Co-ordination Chemistry of Higher Oxidation States. Part 22.[1] *trans*-Dioxo-osmium(VI) Complexes of Diamines, Diphosphines, and Diarsines

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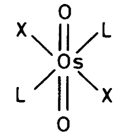
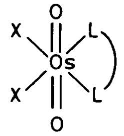
The reactions of tertiary arsines and diarsines with a mixture of OsO_4, concentrated HCl, and ethanol at low temperatures produce the dioxo-osmium(VI) complexes $[OsO_2Cl_2L_2]$ (L = $AsEt_3$, $AsMe_2Ph$, or $AsPh_3$) and $[OsO_2Cl_2(L–L)]$ [L–L = o-$C_6H_4(AsMe_2)_2$, o-$C_6H_4(AsPh_2)_2$, $Ph_2AsCH_2CH_2AsPh_2$, or $Ph_2AsCH{=}CHAsPh_2$]. The corresponding reactions at higher temperatures lead to mixtures containing Os^{VI} complexes and chloro complexes of Os^{III} and Os^{IV}. The diphosphine complexes $[OsO_2Cl_2(L–L)]$ [L–L = o-$C_6H_4(PMe_2)_2$, $Me_2PCH_2CH_2PMe_2$, $Ph_2PCH_2CH_2PPh_2$, or $Ph_2PCH{=}CHPPh_2$] are prepared similarly, but are very difficult to obtain pure, and the bromo complexes $[OsO_2Br_2(L–L)]$ (L–L = diphosphine or diarsine) are obtained from OsO_4, concentrated HBr, EtOH, and L–L. *NNN'N'*-Tetramethylethylenediamine (tmen) produces $[OsO_2X_2(tmen)]$, and $[H_2tmen][OsO_2Cl_4]$ has been characterised as a minor by-product in the case of X = Cl. Bis-ligand complexes $[OsO_2(L–L)_2]^{2+}$ have been obtained only with L–L = o-$C_6H_4(PMe_2)_2$. The complexes have been characterised by i.r., u.v.–visible, ^1H, and ^{31}P n.m.r. spectroscopy and microanalysis. Decomposition in solution is suggested to involve oxygen-atom transfer from the OsO_2^{2+} group to the neutral ligand. The properties and stabilities of the complexes are discussed and the ease of oxidation of the neutral ligands is suggested to be a major factor determining relative stabilities.

The *trans*-dioxo-osmium(VI) group ('osmyl', OsO_2^{2+}) is well known in mono- and di-nuclear esters and in anionic complexes such as $[OsO_2Y_4]^{2-}$ (Y = Cl, Br, OH, CN, OMe, *etc.*).[2] Complexes with various amines are also readily prepared, including $[OsO_2(NH_3)_4]^{2+}$, $[OsO_2(H_2NCH_2CH_2NH_2)_2]^{2+}$, and $[OsO_2(bipy)(OH)_2]$[3–6] (bipy = 2,2'-bipyridyl) but examples with other donors are rare. Walton and co-workers[7,8] showed that the reported '$OsOCl_3(PPh_3)_2$' was a mixture of *trans*-$[OsCl_4(PPh_3)_2]$ and $[OsO_2Cl_2(PPh_3)_2]$ and prepared other examples of the latter type with PR_2Ph and $PRPh_2$ (R = alkyl) which probably have the 'all-*trans*' structure (I). We subsequently prepared[9] analogues with SMe_2 and $SeMe_2$ and type (II) complexes with dithioethers and diselenoethers. The present paper extends this work to tertiary arsines and chelating Group 5B ligands.



(I)



(II)

Results

trans-$[OsO_2Cl_2(AsR_3)_2]$ (R_3 = Me_2Ph, Ph_3, *or* Et_3).—The addition of $AsEt_3$ (2 mmol) to a mixture of OsO_4 (1 mmol), ethanol, and concentrated hydrochloric acid at 0 °C produces a brown solid which has the ^1H n.m.r. spectrum shown in the Figure. The ethyl pattern at higher frequency is characteristic[10,11] of the paramagnetic *trans*-$[OsCl_4(AsEt_3)_2]$, and the second set of ethyl group resonances are typical of a diamagnetic $AsEt_3$ complex. The solid also shows the strong i.r. absorption (840 cm^{-1}) of a *trans*-OsO_2^{2+} unit[2,6,8] suggesting the second species is $[OsO_2Cl_2(AsEt_3)_2]$. The latter is isolated pure by conducting the reaction at −50 °C. Analogues with $AsPh_3$ and $AsMe_2Ph$ were prepared, along with $[OsO_2Cl_2(PMe_2Ph)_2]$ and the known[7,8] $[OsO_2Cl_2(PPh_3)_2]$ and comparison of the physical data (Table 1) shows that all have similar structures, probably the 'all-*trans*' form (I). Attempts to prepare the $SbPh_3$ analogue were unsuccessful. The tertiary arsine complexes are more soluble in common organic solvents, qualitatively less readily reduced than the phosphine analogues, and do not appear to be particularly light sensitive {in contrast to $[OsO_2Cl_2(PPh_3)_2]$}.[7]

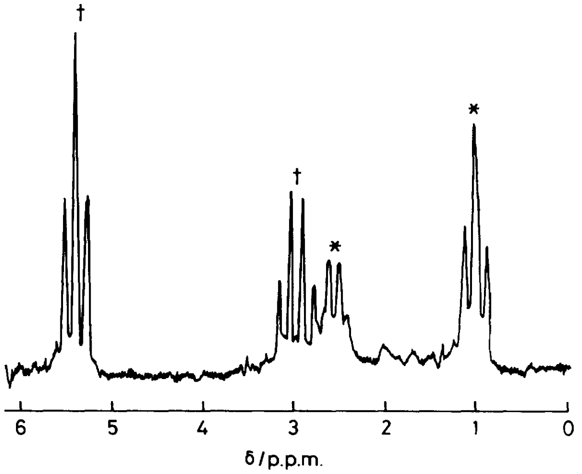


Figure. The ^1H n.m.r. spectrum of the product of the reaction of OsO_4 and $AsEt_3$ in EtOH–HCl(conc.) at 0 °C. The resonances marked (†) are assigned to *trans*-$[OsCl_4(AsEt_3)_2]$ and (*) to $[OsO_2Cl_2(AsEt_3)_2]$ **(19)**

$[OsO_2X_2(L–L)]$ (L–L = *diphosphine or diarsine*, X = Cl *or* Br).—The addition of various diarsines [L–L = o-$C_6H_4(AsPh_2)_2$, o-$C_6H_4(AsMe_2)_2$, $Me_2As(CH_2)_3AsMe_2$, $Ph_2AsCH_2CH_2AsPh_2$, or *cis*-$Ph_2AsCH{=}CHAsPh_2$] to OsO_4–HCl(conc.)–EtOH mixtures (Os:L–L ratio *ca.* 1:1) at low temperatures, followed by thorough washing of the precipitates produced orange to brown powders,

Table 1. Selected physical data

Complex	Colour	$\nu_{asym}(OsO_2)/cm^{-1}$	$\nu(OsX)/cm^{-1}$ (X = Cl or Br)	^1H n.m.r. [δ(Me)/p.p.m.][a,b]	^{31}P n.m.r. (δ/p.p.m.)[a,c]	10^{-3} ν/cm^{-1} ($\varepsilon_{mol}/dm^3\ mol^{-1}\ cm^{-1}$)[d]
(**1**) $[OsO_2Cl_2(tmen)]$	Orange-brown	861	319	2.9		22.7 (40) (sh), 28.3 (40), 31.6 (310)
(**2**) $[OsO_2Br_2(tmen)]$	Brown	846	*ca.* 200 (br)	2.8		18.6 (30), 24.3 (120)
(**3**) $[OsO_2Cl_2(Me_2PCH_2CH_2PMe_2)]$	Tan	842	299 (sh), 288	2.0	35.3	28.9 (2 070), 35.0 (2 390)
(**4**) $[OsO_2Br_2(Me_2PCH_2CH_2PMe_2)]$	Tan	842	195	2.0	37.6	18.7 (230) (sh), 20.4 (470) (sh), 23.1 (1 020), 27.9 (1 140)
(**5**) $[OsO_2Cl_2(Ph_2PCH_2CH_2PPh_2)]$	Tan	838	312		insoluble	25.0 (sh), 31.8 (d.r.), 16.9, 18.6, 24.8, 30.7
(**6**) $[OsO_2Cl_2(Ph_2PCHCHPPh_2)]$	Brown	842	315		19.8	19.4 (660), 24.8 (1 360) (sh), 27.1 (1 470)
(**7**) $[OsO_2Cl_2\{o\text{-}C_6H_4(PMe_2)_2\}]$	Light brown	843	322	2.5	38.6	24.3 (1 200) (sh), 25.1 (5 020) (sh), 26.5 (6 540), 29.2 (10 100)
(**8**) $[OsO_2Cl_2\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}]$	Brown	847	330 (br)		46.0[e]	(d.r.) 16.8, 18.3, 24.8, 29.8
(**9**) $[OsO_2Cl_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$	Dark brown	832	302	2.6		19.5 (450), 26.8 (2 230), 32.2 (2 200)
(**10**) $[OsO_2Cl_2\{o\text{-}C_6H_4(AsPh_2)_2\}]$	Light brown	834	321			25.3 (920) (sh), 27.5 (1 430), 31.7 (5 150)
(**11**) $[OsO_2Cl_2(Ph_2AsCH_2CH_2AsPh_2)]$	Brown	837	312			decomposes
(**12**) $[OsO_2Cl_2(Ph_2AsCHCHAsPh_2)]$	Orange-brown	840	303			19.2 (sh), 24.6 (390) (sh), 28.6 (880) (sh), 31.3 (1 530) (sh)
(**13**) $[OsO_2Br_2(Ph_2AsCHCHAsPh_2)]$	Orange-brown	837	190 (br)			23.0 (770) (sh), 28.1 (2 980), 33.3 (4 930) (sh)
(**14**) $[OsO_2Cl_2\{Me_2As(CH_2)_3AsMe_2\}]$	Buff	843	317	decomposes		21.9 (360) (sh), 28.1 (1 420) (sh), 31.8 (2 770)
(**15**) $[OsO_2Cl_2(PPh_3)_2]$	Light tan	842	307		decomposes	(d.r.) 16.8, 18.5, 24.6, 31.1
(**16**) $[OsO_2Cl_2(PMe_2Ph)_2]$	Brown	833, 839 (sh)	307	2.13	−21.9	19.1 (470), 25.5 (1 290) (sh), 32.9 (14 700)
(**17**) $[OsO_2Cl_2(AsPh_3)_2]$	Buff	842	316			19.7 (350), 29.8 (2 820) (sh)
(**18**) $[OsO_2Cl_2(AsMe_2Ph)_2]$	Light brown	837	309	2.0		18.3 (sh), 20.5 (210), 25.3 (750), 28.4 (1 530) (sh)
(**19**) $[OsO_2Cl_2(AsEt_3)_2]$	Brown	840	304	1.4 (t), 2.3 (quartet)		17.1 (sh), 24.0 (290), 27.8 (2 220) (sh), 29.6 (17 700)
(**20**) $[OsO_2(en)_2]Cl_2$	Pale yellow	833				(d.r.) 20.8, 21.9, 24.9, 30.1
(**21**) $[OsO_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]Cl_2$	Fawn	841		2.6	35.0	25.4 (1 350) (sh), 28.8 (2 270) (sh), (d.r.) 17.0, 18.6, 24.8, 30.4
(**22**) $[OsO_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]Br_2$	Fawn	842		decomposes	decomposes	(d.r.) 16.8, 18.6, 24.8, 29.6

[a] Freshly prepared $[^2H_6]$dmso (dmso = dimethyl sulphoxide) solution unless otherwise indicated. [b] Relative to internal $SiMe_4$. [c] Relative to 85% H_3PO_4 (high frequency positive convention). [d] Freshly prepared dmso solution unless indicated otherwise; d.r. = diffuse reflectance. [e] In CD_2Cl_2.

$[OsO_2Cl_2(L\text{–}L)]$. The spectroscopic properties (Table 1), in particular the strong $\nu_{asym}(OsO_2)$ vibrations in the range 830—850 cm^{-1}, show the presence of the *trans*-OsO_2^{2+} unit* and these materials are assigned structure (**II**).

The synthesis of diphosphine complexes in a pure state proved to be exceptionally difficult. The addition of dichloromethane solutions of $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, or *o*-$C_6H_4(PPh_2)_2$ to OsO_4–HCl(conc.)–EtOH mixtures at various temperatures between 0 and −50 °C produced fawn solids of rather variable analytical composition, with strong $\nu(OsO_2)$ and $\nu(OsCl)$ modes in the i.r. spectra as expected for $[OsO_2Cl_2(\text{diphosphine})]$, but also very strong absorptions at *ca.* 1 100—1 200 cm^{-1} characteristic of phosphine oxide groups.[12] These materials were poorly soluble in organic solvents and appear to be photochemically unstable, darkening rapidly unless kept at low temperatures in the dark. Careful control of the reaction conditions followed by washing of the precipitated solids with copious quantities of ethanol and diethyl ether produced reasonably pure samples of $[OsO_2Cl_2(L\text{–}L)]$ (L–L = $Ph_2PCH_2CH_2PPh_2$ or $Ph_2PCH{=}CHPPh_2$) as judged by analysis and especially by the absence of strong absorptions characteristic of P=O groups. All products obtained with *o*-$C_6H_4(PPh_2)_2$ had intense $\nu(P{=}O)$ vibrations in the i.r. spectra, and these preparations were not pursued. Similar preparations using the alkyldiphosphines $Me_2PCH_2CH_2PMe_2$ and *o*-$C_6H_4(PMe_2)_2$ were more successful and phosphine oxide-free $[OsO_2Cl_2(L\text{–}L)]$ were obtained readily, albeit in poor yield. The successful synthesis of $[OsO_2Cl_2(Me_2PCH_2CH_2PMe_2)]$ contrasts with the failures[7,8] to obtain trialkylphosphine complexes. In separate experiments we obtained no evidence of reaction between phosphine oxide ligands, including PPh_3O and $Ph_2P(O)CH_2CH_2P(O)Ph_2$, and OsO_4–HCl(conc.)–EtOH mixtures, so it seems that the phosphine oxides found in these syntheses are present as free ligands rather than osmium(VI) complexes, a conclusion supported by the $\nu(P{=}O)$ frequencies which were not appreciably different from those of the free ligands. Co-ordinated phosphine oxides have lower $\nu(P{=}O)$ frequencies.[12]

Replacement of the concentrated HCl by HBr in the above preparations afforded $[OsO_2Br_2(L\text{–}L)]$ (L–L = diphosphine or diarsine) which have similar properties to the chloro analogues and only a few representative examples are included in Table 1. Ditertiary stibines $Ph_2Sb(CH_2)_3SbPh_2$ or *o*-$C_6H_4(SbPh_2)_2$ were chlorinated by OsO_4–HCl(conc.)–EtOH mixtures, but a poor yield of the brown complex (**8**) was obtained with the hybrid phosphine–stibine ligand. The phenyldiphosphine complexes are poorly soluble in common organic solvents, and all of the diphosphine complexes decompose easily whilst the arsenic analogues are more readily soluble and apparently more stable.

The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of $[OsO_2X_2(\text{diphosphine})]$ in freshly prepared dimethyl sulphoxide solutions each showed a single strong resonance in the range *ca.* +20 to +50 p.p.m. (relative to H_3PO_4); the large high-frequency co-ordination shifts are characteristic of five-membered chelate rings[13] and confirm structure (**II**). For comparison, (**16**) has $\delta(P) = -21.9$ p.p.m. For (**15**) a single resonance at +26 p.p.m. was found, identical to that of free PPh_3O showing complete decomposition of the complex. The spectra of the diphosphine complexes usually showed other weak resonances some of which could be identified as phosphine oxide or phosphonium salt impurities. The correlation of the main resonance with the $[OsO_2Cl_2(L\text{–}L)]$ species was supported by exposing the solutions to bright sunlight, when the resonance rapidly decreased consistent with the photochemical instability of these Os^{VI} complexes. The 'impurity' signals grew somewhat in intensity as a result of this decomposition, but most of the decomposition products did not appear in the ^{31}P n.m.r. spectra suggesting that paramagnetic Os^{IV} or Os^{III} are the main products. *trans*-$[OsCl_4(PR_3)_2]$ give sharp but greatly shifted (*ca.* 1 200 p.p.m.) ^{31}P n.m.r. spectra,[10] but we have not observed similar spectra for $[OsCl_4(\text{diphosphine})]$ presumably due to unfavourable relaxation times.[14] This limited solution stability frustrated attempts to record ^{17}O n.m.r. spectra but we re-examined our previously reported[9] $[OsO_2Cl_2(SeMe_2)_2]$ and $[OsO_2Cl_2(MeSeCH_2CH_2SeMe)]$ by ^{77}Se n.m.r. spectroscopy. The latter showed two resonances at δ 337.4 and 328.9 p.p.m. (relative to $SeMe_2$) consistent with the presence of *meso* and DL invertomers, the shifts being similar to those of $MeSeCH_2CH_2SeMe$ chelated to other platinum metals.[15] The solution obtained from $[OsO_2Cl_2(SeMe_2)_2]$ showed a single resonance at δ 808 p.p.m. in the ^{77}Se n.m.r. spectrum, not consistent with co-ordinated $SeMe_2$ but indicative of $SeMe_2O$ (lit.,[16] 812 p.p.m.), analogous to the result observed in the production of PPh_3O from the triphenylphosphine complex.

The electronic spectra of the $[OsO_2X_2(L\text{–}L)]$ complexes (Table 1) are dominated by intense absorptions at > *ca.* 24 000 cm^{-1} due to L→Os charge-transfer transitions, and weaker absorptions or shoulders to lower energy may be the *d–d* transitions expected for d^2 Os^{VI}. Diffuse reflectance (d.r.) spectra are similar in profile to the solution spectra although with poorly defined peak maxima. In view of the solution instability the ε_{mol} values in Table 1 should be treated as approximate only, although repetitive scanning of some spectra showed decomposition to be slow over the time taken. All the complexes are diamagnetic, as expected for *trans*-OsO_2^{2+} groups where the strong $O_{p\pi} \longrightarrow Os_{d\pi}$ interactions produce a d_{xy}^2 ground state.[17]

Chemically these $[OsO_2X_2(L\text{–}L)]$ complexes are readily converted to $[OsX_4(L\text{–}L)]$ by heating with HX in aqueous ethanol, although the latter are more readily prepared from $[OsX_6]^{2-}$.[14] The $[OsO_2X_2(PR_3)_2]$ complexes have been shown to be useful starting materials for the preparation of high-valent osmium complexes (see refs. 7, 8, and 18, for example) and the mono- and di-arsine complexes reported here may be similarly valuable. The difficulty of preparing pure samples of the diphosphine complexes (and the poor yields) makes them less attractive in this respect.

$[OsO_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]X_2$ [X = Cl (**21**) *or* Br (**22**)].—We found that addition of excess *o*-$C_6H_4(PMe_2)_2$ to OsO_4–HCl(conc.)–EtOH produced a fawn solid of composition $[OsO_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]Cl_2$ (**21**) with $\nu(OsO_2)$ 841 cm^{-1}, very similar to that of $[OsO_2Cl_2\{o\text{-}C_6H_4(PMe_2)_2\}]$ (843 cm^{-1}), but whereas the latter has a strong $\nu(OsCl)$ at *ca.* 322 cm^{-1}, the former has only weak absorption in the range 350—300 cm^{-1}. If HBr is used in place of HCl, (**22**) is formed with an identical i.r. spectrum to that of the chloride. The bromide is however unstable in solution.

o-Phenylenebis(dimethylphosphine) has a pronounced tendency to form 2:1 complexes with many transition metals,[19] but the production of $[OsO_2(L\text{–}L)_2]^{2+}$ was unexpected. Attempts to obtain $[OsO_2(Me_2PCH_2CH_2PMe_2)_2]^{2+}$ gave only the 1:1 complex (**3**), whilst reaction of a OsO_4–EtOH–HBF_4 mixture with $Me_2PCH_2CH_2PMe_2$ at 0 °C in an attempt to form $[OsO_2(Me_2PCH_2CH_2PMe_2)_2][BF_4]_2$ instantly produced a black osmium oxide. The reaction of OsO_4–HCl(conc.)–EtOH with excess *o*-$C_6H_4(AsMe_2)_2$ afforded a pink solid which had a strong $\nu_{asym}(OsO_2)$ at 858 cm^{-1} and analysed as a complex with L–L:Os *ca.* 2:1. However the u.v.–visible spectrum showed the characteristic features of *trans*-$[OsCl_2\{o\text{-}C_6H_4\text{-}$

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* Various attempts to record Raman spectra gave indifferent results with instant blackening of the samples, not surprising in view of the light sensitivity of some of these materials.

Table 2. Analytical data (%)[a]

Complex	C	H	Other[b]
(1)	18.1 (17.6)	4.2 (3.9)	7.0 (6.8)[c]
(2)	13.9 (14.5)	3.3 (3.2)	5.3 (5.6)[c]
(3)	16.2 (16.3)	3.4 (3.6)	
(4)	13.4 (13.5)	3.0 (3.0)	
(5)	44.6 (45.2)	3.3 (3.5)	
(6)	45.0 (45.3)	3.1 (3.2)	
(7)	24.5 (24.4)	3.3 (3.3)	
(8)	21.4 (20.8)	2.9 (2.8)	
(9)	20.5 (20.7)	2.8 (2.8)	
(10)	42.9 (43.2)	3.0 (2.9)	22.7 (23.0)[d]
(11)	40.1 (39.5)	3.2 (3.0)	23.3 (24.1)[d]
(12)	40.0 (39.6)	2.9 (2.8)	
(13)	35.5 (35.9)	2.6 (2.5)	20.4 (21.7)[d]
(14)	15.8 (15.4)	3.4 (3.3)	34.5 (34.9)[d]
(17)	46.9 (47.2)	3.3 (3.3)	
(18)	29.7 (29.2)	3.4 (3.3)	28.4 (28.9)[d]
(19)	23.8 (23.4)	5.2 (5.0)	31.6 (30.8)[d]
(20)	12.0 (11.6)	3.9 (3.9)	13.3 (13.6)[c]
(21)	34.4 (34.8)	4.6 (4.8)	
(22)	30.7 (30.8)	4.0 (4.1)	

[a] Calculated values are in parentheses. [b] N or Os. [c] Nitrogen. [d] Osmium.

$(AsMe_2)_2\}_2]Cl$[14,20] which is responsible for the unusual pink colour. Our data suggest $[OsO_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2]Cl_2$ is formed in this reaction, but is too unstable to separate from the reduction product $[OsCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2]Cl$.

trans-$[OsO_2(en)_2]Cl_2$ **(20)** (en = ethylenediamine) has been reported previously,[3] and the cation characterised (as the HSO_4^- salt) by a single crystal *X*-ray study.[21] Spectroscopic data on this are included in Table 1 for comparison.

Diamine Complexes.—None of the phosphine or arsine complexes produced above yielded crystals suitable for an *X*-ray study, and in the hope of obtaining more tractable materials we investigated *N*-alkylated diamine complexes. The addition of *NNN'N'*-tetramethylethylenediamine (tmen) to OsO_4–HCl(conc.)–EtOH resulted in black precipitates, presumably osmium oxides. However addition of tmen•2HCl to an aqueous solution of potassium osmate(VI), $K_2[OsO_2(OH)_4]$ (*cf.* ref. 3), readily afforded an orange-brown powder $[OsO_2Cl_2(tmen)]$. The bromo analogue was obtained from tmen•2HBr, but this reaction fails with $o\text{-}C_6H_4(NMe_2)_2$•2HCl. Excess amine hydrochloride failed to give 2:1 complexes {and conversely a 1:1 ratio of en•2HCl:$K_2[OsO_2(OH)_4]$ still produced **(20)**}.

The $[OsO_2X_2(tmen)]$ complexes are rather stable powders but disappointingly have poor solubility in organic solvents or water, and attempts to grow single crystals *in situ* were made. Most failed, producing powdered $[OsO_2X_2(tmen)]$, but one gave a few small crystals. A single-crystal *X*-ray study showed[22] these to be $[H_2tmen][OsO_2Cl_4]$. Since subsequent studies showed that even in the presence of excess HX, $[OsO_2X_2(tmen)]$ were the major products it seems likely that $[H_2tmen][OsO_2Cl_4]$ is a minor by-product or hydrolysis product. We note that $[Pt(tmen)(\eta^2\text{-}C_2H_4)Cl]^+$ in concentrated aqueous HCl gave $[Pt(tmen)Cl_2]$ and $[Pt(Htmen)Cl_3]$ with minor amounts of $[H_2tmen][PtCl_4]$ and $[H_2tmen][PtCl_6]$, the proportion of the $[H_2tmen]^{2+}$ salts increasing with longer reaction times.[23] The i.r. spectrum of $[H_2tmen][OsO_2Cl_4]$ has $\nu(OsO_2)$ 847 and $\nu(OsCl)$ 298 cm^{-1}, in good agreement with $Cs_2[OsO_2Cl_4]$ (845 and 308 cm^{-1} respectively),[9] and clearly different from that of **(1)** (Table 1).

Discussion

The complexes reported here and those of the type $[OsO_2X_2L_2]$ (X = Cl or Br; L = PR_3, SR_2, *etc.*) described elsewhere[7–9] are rare examples of heavy Group 5B and 6B donors bound to a transition metal centre of very high formal oxidation state (Os^{VI}). The only other examples of M^{VI} species are the nitrido complexes $[Os(N)X_3(ER_3)_2]$ and $[Ru(N)X_3(ER_3)_2]$[24] (E = P, As, or Sb) and a few tungsten(VI) complexes, including $[WOCl_4\{o\text{-}C_6H_4(AsMe_2)_2\}]$,[25] $[(WSCl_4)_2(MeSCH_2CH_2SMe)]$,[26] and $[WCl_6(SMe_2)]$.[27]

The isolated dioxo-osmium(VI) complexes are all rather unstable and qualitatively this stability varies with halide as expected (Cl > Br) but with the neutral donors the order is unusual (S > As ~ Se > P). Thio- and seleno-ethers are usually less able to bond effectively to high-oxidation-state metal centres than are phosphines and arsines.[15,19,28] The formation of $[OsO_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]^{2+}$ by this diphosphine alone can be viewed as a successful competition of the second diphosphine molecule with halide for the osmium, and seems more in keeping with the expected donor ability. In fact the observed 'stability' order with neutral ligands reflects the ease of oxidation of the free ligands, and indicates that in these systems there is a competition between complexation and oxidation of the neutral ligand by the osmium(VI). The SR_2 and AsR_3 are less easily oxidised than SeR_2 or PR_3 which accounts for the easier preparation and better yields of complexes of the former ligands, and the greater apparent stability once isolated. Our successful preparation of $[OsO_2Cl_2(Me_2PCH_2CH_2PMe_2)]$ contrasted with the failure[8] to obtain $[OsO_2Cl_2(PR_3)_2]$ (R = alkyl) supports this argument since the chelating ligand will produce less labile complexes.

The decomposition products of $[OsO_2Cl_2L_2]$ [L = PPh_3 or $SeMe_2$], identified as PPh_3O and $SeMe_2O$, indicates that decomposition may involve direct attack of the neutral ligand on the osmyl oxygen. Such oxygen-atom transfer reactions are well documented for a variety of high-valent M=O species.[29–31] The analogy with the study of Pawson and Griffith[24] on $[OsNCl_4]^-$ + L systems should be noted; $[OsNCl_3L_2]$ (L = AsR_3 or SbR_3) can be isolated directly whereas PR_3 ligands bring about reduction to the Os^{IV} phosphine imidates $[Os(NPR_3)Cl_3(PR_3)_2]$. These phosphine imidate moieties are analogous to the $OsOPR_3$ intermediates assumed but rarely detected in the oxo systems [see, however, ref. 30 for an $Ru(OPR_3)$ intermediate].

Experimental

Physical measurements were made as described in previous parts of this series. Osmium analyses were performed as described.[9] The phenyldiphosphine complexes gave low and poorly reproducible analyses by this method which appear to result from difficulty in completely destroying the ligands without some loss of OsO_4. Similar problems have been reported in other systems. Analytical data are given in Table 2.

$[OsO_2Cl_2(Ph_2AsCH{=}CHAsPh_2)]$ **(12)**.—To a solution of OsO_4 (0.099 g, 0.39 mmol) in a mixture of ethanol (3 cm^3) and concentrated hydrochloric acid (0.5 cm^3) was added $Ph_2AsCH{=}CHAsPh_2$ (0.192 g, 0.40 mmol) dissolved in CH_2Cl_2 (1 cm^3) dropwise *via* a syringe at 0 °C. The mixture was stirred for *ca.* 10 min after which time an orange-brown powder had deposited. This was collected and washed with ethanol (3 × 10 cm^3) and diethyl ether (2 × 10 cm^3) and dried *in vacuo* (0.18 g, 59%).

The complexes **(13)** and **(10)** were prepared by an analogous route. The complexes **(5)** and **(6)** were similarly made except that the reactions were carried out in darkness and products carefully washed with CH_2Cl_2 before any spectroscopic or analytical data were obtained.

$[OsO_2Cl_2(tmen)]$ (**1**).—$K_2[OsO_2(OH)_4]$ prepared from KOH(aq)–OsO_4–EtOH was dissolved in water. An excess of tmen•2HCl was prepared from tmen and concentrated hydrochloric acid, and dissolved in water. The two solutions were combined resulting in a copper coloured solution. After leaving for 24 h at 0 °C, orange-brown crystals had been deposited which were isolated by filtration, washed with copious quantities of diethyl ether, and dried *in vacuo*. Complex (**2**) was similarly prepared using concentrated HBr.

$[OsO_2Cl_2(Me_2PCH_2CH_2PMe_2)]$ (**3**).—Osmium tetraoxide (0.220 g, 0.87 mmol) was dissolved in EtOH–HCl(*ca.* 10:1 v/v) (8 cm^3). This mixture was purged with nitrogen and cooled to 0 °C. $Me_2PCH_2CH_2PMe_2$ (0.150 g, 1.00 mmol) was added dropwise to this mixture giving a tan precipitate. The mixture was then stirred in the dark for *ca.* 10 min. The tan solid was then collected and washed with ethanol (3 × 10 cm^3) and diethyl ether (3 × 10 cm^3) and dried *in vacuo*. Complex (**4**) was prepared by a similar route.

$[OsO_2Cl_2\{o\text{-}C_6H_4(PMe_2)_2\}]$ (**7**).—Osmium tetraoxide (0.236 g, 0.93 mmol) was dissolved in EtOH–HCl(*ca.* 10:1 v/v) (8 cm^3). This mixture was purged with nitrogen and $o\text{-}C_6H_4(PMe_2)_2$ (0.190 g, 0.96 mmol) was added dropwise, *via* a syringe, over a period of a few minutes at room temperature. The light brown solid deposited was collected, washed with ethanol (3 × 10 cm^3) and diethyl ether (3 × 10 cm^3), and dried *in vacuo*.

$[OsO_2Cl_2\{o\text{-}C_6H_4(PMe_2)(SbMe_2)\}]$ (**8**).—To a nitrogen-purged mixture of OsO_4 (0.217 g, 0.85 mmol) dissolved in EtOH–HCl(*ca.* 10:1 v/v) (8 cm^3), cooled to 0 °C, was added $o\text{-}C_6H_4(PMe_2)(SbMe_2)$ (0.395 g, 1.40 mmol) dropwise *via* a syringe over a period of 5 min. The mixture was then stirred in darkness for 30 min during which time a brown solid was deposited. This was collected, washed with ethanol (3 × 15 cm^3) and diethyl ether (3 × 15 cm^3), and dried *in vacuo* (0.05 g, 10%). Prior to obtaining analytical data the product was carefully washed with dichloromethane–diethyl ether to remove any oxidised ligand or decomposition products.

$[OsO_2Cl_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$ (**9**).—Osmium tetraoxide (0.092 g, 0.36 mmol) was dissolved in EtOH–HCl(*ca.* 10:1 v/v) (2 cm^3), purged with nitrogen, and cooled to *ca.* −50 °C in a slush bath. $o\text{-}C_6H_4(AsMe_2)_2$ (0.103 g, 0.36 mmol) was added dropwise *via* a syringe. The mixture was stirred and allowed to warm to 0 °C over a period of *ca.* 40 min. During this time a dark brown solid was deposited which was isolated using a frit-stick under nitrogen, washed with nitrogen-purged ethanol (2 × 5 cm^3) and diethyl ether (2 × 5 cm^3), and dried *in vacuo*.

$[OsO_2Cl_2(Ph_2AsCH_2CH_2AsPh_2)]$ (**11**).—To a mixture of OsO_4 (0.072 g, 0.28 mmol) dissolved in EtOH–HCl(*ca.* 10:1 v/v) (3 cm^3) was added $Ph_2AsCH_2CH_2AsPh_2$ (0.136 g, 0.28 mmol) dissolved in CH_2Cl_2 (1 cm^3) over a period of 5 min at room temperature. The mixture was then placed in ice at 0 °C for 30 min and a brown solid was produced. This was isolated, washed with ethanol (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3), and dried *in vacuo* (0.057 g, 25%).

$[OsO_2Cl_2\{Me_2As(CH_2)_3AsMe_2\}]$ (**14**).—Osmium tetraoxide (0.065 g, 0.26 mmol) was dissolved in EtOH–HCl(*ca.* 10:1 v/v) (2 cm^3). This mixture was purged with nitrogen prior to dropwise addition of $Me_2As(CH_2)_3AsMe_2$ (0.080 g, 0.32 mmol) at *ca.* −50 °C. The mixture was stirred and gradually allowed to warm to *ca.* −20 °C under nitrogen. At this point a buff solid had been deposited which was collected under nitrogen, washed with deoxygenated diethyl ether (15 cm^3), and dried *in vacuo*. The complexes (**18**) and (**19**) were prepared by a similar route.

$[OsO_2Cl_2(PMe_2Ph)_2]$ (**16**).—Dimethylphenylphosphine (0.356 g, 2.78 mmol) was added dropwise to a stirred, nitrogen-purged solution of OsO_4 (0.237 g, 0.93 mmol) dissolved in EtOH–HCl(*ca.* 10:1 v/v) (8 cm^3) over a period of 5 min; this produced a red solution. The mixture was then stirred in the dark for *ca.* 4 h. An orange-brown powder was precipitated, isolated by filtration, washed with ethanol (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3), and dried *in vacuo*.

$[OsO_2Cl_2(PPh_3)_2]$ (**15**).—To a stirred solution of OsO_4 (0.234 g, 0.92 mmol) dissolved in EtOH–HCl(*ca.* 10:1 v/v) was added PPh_3 (0.500 g, 1.91 mmol) dissolved in CH_2Cl_2 (5 cm^3) over a period of 10 min. A light tan powder was deposited which was isolated, washed with ethanol (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3), and dried *in vacuo*. Prior to obtaining analytical data the solid was washed with copious quantities of dichloromethane and dried *in vacuo* to remove any soluble decomposition products. The $AsPh_3$ analogue (**17**) was prepared by a similar route.

$[OsO_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]Br_2$ (**22**). To a nitrogen-purged mixture of OsO_4 (0.189 g, 0.74 mmol) dissolved in EtOH–HBr(*ca.* 10:1 v/v) (8 cm^3) was added an excess of $o\text{-}C_6H_4(PMe_2)_2$ (0.36 g, 1.8 mmol) at 0 °C. The mixture immediately gave a fawn powder which was isolated after *ca.* 20 min, washed with ethanol (3 × 15 cm^3) and diethyl ether (3 × 10 cm^3), and dried *in vacuo*. The chloride analogue (**21**) was similarly made using concentrated hydrochloric acid.

Complex (**20**) was prepared by the method of Malin and Taube.[3]

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