vpy = 4-vinylpyridine. Use of the copolymers for electron transport studies has been assessed [94]. Polymers based on poly(4-vinylpyridine) or poly(*N*-vinylimidazole) with *bis*(bpy)osmium(II) centres have been prepared in stepwise reactions; the excited state and redox properties of the osmium centres are retained upon attachment of the polymer units [95]. Conductance measurements have been made for electropolymerisation films which include the complexes [Os(vbpy)₃]²⁺, [Os(vbpy)(phendione)]²⁺, [Os(vbpy)(NH₂phen)]²⁺ and [Os(5-Clphen)₃]²⁺ [96]. An investigation has been carried out of the reductive polymerisation of [Os(bpy)₂(vpy)₂]²⁺ to produce films on evaporated gold electrodes [97]. Charge transfer rates in thin films of the polymeric polynuclear complex [Os(bpy)₂(pvp)₁₀Cl]Cl where pvp = polyvinylpyridine have been investigated [98].



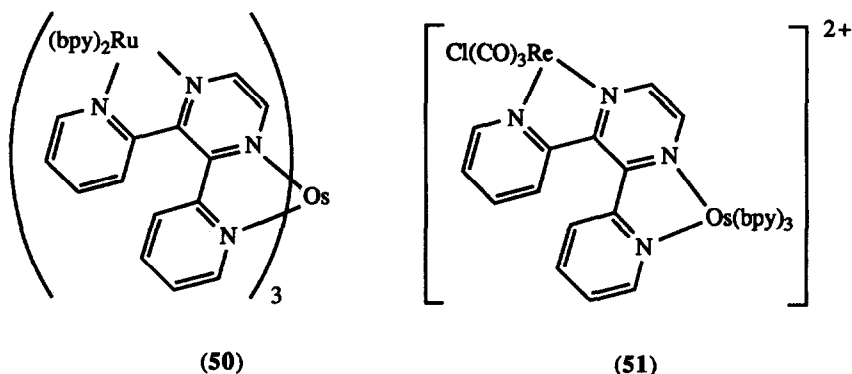
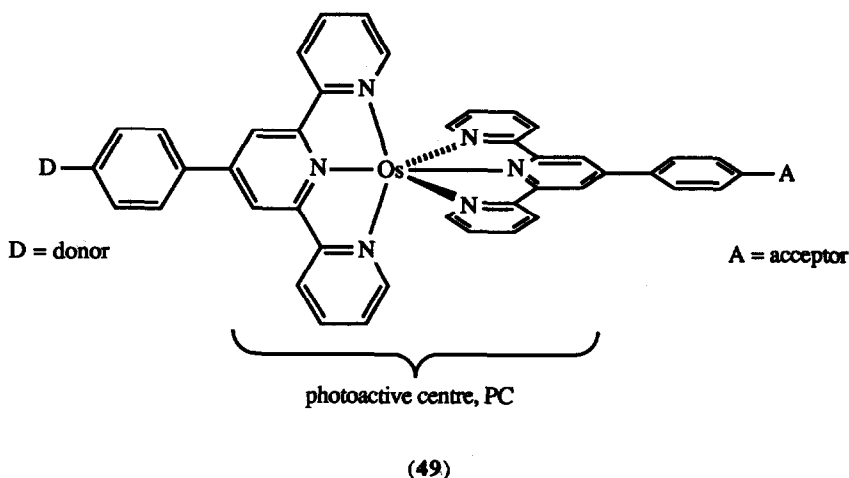
(47)



(48)

The family of ligands (33) have been incorporated into osmium(II) systems to provide a linear array of {donor-photoactive-acceptor}-centres, (49). Complexes have been characterised by

^1H NMR and UV-vis spectroscopy; cyclic voltammetry and emission spectroscopic studies on the new complexes have been carried out. There is efficient intramolecular electron transfer across each complex from the MLCT excited state [99].

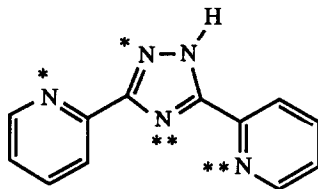


The heterometallic complex (50) has been synthesised and its absorption spectral, luminescence, and electrochemical properties have been reported. Luminescence occurs from the osmium(II) containing central unit; an "antenna" effect is observed in which the osmium-core collects the energy absorbed by the surrounding ruthenium-containing chromophores [100]. A related complex is [(51)][PF₆]₂; the electronic spectral, photochemical, and electrochemical properties of (51) have been investigated [101]. In work by the same authors, the same nitrogen-donor ligand, L, as in (51) has been incorporated into the complex cation [OsL₃]²⁺; a related complex with H₂L = 4,4'-(HO₂C)₂bpy has also been reported. The electronic spectrum of the cation [OsL₃]²⁺ has been interpreted. The absorption spectrum is essentially pH independent except in strongly acidic solution where protonation occurs to give [OsL₂(HL)]³⁺; there is an

associated red shift in the MLCT from 480 to 528 nm. Above pH 7, the emission spectrum is independent of the pH of the solution, but the protonated species is non-emissive. The MLCT excited state is very much more basic than the ground state [102].

An X-ray diffraction study of $[\text{OsL}_3][\text{SO}_4]$ in which $\text{L} = 4,7\text{-Ph}_2\text{phen}$ has been carried out [103].

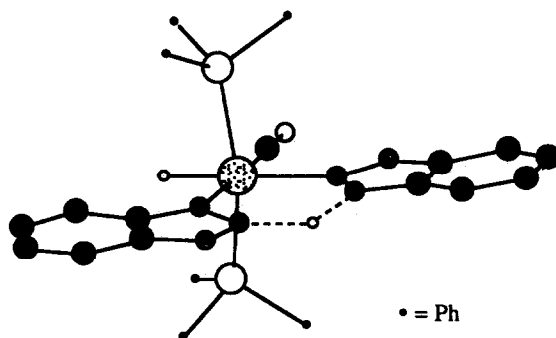
The reaction of $\text{Ru}(\text{bpy})_2\text{Cl}_2$ with HL yields $[\text{Ru}(\text{bpy})_2\text{L}]^+$ where HL = (52). Further reaction with $\text{Os}(\text{bpy})_2\text{Cl}_2$ leads to the heterometallic dinuclear complex $[(\text{bpy})_2\text{Ru}(\mu\text{-L})\text{Os}(\text{bpy})_2]^{3+}$ in which the donor sets indicated in (52) may be associated with either the osmium(II) or ruthenium(II) centres. The isomers produced are discussed. The synthesis of the complex $[(\text{Ru}(\text{bpy})_2)_2(\mu\text{-L})](\text{CF}_3\text{SO}_3)_3$ has also been successful and the molecular structure has been determined crystallographically; limited structural data are available for $[(\text{bpy})_2\text{Ru}(\mu\text{-L})\text{Os}(\text{bpy})_2](\text{CF}_3\text{SO}_3)_3$ but the results obtained are consistent with a structure related to that of $[(\text{Ru}(\text{bpy})_2)_2(\mu\text{-L})](\text{CF}_3\text{SO}_3)_3$ with an isomorphous replacement of one osmium for ruthenium atom. Spectroscopic and electrochemical data for the complexes are discussed [104].



..... and **.....** are two bidentate donor sets (see text)

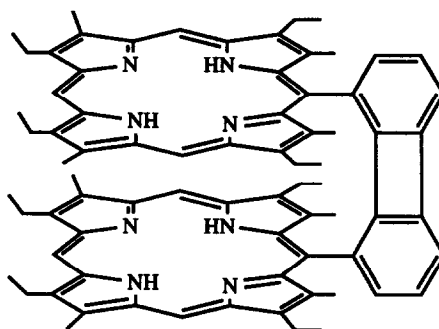
(52)

The reactions of $\text{OsH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3$ and $\text{OsH}_2(\text{CO})(\text{PPh}_3)_3$ with benzenetriazole, HL, have been reported. The reaction with the dihydride yields complex (53), the structure of which has been determined by X-ray crystallography. There are two triazole ligands, one protonated and one not. The two ligands are connected by a hydrogen bond; pertinent bond distances in complex (53) are $\text{Os-N} = 2.160$ (5), 2.176 (7) Å, $\text{Os-P} = 2.354$ (3), 2.452 (9) Å, $\angle \text{N-Os-N} = 91.8$ (2)° [105].



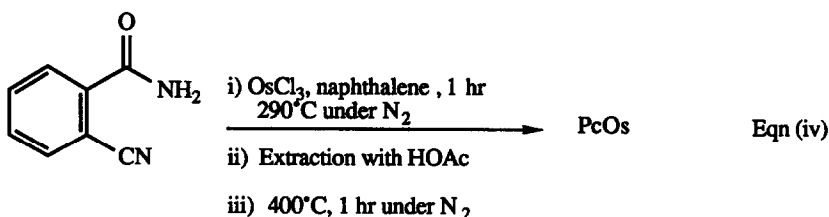
(53)

Several osmium(II) porphyrinato complexes have been documented. The first example of a porphyrin complex in which the metal atom binds to dihydrogen has been reported; the complex is $\text{Os}(\text{OEP})(\eta^2\text{-H}_2)$ and it is prepared by the reaction of $[\text{Os}(\text{OEP})]_2$ with potassium metal in thf followed by hydrolysis and treatment with PhCO_2H . The complex $\text{Os}(\text{OEP})(\eta^2\text{-H}_2)$ is characterised in the ^1H NMR spectrum by a resonance at $\delta -30$; $\text{Os}(\text{OEP})(\eta^2\text{-HD})$ has also been prepared and studied by ^1H NMR spectroscopy [106]. The reaction of H_4L , (54), with $\text{Os}_3(\text{CO})_{12}$ followed by treatment with pyridine gives $\text{Os}_2(\text{py})_2\text{L}(\text{CO})_2$; photolysis in the presence of pyridine then affords $\text{Os}_2(\text{py})_4\text{L}$. The latter is a precursor to Os_2L . Related reaction sequences have been used to prepare $\text{OsH}_2(\text{py})_2\text{L}$ and OsRuL [107].



(54)

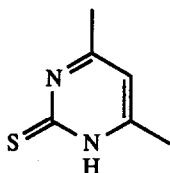
The phthalocyanine complex OsPc has been synthesised from OsCl_3 according to Eqn (iv); note that the preparation is advantageous because it does not use the toxic osmium tetroxide. The product is a blue-black powder and the infrared spectrum is identical to that of RuPc . Adducts of the type PcOsL_2 for $\text{L} = \text{py}$, $^t\text{BuNC}$, picoline, dmsO and other ligands have been reported [108].



6.5.2 Complexes with nitrogen-sulphur donor ligands

The osmium(II) complex $\text{OsCl}_2(\text{PPh}_3)_3$ reacts with HL , (55), to give orange $\text{OsL}_2(\text{PPh}_3)_2$ in which the phosphine ligands are *trans* to one another and ligand L^- functions as an *N,S*-donor

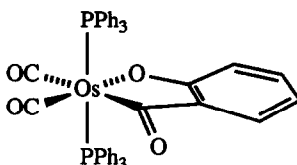
set. Reaction of HL with $\text{Os}(\text{CO})\text{H}_2(\text{PPh}_3)_3$ gives the yellow complex $\text{OsH}(\text{L})(\text{CO})(\text{PPh}_3)_2$ which reacts further with HL [109].



(55)

6.5.3 Complexes with oxygen donor ligands

The reaction of $\text{Os}(\text{CO})\text{H}_2(\text{PPh}_3)_3$ with 2-hydroxybenzaldehyde gives the complex (56) in which the two phosphine ligands are mutually *trans* [110].



(56)

6.5.4 Complexes with phosphorus donor ligands

Many of the complexes in the preceding sections have contained phosphorus donor ligands but in this section, we focus on those complexes in which the phosphorus ligand is the main ligand of interest.

A trend in ^{187}Os NMR spectral shifts as a function of R has been established in the series of compounds $\text{CpOsR}(\text{PPh}_3)_2$ for R = H, Me, Cl. With respect to $\delta = 0$ for OsO_4 , values are $\delta = -2595$ for R = Cl, $\delta = -4411$ for R = Me and $\delta = -5186$ for R = H. The data has been collected indirectly by the use of 2D-NMR spectroscopy [111].

Activation of a C-H bond in PMe_3 is observed during the thermolysis of *cis*-(Me_3P) $_4\text{Os}(\text{H})\text{R}$ where R = neo-pentyl. At 80°C , the complex produced is *fac*-(Me_3P) $_3\text{Os}(\text{H})(\eta^2\text{-CH}_2\text{PMe}_2)$. The kinetics of the reaction have been studied in detail [112]. A series of phosphine containing complexes involving a variety of other ligands has been prepared and characterised; these include $\text{Os}(\eta^2\text{-L})(\text{PH}_2)(\text{CO})(\text{PPh}_3)_2$ where the chelating ligands are derived from HL = HOAc, Hacac, HNO_2 , and $N,N'\text{-Me}_2\text{NCS}_2\text{H}$. Reactions of $\text{OsX}(\text{PH}_2)(\text{CO})_2(\text{PPh}_3)_2$ (X = H, Cl, OAc) with a variety of electrophiles including transition metal fragments are reported [113].

The *bis*(phosphine) $(c\text{-C}_6\text{H}_{11})_2\text{PCH}_2\text{CH}_2\text{P}(c\text{-C}_6\text{H}_{11})_2$, *P-P*, reacts with $[\text{OsCl}_6]^{2-}$ in $\text{MeOCH}_2\text{CH}_2\text{OH}$ to yield the red octahedral complex *trans*- $\text{Os}(P\text{-}P)_2\text{Cl}_2$. On heating in 1,2-dichlorobenzene, isomerisation to the yellow complex *cis*- $\text{Os}(P\text{-}P)_2\text{Cl}_2$ occurs. Halide exchange and isomerisation results when *cis*- $\text{Os}(P\text{-}P)_2\text{Cl}_2$ is treated with LiBr, the product being *trans*- $\text{Os}(P\text{-}P)_2\text{Br}_2$. With tetraphenylborate anion in ethanol, chloride abstraction from *cis*- $\text{Os}(P\text{-}P)_2\text{Cl}_2$ occurs to give the five-coordinate complex $[\text{Os}(P\text{-}P)_2\text{Cl}]^+$, isolated as the $[\text{BPh}_4]^-$ salt. The same reaction in the presence of LiBr leads to $[\text{Os}(P\text{-}P)_2\text{Br}]^+$ and when this is treated with LiBr in $\text{MeOCH}_2\text{CH}_2\text{OH}$, *cis*- $\text{Os}(P\text{-}P)_2\text{Br}_2$ is formed [114].

Phosphine hydrido osmium(II) complexes are discussed in Section 6.5.5.

6.5.5 Complexes with hydride ligands

The reaction of MgH_2 with osmium has been shown to give the new species $\text{Mg}_2[\text{OsH}_6]$. Powder studies (X-ray and neutron) have been carried out on the sample. For the deuterated complex anion, $\text{Os-D} = 1.68 (1) \text{ \AA}$ [115].

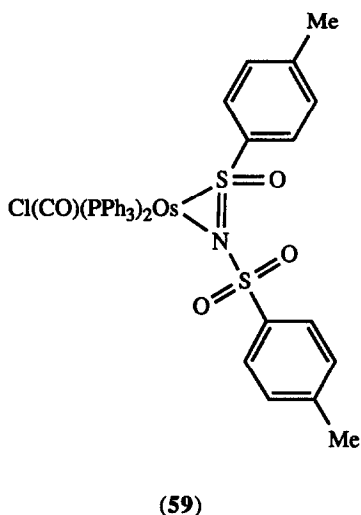
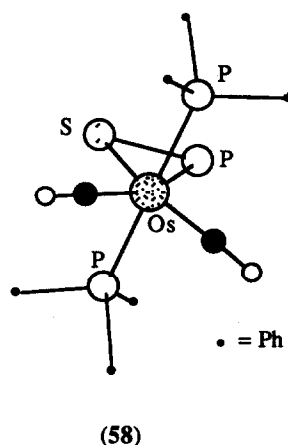
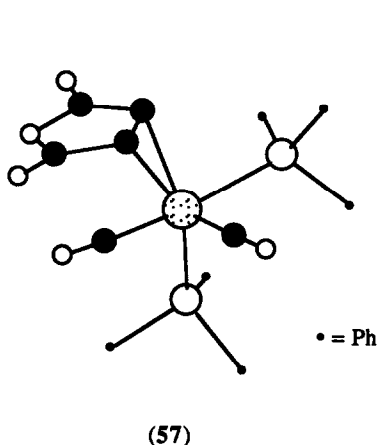
Protonation of OsH_2L_4 ($\text{L} = \text{PPh}(\text{OEt})_2$ or $\text{P}(\text{OEt})_3$) gives $[\text{OsH}(\eta^2\text{-H}_2)\text{L}_4]^+$, isolated as the tetraphenylborate salt and characterised in the infrared spectrum by an absorption at 1958 cm^{-1} assigned to the mode $\nu_{\text{O}_2\text{H}}$. $[\text{OsH}(\eta^2\text{-H}_2)\text{L}_4]^+$ reacts with 4-MeC₆H₄NC to give $[\text{OsH}(4\text{-MeC}_6\text{H}_4\text{NC})\text{L}_4]^+$; with phosphines, the product is $[\text{OsH}(\text{PR}_3)_4]^+$. Comparisons are made between the new hydrido complexes and their iron and ruthenium analogues [116].

6.6 LOW OXIDATION STATES OF OSMIUM AND HETEROMETALLIC COMPLEXES

The synthesis and characterisation of the complex $(\eta^2\text{-maleic anhydride})\text{dicarbonyl-bis}(\text{triphenylphosphine})\text{osmium}$ has been reported. The structure of the complex, (57), has been determined crystallographically [117]. In related investigations, the protonation of $\text{Os}(\text{O}_2\text{Ac})(\text{PH}_2=\text{E})(\text{CO})_2(\text{PPh}_3)_2$ ($\text{E} = \text{S}$ or Se) followed by treatment with base is shown to give $\text{Os}(\eta^2\text{-PH}=\text{E})(\text{CO})_2(\text{PPh}_3)_2$. For $\text{E} = \text{S}$, the new complex, (58), has been structurally characterised. The phosphorus and sulphur atom positions in (58) in the thioxophosphane ligand have not been distinguished; pertinent distances are $\text{Os-P/S} = 2.457 (3), 2.443 (3) \text{ \AA}$ and $\text{P-S} = 2.090 (5) \text{ \AA}$. The complexes $\text{Os}(\eta^2\text{-PH}=\text{E})(\text{CO})_2(\text{PPh}_3)_2$ can be reversibly protonated [118].

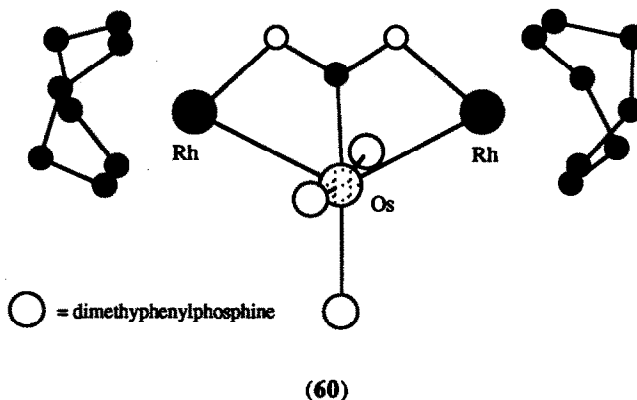
The coordination chemistry of iminooxosulphuranes and related complexes has been studied. A series of complexes of the type $\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSA})$ where $\text{A} = \text{O}, \text{CH}_2, \text{S}$ or NR and $\text{R} = \text{C}_6\text{H}_4\text{-4-Me}, \text{C}_6\text{H}_4\text{-2-Me}$ or $\text{SO}_2\text{-C}_6\text{H}_4\text{-4-Me}$. Ligand displacement occurs in the reaction of $\text{OsCl}(\text{NO})(\text{PPh}_3)_2\text{L}$ ($\text{L} = \text{alkene}$ or $\text{triphenylphosphine}$) with SO_2 gives the yellow complex $\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{SO}_2)$. This complex can also be prepared from $\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{CO})$ in liquid SO_2 . $\text{OsCl}(\text{NO})(\text{PPh}_3)_2\text{L}$ ($\text{L} = \text{alkene}, \text{PPh}_3$ or SO_2) reacts with 4-Me-C₆H₄SO₂NSO (tosylNSO) to yield the yellow complex $\text{OsCl}(\text{NO})(\text{PPh}_3)_2(\text{OSNtos})$ which shows a characteristic infrared absorption ν_{NO} at 1768 cm^{-1} . Related reactions are described. Infrared and ^1H and ^{31}P

NMR spectroscopic results for the new complexes are reported and the coordination modes of the iminoxosulphurane and related ligands are discussed [119]. In work from the same authors, the synthesis and characterisation of the complex $\text{OsCl}\{\text{SR}(\text{NSO}_2\text{R})\text{O}\}(\text{CO})(\text{PPh}_3)_2$ (59) where $\text{R} = 4\text{-MeC}_6\text{H}_4$ has been described [120]. Related compounds were described in Section 6.4.4 [73-75].



Tri- and *tetrakis*(pyrazolyl)borate salts, $[\text{HBpz}_3]^-$ and $[\text{Bpz}_4]^-$, react with the diosmium carbonyl compound $[\text{Os}(\text{OAc})(\text{CO})_3]_2$ to yield $[\text{Os}(\text{RBpz}_3)(\text{CO})_2]_2$ ($\text{R} = \text{H}$ or pz); related ruthenium complexes are also reported. Each (pyrazolyl)borato ligand is coordinated in an N,N',N'' -mode to an individual osmium atom. Treating $[\text{Os}(\text{RBpz}_3)(\text{CO})_2]_2$ with chlorinated organic solvents or bromine gives $\text{Os}(\text{RBpz}_3)(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}$ or Br) [121]. The heterometallic complex $(\eta^6\text{-}p\text{-cymene})\text{OsCl}(\mu\text{-S})_2\text{W}(\mu\text{-S})_2\text{Os}(\eta^6\text{-}p\text{-cymene})$ ($p\text{-cymene} = 4\text{-MeC}_6\text{H}_4\text{CHMe}_2$) forms

when $[(p\text{-cymene})\text{OsCl}_2]_2$ is treated with $[\text{PPh}_4]_2[\text{WS}_4]$ in acetonitrile. The complex contains two osmium centres connected by a bridging $[\text{WS}_4]$ -unit and the latter is considered to be a three electron donor to each terminal osmium centre [122]. The red heterodinuclear complex $(\text{cod})\text{RhH}_3\text{Os}(\text{PMe}_2\text{Ph})_3$ reacts with carbon dioxide in benzene or thf to give yellow $\{(\text{cod})\text{Rh}\}_2\text{Os}(\mu\text{-H})_2(\text{PMe}_2\text{Ph})_3\text{CO}_2$, (60), $\text{H}_2\text{Os}(\text{CO})(\text{PMe}_2\text{Ph})_3$, and H_2O . The complex (60) has been fully characterised; the mode of attachment of the CO_2 molecule is of interest and pertinent bond parameters for the CO_2 unit are $\text{C-O} = 1.309$ (22) and 1.300 (21) Å, $\angle\text{O-C-O} = 116.3$ (16)°. Adducts with ZnBr_2 and NaBPh_4 are reported; in the zinc(II) bromide case, structural characterisation shows that the zinc atom is associated with the two oxygen atoms of the CO_2 -unit and bond parameters change to $\text{C-O} = 1.290$ (14), 1.322 (14) Å, $\angle\text{O-C-O} = 112.2$ (10)° [123].



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