Co-ordination Chemistry of Higher Oxidation States. Part 38.[1] Synthesis, Spectroscopic and Electrochemical Studies of some *trans*-Dihalogenoosmium Complexes. Crystal Structure of *trans*-$[Os(PMe_3)_4Cl_2]BF_4$†

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The complexes *trans*-$[Os(PMe_3)_4X_2]$ (X = Cl or Br) have been obtained from $[Os(PPh_3)_3X_2]$ and PMe_3, and *trans*-$[OsL_4X_2]$ [L = PMe_2Ph, $AsMe_3$, $SbPh_3$ or pyridine (py)] by reduction of appropriate osmium(III) complexes in the presence of L. The complexes *cis*-$[Os(PR_3)_4X_2]$ are formed by isomerisation of the *trans* analogues in chlorinated solvents, and in other ways. Air oxidation of the osmium(II) complexes gives *trans*-$[OsL_4X_2]BF_4$ (L = PMe_3 or $AsMe_3$), but formation of *trans*-$[OsL_4X_2]BF_4$ (L = PMe_2Ph, $SbPh_3$ or py) and *cis*-$[Os(PMe_2Ph)_4Cl_2]BF_4$ requires HNO_3 as oxidant. Use of concentrated HNO_3 gives *trans*-$[OsL_4X_2]^{2+}$ (L = PMe_3, PMe_2Ph or $AsMe_3$) in solution, but these have not been isolated. The complexes have been characterised by IR, UV–VIS, and NMR spectroscopies, and the effect of stereochemistry and L and X upon the Os^{II}–Os^{III} and Os^{III}–Os^{IV} redox potentials probed by cyclic voltammetry. The crystal structure of *trans*-$[Os(PMe_3)_4Cl_2]BF_4$ has been determined: orthorhombic, space group *Fddd*, $a = 8.104(4)$, $b = 32.195(11)$, $c = 38.540(9)$ Å, and $Z = 16$. The cation has Os–P 2.419(5) and 2.398(5) Å and Os–Cl 2.352(4) Å, and shows deviations of the OsP_4 unit from planarity due to steric interactions. There is no evidence that *mer*-$[IrL_3Cl_3]$ (L = $PEtPh_2$, $AsMe_2Ph$, $SbPh_3$ or SMe_2) can be oxidised either chemically or electrochemically to stable iridium(IV) cations.

We have recently described[2,3] some systematic studies of the effects of varying the neutral ligands (L = PR_3, AsR_3, SbR_3, *etc.*) and halide (X = Cl or Br) upon the stability and redox potentials of the *trans*-$[OsL_2X_4]$–$[OsL_2X_4]^-$ and *mer*- and *fac*-$[OsL_3X_3]^+$–$[OsL_3X_3]$ systems. The present paper extends these studies to complexes with four neutral ligands. Such complexes are rather rare for osmium, and most readily obtained for Os^{II} as $[OsL_4X_2]$,[4–11] although detailed characterisations have been provided only for the *trans* isomers where L = PMe_3 or PMe_2Ph and X = Cl.

Results and Discussion

Synthesis of Osmium(II) *Complexes.*—The *trans*-$[Os(PMe_3)_4X_2]$ complexes were made by phosphine exchange between $[Os(PPh_3)_3X_2]$ and PMe_3.[4,5] A similar route using PMe_2Ph was unsatisfactory, and *trans*-$[Os(PMe_2Ph)_4X_2]$ were obtained directly from OsO_4 or $Na_2[OsX_6]$, HX and excess of PMe_2Ph in ethanol.[11] The only previously reported arsine complexes with this stoichiometry are $[OsL_4X_2]$ (L = $AsMe_2Ph$ or $AsMePh_2$) obtained by Dwyer *et al.*,[9] and characterised only by halide analysis. Several attempts to prepare the $AsMe_2Ph$ complexes using their route gave materials which were identified by chemical analysis, IR and ^1H NMR spectroscopies as the halide-bridged dimers $[Os_2(AsMe_2Ph)_6X_3]H_2PO_2$. The presence of the $H_2PO_2^-$ anion results from the large excess of hypophosphorous acid used as a reducing agent. In the proton NMR spectra, each sample exhibited only a single AsMe resonance assignable to the dimer, which is expected to have the familiar[6] $[L_3Os(\mu\text{-}X)_3OsL_3]^+$ structure. Halide analyses differ little for the two formulations. There was no apparent reaction between *trans*-$[Os(SbPh_3)_4Cl_2]$ and $AsMe_3$ in hexane even after 3 d, in marked contrast to the facile reaction of PMe_3 with $[Os(PPh_3)_3X_2]$, reflecting the very different kinetics of ligand replacement in the five-co-ordinate complex and the very inert $t_{2g}{}^6$ configuration in O_h symmetry. The reduction of mixtures of $[OsX_6]^{2-}$ and $AsMe_3$ in EtOH–water with H_3PO_2, or better the reduction of *mer*-$[Os(AsMe_3)_3X_3]$ in tetrahydrofuran with amalgamated zinc in the presence of $AsMe_3$, appeared to give *trans*-$[Os(AsMe_3)_4X_2]$, but we were unable to isolate solid complexes. The products were clear yellow oils, with single ^1H NMR resonances, and weak absorptions at *ca.* 26 000 cm^{-1} in the UV–VIS spectra consistent with the expected *trans* complexes. Air oxidation of the oils in acetone or ethanol solution in the presence of HBF_4 gave the corresponding osmium(III) complexes.

The *trans*-$[Os(SbPh_3)_4X_2]$ complexes were prepared by prolonged reflux of *mer*-$[Os(SbPh_3)_3X_3]$ with excess of $SbPh_3$ in 2-ethoxyethanol with addition of $NaBH_4$ as reducing agent. The formation of six-co-ordinate $[OsL_4X_2]$ with $SbPh_3$, compared with the five-co-ordinate complexes obtained with PPh_3,[12,13] is probably attributable to the significantly smaller cone angle of the stibine. In the cases of *trans*-$[Os(py)_4X_2]$ (py = pyridine), Buckingham *et al.*'s method[7] from $K_2[OsX_6]$ and pyridine in glycerol was used, although with a modified work-up procedure. In this case the glycerol serves as both solvent and reducing agent.[14] Attempts to prepare tetrakis(ligand)osmium(II) complexes with Group 16 donors such as Me_2S have been unsuccessful so far, although *trans*-$[Os(dmso)_4X_2]$ (dmso = dimethyl sulphoxide) are known,[15] and an X-ray study of the bromo complex showed the dmso ligands were S-co-ordinated to the osmium.[16]

The complexes *cis*-$[Os(PMe_2Ph)_4X_2]$ were made by heating OsO_4, HX, and excess of PMe_2Ph in 2-methoxyethanol,[11] and *cis*-$[Os(PMe_3)_4X_2]$ by isomerisation of the *trans* isomers in CH_2Cl_2 under nitrogen. The latter complexes were obtained by

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† *trans*-Dichlorotetrakis(trimethylphosphine)osmium(III) tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Selected spectroscopic data

trans Isomers	Colour	ν(Os–X)[a]/cm^{-1}	E_{max} /10^3 cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1})[b]
$[Os(py)_4Cl_2]$	Dark red	300	21.74 (7570), 26.00 (17 460)
$[Os(py)_4Br_2]$	Orange-brown	196	17.70 (2000), 20.15 (12 000), 26.75 (16 250)
$[Os(PMe_3)_4Cl_2]$	Yellow	284	26.95 (240)
$[Os(PMe_3)_4Br_2]$	Orange-yellow	187	25.51 (220)
$[Os(PMe_2Ph)_4Cl_2]$	Yellow	298	26.32 (470), 30.12 (sh)
$[Os(PMe_2Ph)_4Br_2]$	Yellow	n.o.	24.88 (230), 30.12 (sh)
$[Os(SbPh_3)_4Cl_2]$	Yellow-brown	n.o.	23.31 (820)
$[Os(SbPh_3)_4Br_2]$	Brown	n.o.	20.75 (sh), 22.22 (1110)
$[Os(py)_4Cl_2]NO_3$	Khaki	330	22.70 (446), 25.77 (820), 29.41 (1190), 32.30 (sh)
$[Os(py)_4Br_2]NO_3$	Brown	n.o.	20.80 (1330), 23.15 (3200), 24.40 (4130), 32.78 (11 200)
$[Os(PMe_3)_4Cl_2]BF_4$	Pink	308	19.19 (2100), 20.83 (sh), 31.06 (3860)
$[Os(PMe_3)_4Br_2]BF_4$	Purple	215	17.45 (3880), 19.16 (sh), 26.53 (2340)
$[Os(PMe_2Ph)_4Cl_2]BF_4$	Purple	311	17.99 (1910), 19.45 (sh), 28.33 (sh), 31.35 (3160)
$[Os(PMe_2Ph)_4Br_2]BF_4$	Green	225	16.50 (3850), 17.99 (sh), 25.38 (1780), 27.32 (1630)
$[Os(AsMe_3)_4Cl_2]BF_4$	Pink	312	19.42 (1100), 21.10 (sh), 27.78 (sh), 31.15 (1720)
$[Os(AsMe_3)_4Br_2]BF_4$	Blue-purple	227	17.70 (2870), 19.46 (700), 27.25 (1700), 31.65 (sh)
$[Os(SbPh_3)_4Cl_2]BF_4$	Green	311	15.06 (985), 15.95 (sh), 25.91 (1745), 33.58 (34 550)
$[Os(SbPh_3)_4Br_2]BF_4$	Green	n.o.	13.80 (3120), 15.27 (sh), 24.63 (2810), 32.78 (48 620)
cis Isomers			
$[Os(PMe_3)_4Cl_2]$	Yellow	283, 300	—[c]
$[Os(PMe_3)_4Br_2]$	Yellow	n.o.	—
$[Os(PMe_2Ph)_4Cl_2]$	Pale yellow	244, 275	—
$[Os(PMe_2Ph)_4Br_2]$	Yellow	n.o.	—
$[Os(PMe_2Ph)_4Cl_2]BF_4$	Purple	272, 308	15.60 (410), 19.05 (1030), 27.55 (910), 33.56 (2880)

[a] Nujol mull, n.o. = not observed or assigned. [b] In CH_2Cl_2. [c] *cis* Complexes have no clearly defined absorption at $< 30\,000$ cm^{-1}.

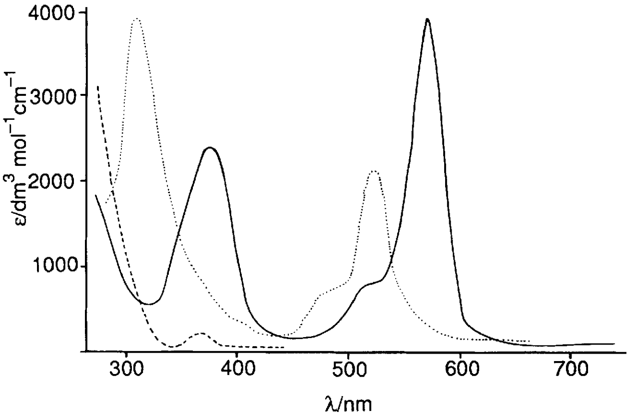

Fig. 1 The UV–VIS spectra of *trans*-$[Os(PMe_3)_4Cl_2]$ (– – – –), *trans*-$[Os(PMe_3)_4Cl_2]BF_4$ (· · · ·) and *trans*-$[Os(PMe_3)_4Br_2]BF_4$ (——), all in CH_2Cl_2 solution

Werner and co-workers[5] by reaction of the *trans* isomers with sodium dihydronaphthylide in tetrahydrofuran to form $[Os(PMe_3)_3(\eta^2\text{-}Me_2PCH_2)H]$, and treatment with HX. Unless oxygen is rigorously excluded the *cis* isomers are contaminated with *trans*-$[Os(PMe_3)_4X_2]^+$.

Properties of Osmium(II) *Complexes*.—Selected spectroscopic data are given in Table 1. As expected for low-spin d^6 Os^{II} the complexes are diamagnetic, and, the pyridine complexes apart, are pale yellow or brown solids. The pyridine complexes are deeply coloured, and their UV–VIS spectra reveal intense absorptions in the range 20 000–30 000 cm^{-1}. These are typical of d^6 polypyridyl complexes[14,17] and can be assigned as metal-to-ligand charge transfer (c.t.) transitions involving the metal t_{2g} and the pyridine π^* orbitals. In contrast the other *trans* complexes have only single weak absorptions at $< 30\,000$ cm^{-1} which can be assigned as d–d transitions, specifically as $^1A_{1g} \rightarrow {}^1E_g$ in D_{4h} symmetry. The $^{31}P\text{-}\{^1H\}$ NMR spectra of the *trans* phosphine complexes contain single broad resonances which in the cases of *trans*-$[Os(PMe_3)_4X_2]$ were little changed by cooling the solution to 190 K. However the single resonances observed at room temperature for *trans*-$[Os(PMe_2Ph)_4X_2]$ broadened when the solutions were cooled, and at the lowest temperature achieved (190 K) showed evidence of several overlapping resonances. It was suggested by Coombe *et al.*[11] that the chloride was not a genuine P_4X_2 complex but that one phosphine was either π bonded to the metal or agostically bound. However since the complexes can be oxidised to *trans*-$[Os(PMe_2Ph)_4X_2]^+$ by nitric acid (below), all four phosphines must be P-bonded to the metal, and the spectral changes are explained by the presence of restricted rotation about the Os–P bonds due to the crowded nature of the cation, as observed for some iridium(III) analogues by Deeming *et al.*[18] The smaller cone angle of PMe_3 presumably reduces the barriers to rotation (although the NMR resonances are unusually broad), and individual resonances are not resolved. On standing in solution in chlorocarbon solvents the PMe_2Ph complexes rapidly isomerise to the *cis* forms,[11] the reaction being complete in a few hours at room temperature. Isomerisation also occurs for the PMe_3 complexes, but complete conversion into the *cis* isomers (as monitored by ^{31}P NMR spectroscopy) takes several days, and is complicated by the ease with which the *trans* isomers oxidise to Os^{III} in air. The arsine and stibine complexes show no sign of isomerisation in chlorocarbon solvents over several days.

Synthesis of Osmium(III) *Complexes*.—The *trans*-$[Os(EMe_3)_4X_2]BF_4$ (E = P or As) complexes were easily made by air oxidation of the osmium(II) complexes in ethanol in the presence of HBF_4. However for the synthesis of the other complexes (Table 1) nitric acid was cautiously added to a suspension of the osmium(II) complex in aqueous HBF_4. The pyridine complexes were initially made as tetrafluoroborates, but these proved to be poorly soluble in organic solvents, and the nitrate salts were prepared instead by HNO_3 oxidation of the osmium(II) complexes in dilute aqueous HX. Nitric acid oxidation of the corresponding *cis* osmium(II) complex produced *cis*-$[Os(PMe_2Ph)_4Cl_2]BF_4$, but the analogous bromide was not obtained analytically pure.

Properties. The *trans*-$[OsL_4X_2]BF_4$ complexes are deeply coloured, air stable and readily soluble in most organic solvents, in which they are 1:1 electrolytes. The assignments of the UV–VIS spectra (Table 1, Fig. 1) follow from those of the

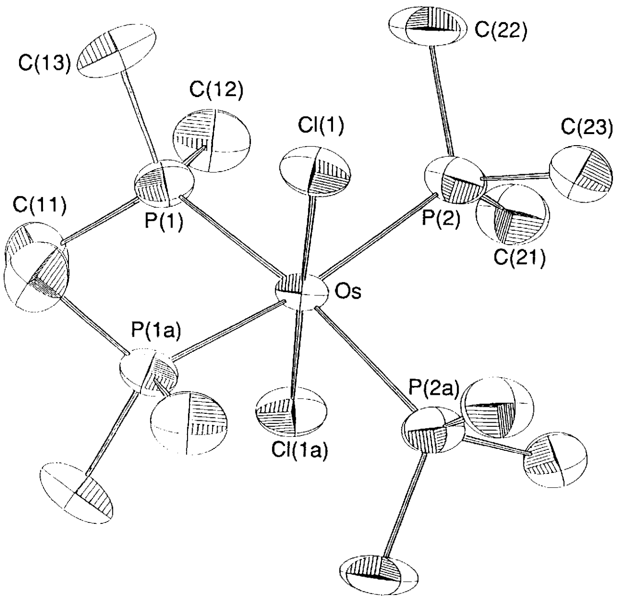

Fig. 2 The cation *trans*-$[Os(PMe_3)_4Cl_2]^+$ showing the atom numbering scheme. Hydrogen atoms are omitted for clarity and the thermal ellipsoids are drawn at the 40% probability level

Table 2 Bond lengths (Å) and angles (°) for *trans*-$[Os(PMe_3)_4Cl_2]BF_4$

Os–Cl(1)	2.352(4)	B–F(1)	1.32(2)
Os–P(1)	2.419(5)	B–F(2)	1.32(2)
Os–P(2)	2.398(5)		
P(1)–C(11)	1.82(2)	P(2)–C(21)	1.81(2)
P(1)–C(12)	1.81(2)	P(2)–C(22)	1.84(2)
P(1)–C(13)	1.81(2)	P(2)–C(23)	1.84(2)
P · · · Cl (min.)	3.14	C–H (fixed)	0.95
P · · · P (min.)	3.42		
Cl(1)–Os–P(1)	97.3(2)	P(1)–Os–P(2)	91.2(2)
Cl(1)–Os–P(2)	82.6(2)	P(1)–Os–P(1a)	89.8(3)
Cl(1)–Os–P(2a)	96.8(2)	P(1)–Os–P(2a)	165.9(2)
Cl(1)–Os–P(1a)	83.3(2)	P(2)–Os–P(2a)	91.2(3)
Cl(1)–Os–Cl(1a)	179.3(3)		
Os–P(1)–C(11)	115.4(6)	Os–P(2)–C(21)	117.5(7)
Os–P(1)–C(12)	114.8(7)	Os–P(2)–C(22)	116.0(7)
Os–P(1)–C(13)	118.0(7)	Os–P(2)–C(23)	115.3(7)
C(11)–P(1)–C(12)	98.5(9)	C(21)–P(2)–C(22)	104.1(10)
C(11)–P(1)–C(13)	105.7(10)	C(21)–P(2)–C(23)	104.1(11)
C(12)–P(1)–C(13)	101.9(9)	C(22)–P(2)–C(23)	97.1(9)
F(1)–B–F(2)	108(1)	F(1)–B–F(2b)	109(1)
F(1)–B–F(1b)	110(1)	F(2)–B–F(2b)	112(1)

Symmetry codes: a 0.25 − *x*, 0.25 − *y*, *z*; b 1.25 − *x*, *y*, 0.25 − *z*.

Table 3 Ultraviolet–visible spectra of the *trans* osmium(IV) cations *

Complex	Colour	E_{max} /10^3 cm^{-1}
$[Os(PMe_3)_4Cl_2]^{2+}$	Blue	14.5, 15.25 (sh)
$[Os(PMe_3)_4Br_2]^{2+}$	Green	13.8
$[Os(PMe_2Ph)_4Cl_2]^{2+}$	Brown	13.0
$[Os(PMe_2Ph)_4Br_2]^{2+}$	Brown	12.7
$[Os(AsMe_3)_4Cl_2]^{2+}$	Green	14.0, 14.9 (sh)
$[Os(AsMe_3)_4Br_2]^{2+}$	Brown	13.4, 13.9

* *In situ* in concentrated HNO_3 solution.

osmium(III) complexes of types $[OsL_2X_4]^-$ and $[OsL_3X_3]$.[2,3] For osmium(III) $t_{2g}{}^5$ complexes the major features are expected to be ligand $\longrightarrow t_{2g}(Os)$ c.t. transitions, and since the symmetry of the *trans* cations is relatively high (D_{4h}), assignments in terms of separate L→Os and X→Os transitions are reasonable. From previous studies[2,3] the strong features at $> ca.$ 28 000 cm^{-1} for the chlorides and $> ca.$ 25 000 cm^{-1} for the bromides are $\pi(X) \longrightarrow t_{2g}(Os)$ charge-transfer bands. The strong features at $< ca.$ 21 000 cm^{-1} for the heavy Group 15 donor complexes are similarly readily assigned as σ(P, As or Sb) $\longrightarrow t_{2g}(Os)$. The spectra are very similar to those of the more familiar *trans*-$[Os(diphosphine)_2X_2]^+$.[19] The spectra of the pyridine complexes are different in that several strong bands are present between 20 000 and 30 000 cm^{-1} and in addition to the $\pi(X) \longrightarrow t_{2g}(Os)$, $\pi(pyridine) \longrightarrow t_{2g}(Os)$ c.t. bands are expected.[20]

Structure of trans-$[Os(PMe_3)_4Cl_2]BF_4$.—The structure of a discrete cation is shown in Fig. 2 and Table 2 lists the bond lengths and angles. The osmium atom is located on a two-fold axis parallel to *z* and the cation has the *trans* configuration. The Os–Cl distance [2.352(4) Å] lies in the range found for other Os^{III}–Cl(*trans* Cl) distances {*e.g.* 2.363(2) Å in $[Os(NH_3)(PPh_3)_2Cl_3]$[21]} and supports the view that increasing osmium oxidation state is accompanied by decreasing Os–Cl distances. The Os–P distances seem unexceptional when compared with published data. The angles around the osmium are of some interest and this is most clearly illustrated by looking at the four Cl(1)–Os–P angles (Table 2). These show an alternating sequence greater than and less than 90° with on average a 7.0° change from the idealised value. The four P atoms thus form a very flattened tetrahedron with the two Cl atoms positioned over the two long (*trans*) edges. This is presumably a consequence of the steric requirements of the four trimethylphosphine ligands. A similar effect is found[18] in *trans*-$[Ir(PMe_2Ph)_4Cl_2]^+$. The Os–P–C angles have an average value of 116(1)° while the C–P–C angles [102(3)° (av.)] are essentially unchanged from the value[22] in free PMe_3 (99°). The BF_4^- anion is well documented, and in the present example shows no evidence for the disorder that is commonly encountered. The B atom is on a two-fold axis.

Osmium(IV) *Complexes*.—The electrochemical studies (below) show that the osmium(III) phosphine and arsine complexes undergo reversible 1e oxidations. The *trans*-$[Os(PMe_3)_4X_2]BF_4$ complexes dissolve in cold concentrated nitric acid to give deep blue (X = Cl) or green (X = Br) solutions which are stable for some hours at room temperature. The UV–VIS spectra contain broad absorptions at 13 000–15 000 cm^{-1} with clearly defined shoulders on the high-energy side, which are very similar to those observed[19] for *trans*-$[Os(diphosphine)_2X_2]^{2+}$, and show that *trans*-$[Os(PMe_3)_4X_2]^{2+}$ have been formed. Dilution of these solutions with water causes immediate decomposition to the osmium(III) analogues. All attempts to isolate these osmium(IV) complexes by the addition of HBF_4 or even 70% $HClO_4$ at −20 °C have failed. Similar osmium(IV) complexes are formed in solution by PMe_2Ph and $AsMe_3$ (Table 3), and again dilution with water regenerates the osmium(III) complexes. However there was no evidence for the formation of such complexes by $SbPh_3$, and whilst *trans*-$[Os(py)_4X_2]$ dissolve in concentrated HNO_3 to give green-brown solutions these have ill defined peaks in the UV–VIS spectra, and the osmium(III) complexes are not reformed on dilution or reduction. It seems likely that the species present are not *trans*-$[Os(py)_4X_2]^{2+}$. The *cis*-$[Os(PR_3)_4X_2]$ complexes similarly appear to decompose on dissolution in concentrated HNO_3.

Electrochemical Studies.—Cyclic voltammetry was used to determine the formal potentials of the Os^{II}–Os^{III}, and in some cases the Os^{III}–Os^{IV}, couples. Voltammograms were recorded at potential scan rates over the range 0.05–0.2 V s^{-1}, at a polished, vitreous carbon-disc electrode for 0.5×10^{-3} mol dm^{-3} solutions of the complexes in CH_2Cl_2 or MeCN, containing 0.1 mol dm^{-3} $NBu^n_4BF_4$. The results are listed in Table 4 and a typical example is shown in Fig. 3.

All of the complexes *trans*-$[OsL_4X_2]^{0/+}$ (L = PR_3, AsR_3 or py) gave reversible Os^{II}–Os^{III} couples. Reversible couples were

Table 4 Electrochemical data, $E_e°$/V *vs.* SCE

	Os^{II}–Os^{III}		Os^{III}–Os^{IV}
trans Isomers	CH_2Cl_2 [a]	MeCN [b]	MeCN
$[Os(PMe_2Ph)_4Cl_2]^{0/+}$	+0.26	+0.19	+1.41
$[Os(PMe_2Ph)_4Br_2]^{0/+}$	—	+0.23	+1.37
$[Os(PMe_3)_4Cl_2]^{0/+}$	—	+0.02	+1.28
$[Os(PMe_3)_4Br_2]^{0/+}$	—	+0.12	+1.29
$[Os(AsMe_3)_4Cl_2]^{0/+}$	—	−0.03	+1.28
$[Os(AsMe_3)_4Br_2]^{0/+}$	—	+0.03	+1.25
$[Os(SbPh_3)_4Cl_2]^{0/+}$	+0.43	(+0.46)[c]	(+1.63)[d]
$[Os(SbPh_3)_4Br_2]^{0/+}$	+0.48	(+0.47)[c]	(+1.60)[d]
$[Os(py)_4Cl_2]^{0/+}$	+0.45	—	—
$[Os(py)_4Br_2]^{0/+}$	+0.49	+0.33	—
cis Isomers			
$[Os(PMe_2Ph)_4Cl_2]^{0/+}$	+0.73	+0.63	—
$[Os(PMe_2Ph)_4Br_2]^{0/+}$	+0.80	—	—
$[Os(PMe_3)_4Cl_2]^{0/+}$	+0.69	—	—
$[Os(PMe_3)_4Br_2]^{0/+}$	+0.73	—	—

[a] Recorded in CH_2Cl_2; ferrocene couple at +0.57 V. [b] Recorded in MeCN; ferrocene couple at +0.41 V. [c] Quasi-reversible. [d] Irreversible.

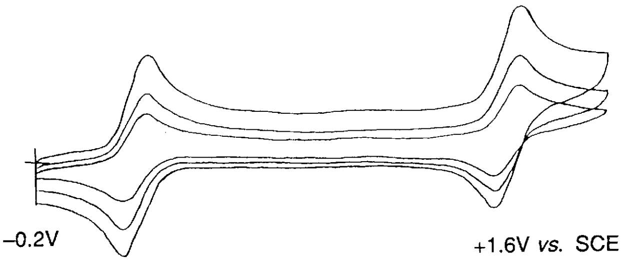

Fig. 3 Cyclic voltammogram of *trans*-$[Os(PMe_3)_4Br_2]$ in MeCN run at potential scan rates of 0.05, 0.1 and 0.2 V s^{-1}

also observed for *trans*-$[Os(SbR_3)_4X_2]$ in CH_2Cl_2, but *trans*-$[Os(SbPh_3)_4X_2]^+$ gave irreversible couples in MeCN, possibly due to the very low solubility of the osmium(II) complexes in this solvent. Reversible Os^{III}–Os^{IV} couples were also observed for the phosphine and arsine complexes, but *trans*-$[Os(SbPh_3)_4X_2]^+$ gave only quasi-reversible oxidations. The *trans*-$[Os(py)_4X_2]^+$ complexes gave a number of oxidations at more positive potentials, but the Os^{III}–Os^{IV} couple not be identified.

The *cis*-$[OsL_4X_2]^{0/+}$ complexes gave reversible Os^{II}–Os^{III} couples at potentials 0.7–0.8 V, more positive than those of the *trans* analogues. No Os^{III}–Os^{IV} couples were identified out to +2 V in MeCN, but a reversible couple was evident at more positive potentials than those of the Os^{II}–Os^{III} couples. From the small peak height and the observed value of $E°$ these couples were identified as due to small amounts of *mer*-$[OsL_3X_3]$[3] formed as a decomposition product (UV–VIS spectra of the starting materials ruled out their initial presence).

It can be seen from the data in Table 4 that varying the halide has little effect upon the redox potentials. However, as previously observed,[2,3] replacing alkyl substituents by phenyl groups shifts the potentials to more positive values, and this appears to be a greater effect than changing P for As as donor. The more positive Os^{II}–Os^{III} potential for the stibine complexes could be partly due to this effect, but unfortunately the osmium trialkylstibine complexes are unknown, previous attempts to prepare them[2] producing intractable oils. The differences in redox potential between corresponding *cis* and *trans* complexes show that the stereochemistry has a large effect.[2,3] We note that for the few examples where redox potentials have been reported previously[6,11] the results are in agreement with those reported here.

Iridium Complexes.—Previous studies[23] have shown that iridium(IV) complexes of types $[IrLCl_5]^-$, *trans*-$[IrL_2X_4]$ and *cis*-$[Ir(L–L)X_4]$ (L = PR_3, AsR_3, SR_2, *etc.*; X = Cl or Br; L–L = dithioether, diimine, *etc.*) are readily obtained, but the only reported examples with less than four co-ordinated halide ligands are the aqua species *mer*- and *fac*-$[Ir(H_2O)_3Cl_3]^+$ obtained in solution only.[24] In view of the osmium results (above and ref. 3), we re-examined a series of iridium(III) complexes $[IrL_3Cl_3]$ to see if there was evidence for the formation of the iridium(IV) analogues. The complexes *mer*-$[IrL_3Cl_3]$ (L = $PEtPh_2$, $AsMe_2Ph$, SMe_2, py or $SbPh_3$) and *fac*-$[Ir(PEtPh_2)_3Cl_3]$ were made by literature methods. Cyclic voltammetry in CH_2Cl_2 solution showed no evidence for any oxidation process within the potential range 0–1.6 V *vs.* saturated calomel electrode (SCE) for *mer*- and *fac*-$[Ir(PEtPh_2)_3Cl_3]$, *mer*-$[Ir(AsMe_2Ph)_3Cl_3]$ and *mer*-$[Ir(py)_3Cl_3]$. For *mer*-$[Ir(SMe_2)_3Cl_3]$ and *mer*-$[Ir(SbPh_3)_3Cl_3]$ there was evidence of some completely irreversible oxidation at highly positive potentials, but the lack of a corresponding reduction wave showed the products were not stable on the time-scale of cyclic voltammetry. Attempted chemical oxidation of these complexes with either Cl_2 in CH_2Cl_2 or concentrated HNO_3 was also unsuccessful. The triphenylstibine complex was completely decomposed to $[IrCl_6]^{2-}$ by excess of Cl_2, but no reaction was apparent in the other cases.

Experimental

The osmium starting materials were obtained and physical measurements were made as described previously.[3] All syntheses were carried out under a nitrogen atmosphere. Recrystallisations of the osmium(II) complexes were also performed with exclusion of oxygen.

trans-$[Os(py)_4Cl_2]$.—This was made by a modification of the method of Buckingham *et al.*[7] Powdered $[NH_4]_2[OsCl_6]$ (1.0 g, 2.3 mmol) was suspended in glycerol (20 cm^3), pyridine (5 cm^3) was added, and the mixture stirred at 80–90 °C for 3 h. The dark red solution was poured into water (100 cm^3), and extracted with CH_2Cl_2 (3 × 50 cm^3). The CH_2Cl_2 extracts were dried ($MgSO_4$) and evaporated to *ca.* 10 cm^3. On standing at 0 °C overnight dark red crystals separated (0.5 g, 40%). A further crop could be obtained by concentrating the solution, but was contaminated with *fac*-$[Os(py)_3Cl_3]$ (Found: C, 41.7; H, 3.4; N, 9.3. $C_{20}H_{20}Cl_2N_4Os$ requires C, 41.6; H, 3.5; N, 9.7%). The complex *trans*-$[Os(py)_4Br_2]$ was made similarly from $K_2[OsBr_6]$ in 55% yield (Found: C, 36.0; H, 3.2; N, 8.5. $C_{20}H_{20}Br_2N_4Os$ requires C, 36.0; H, 3.0; N, 8.4%).

trans-$[Os(PMe_3)_4Cl_2]$.—This complex was made using the method of Werner and Gotzig,[5] namely reaction of green $[Os(PPh_3)_3Cl_2]$[12] with PMe_3 at room temperature in hexane. The solid product was filtered off, washed with hexane and recrystallised from deoxygenated actone. ^{31}P-{^1H} NMR (CH_2Cl_2): δ −49 (s) ($W_{\frac{1}{2}}$ = 300 Hz). The complex *trans*-$[Os(PMe_3)_4Br_2]$ was prepared similarly from $[Os(PPh_3)_3Br_2]$[12] (35%) (Found: C, 21.8; H, 5.4. $C_{12}H_{36}Br_2OsP_4$ requires C, 22.0; H, 5.5%). ^{31}P-{^1H} NMR (CH_2Cl_2): δ −56.0 (s) ($W_{\frac{1}{2}}$ = 360 Hz).

trans-$[Os(PMe_2Ph)_4Cl_2]$.—A deoxygenated ethanol (35 cm^3) solution of OsO_4 (0.3 g, 1.18 mmol) and concentrated hydrochloric acid (3 cm^3) was treated with PMe_2Ph (1.64 g, 11.9 mmol) and the mixture heated to reflux under nitrogen for *ca.* 4 h and then cooled. After standing for 16 h at room temperature a yellow solid separated from the red solution and was filtered off, washed with ethanol until free from red powder and dried *in vacuo* (0.23 g, 24%) (Found: C, 47.4; H, 5.3. $C_{32}H_{44}Cl_2OsP_4$ requires C, 47.2; H, 5.4%). ^{31}P-{^1H} NMR (CH_2Cl_2): δ −52.8 (s) ($W_{\frac{1}{2}}$ = 680 Hz).

trans-$[Os(PMe_2Ph)_4Br_2]$.—The salt $Na_2[OsBr_6]$ (1.0 g, 1.4

mmol) and PMe_2Ph (1.5 g, 11 mmol) were refluxed under nitrogen in a mixture of ethanol (25 cm^3) and water (15 cm^3) until the ^{31}P-{^1H} NMR spectrum of a portion of the mixture showed that it contained largely the desired product. The reaction mixture was cooled, filtered and the solid dried *in vacuo* (0.9 g, 71%) (Found: C, 42.7; H, 5.1. $C_{32}H_{44}Br_2OsP_4$ requires C, 42.6; H, 4.9%). ^{31}P-{^1H} NMR (CH_2Cl_2): δ −59.6 (s) ($W_{\frac{1}{2}}$ = 240 Hz).

cis-[$Os(PMe_3)_4Cl_2$].—The corresponding *trans* isomer was dissolved in deoxygenated CH_2Cl_2 and the solution allowed to stand for 7 d with rigorous exclusion of oxygen. The solvent was removed *in vacuo*, the yellow powder washed with diethyl ether and dried (Found: C, 25.7; H, 6.3. $C_{12}H_{36}Cl_2OsP_4$ requires C, 25.5; H, 6.4%). ^{31}P-{^1H} NMR (CH_2Cl_2): δ −44 (t) and −48.2 (t) [^2J(PP) = 17 Hz]. The complex *cis*-[$Os(PMe_3)_4Br_2$] was made similarly (Found: C, 22.2; H, 5.6. $C_{12}H_{36}Br_2OsP_4$ requires C, 22.0; H, 5.5%). ^{31}P-{^1H} NMR (CH_2Cl_2): δ −50.9 (t) and −54.3 (t) [^2J(PP) = 18 Hz].

cis-[$Os(PMe_2Ph)_4Cl_2$].—The complex *mer*-[$Os(PMe_2Ph)_3Cl_3$] (0.49 g, 0.69 mmol) was heated to reflux with PMe_2Ph (0.5 cm^3) in 2-ethoxyethanol (25 cm^3) for 1 h until the mixture had become yellow, and was then evaporated under reduced pressure to *ca.* 10 cm^3. Acetone (5 cm^3) was added and the mixture refrigerated. The yellow solid was filtered off, washed with acetone (5 cm^3) and dried *in vacuo* (0.36 g, 64%) (Found: C, 47.1; H, 5.5. $C_{32}H_{44}Cl_2OsP_4$ requires C, 47.2; H, 5.4%). ^{31}P-{^1H} NMR ($CHCl_3$): δ −43.3 and −44.2 (broad with ill defined coupling).[11]

The complex *cis*-[$Os(PMe_2Ph)_4Br_2$] was prepared similarly from *mer*-[$Os(PMe_2Ph)_3Br_3$] (53%) (Found: C, 42.8; H, 5.0. $C_{32}H_{44}Br_2OsP_4$ requires C, 42.6; H, 4.9%). ^{31}P-{^1H} NMR (CH_2Cl_2): δ −48.8 (t) and −53.8 (t) [^2J(PP) = 16 Hz].

trans-[$Os(SbPh_3)_4Cl_2$].—The complex *mer*-[$Os(SbPh_3)_3Cl_3$] (0.3 g, 0.22 mmol)[10] was dissolved in CH_2Cl_2 (10 cm^3) and $SbPh_3$ (*ca.* 0.2 g) in 2-ethoxyethanol (10 cm^3) was added. After gentle warming, $NaBH_4$ was slowly added until the colour change from green to yellow was complete. Cooling of the mixture, followed by filtration, yielded a yellow solid which was rinsed with water and hydrochloric acid and recrystallised from a chloroform–ethanol mixture (0.22 g, 60%) (Found: C, 51.9; H, 3.7. $C_{72}H_{60}Cl_2OsSb_4$ requires C, 51.7; H, 3.6%). The complex *trans*-[$Os(SbPh_3)_4Br_2$] was similarly made from *mer*-[$Os(SbPh_3)_3Br_3$][3] (45%) (Found: C, 49.0; H, 3.4. $C_{72}H_{60}Br_2OsSb_4$ requires C, 49.1; H, 3.4%).

[$Os_2(AsMe_2Ph)_6X_3$]H_2PO_2 (X = Cl *or* Br).—These complexes were formed in attempts to make *trans*-[$Os(AsMe_2Ph)_4X_2$] using the method of Dwyer *et al.*[9] A nitrogen-purged solution of $Na_2[OsX_6]$ (0.7 mmol) and aqueous HX (5 cm^3) in ethanol (15 cm^3) was treated with $AsMe_2Ph$ (0.6 g) under a stream of nitrogen. Hypophosphorous acid (3 cm^3) was added and the solution heated to reflux under nitrogen. Reflux was continued, with *ca.* 2 cm^3 additional H_3PO_2 being added every 30 min, until the solution became yellow, whereupon excess of water was added and the mixture shaken with light petroleum (b.p. 40–60 °C, 15 cm^3). The yellow solid thus formed was filtered off and dried *in vacuo*: X = Cl (Found: C, 34.7; H, 4.1. $C_{48}H_{68}As_6Cl_3O_2Os_2P$ requires C, 35.0; H, 4.1%); ^1H NMR ($CDCl_3$): δ 1.75 (s, 6 H) and 7.4 (m, 5 H); IR: ν(P–H) 2322 cm^{-1} (H_2PO_2). X = Br (Found: C, 32.4; H, 4.2. $C_{48}H_{68}As_6Br_3O_2Os_2P$ requires C, 32.4; H, 3.8%); ^1H NMR ($CDCl_3$): δ 1.8 (s, 6 H) and 7.5 (m, 5 H); IR: ν(P–H) 2322 cm^{-1} (H_2PO_2).

trans-[$Os(PMe_2Ph)_4Cl_2$]BF_4.—The complex *trans*-[$Os(PMe_2Ph)_4Cl_2$] (0.41 g, 0.5 mmol) was suspended in 40% HBF_4 (15 cm^3), cooled in ice, and concentrated HNO_3 (1 cm^3) added. The mixture was stirred at 0 °C for 10 min, the purple solid filtered off, rinsed with water, and dried *in vacuo* (0.27 g, 60%) (Found: C, 42.8; H, 5.0. $C_{32}H_{44}BCl_2F_4OsP_4$ requires C, 42.7; H, 4.9%). The complex *trans*-[$Os(PMe_2Ph)_4Br_2$]BF_4 was prepared analogously, except that the oxidation to the green product was carried out at room temperature, complete reaction being achieved in 5 min (75%) (Found: C, 38.8; H, 4.4. $C_{32}H_{44}BBr_2F_4OsP_4$ requires C, 38.8; H, 4.4%), Λ_m (10^{-3} mol dm^{-3} MeCN) = 130 ohm^{-1} cm^2 mol^{-1}.

trans-[$Os(PMe_3)_4Cl_2$]BF_4.—To a nitrogen-purged solution of OsO_4 (0.3 g, 1.18 mmol) and concentrated HCl (3 cm^3) in ethanol (30 cm^3) was added a 1.0 mol dm^{-3} solution (10 cm^3) of PMe_3 (10 mmol) in toluene and the mixture refluxed under nitrogen for 3 h, producing *mer*-[$Os(PMe_3)_3Cl_3$] in solution. More ligand solution (5 cm^3) was then added and the reflux continued until the solution became yellow. After standing in air for *ca.* 16 h the mixture had become pink and addition of 40% aqueous HBF_4 (10 cm^3) followed by concentration to 30 cm^3 under reduced pressure and refrigeration for 3 d produced pink crystals of suitable quality for X-ray analysis. These were filtered off and dried *in vacuo* (0.43 g, 56%) (Found: C, 21.9; H, 5.4. $C_{12}H_{36}BCl_2F_4OsP_4$ requires C, 22.0; H, 5.5%), Λ_m (10^{-3} mol dm^{-3} MeCN) = 151 ohm^{-1} cm^2 mol^{-1}.

trans-[$Os(PMe_3)_4Br_2$]BF_4.—The acetone solution remaining from the recrystallisation of *trans*-[$Os(PMe_3)_4Br_2$] was treated with 40% aqueous HBF_4 (20 cm^3) and concentrated under reduced pressure until precipitation occurred. The purple solid was isolated by filtration, washed with distilled water and dried *in vacuo* (30%) (Found: C, 20.0; H, 5.3. $C_{12}H_{36}BBr_2F_4OsP_4$ requires C, 19.4; H, 4.9%).

trans-[$Os(AsMe_3)_4Cl_2$]BF_4.—The salt $K_2[OsCl_6]$ (0.48 g, 1.0 mmol) was suspended in water (5 cm^3)–butanol (15 cm^3), $AsMe_3$ (0.48 g, 4.0 mmol) added and the mixture heated to reflux. Hypophosphorous acid (1 cm^3) was added and the reflux continued for 2 h, after which the solvents were removed *in vacuo*, to yield a crude orange solid, *mer*-[$Os(AsMe_3)_3Cl_3$]. This was redissolved in tetrahydrofuran (15 cm^3) under Ar, and $AsMe_3$ (0.24 g, 2.0 mmol) and amalgamated zinc (*ca.* 2 g) added. The mixture was refluxed for 1 h, by which time a clear yellow solution had formed. The zinc was removed, and the filtrate concentrated *in vacuo* to a clear pale yellow oil. This was dissolved in the minimum volume of acetone, HBF_4 (40%, 10 cm^3) was added, and the mixture stirred in air overnight. The resulting red solution was concentrated to *ca.* 5 cm^3, and on standing at 0 °C deposited red crystals (40%) (Found: C, 17.5; H, 4.5. $C_{12}H_{36}As_4BCl_2F_4Os$ requires C, 17.4; H, 4.3%). The complex *trans*-[$Os(AsMe_3)_4Br_2$]BF_4 was made similarly (35%) (Found: C, 15.6; H, 4.1. $C_{12}H_{36}As_4BBr_2F_4Os$ requires C, 15.7; H, 3.9%).

trans-[$Os(SbPh_3)_4X_2$]BF_4.—These complexes were prepared similarly to *trans*-[$Os(PMe_2Ph)_4Cl_2$]BF_4, by room-temperature oxidation of the osmium(II) compound suspended in aqueous HBF_4 with concentrated HNO_3. The yields were *ca.* 40%. X = Cl (Found: C, 48.7; H, 3.5. $C_{72}H_{60}BCl_2F_4OsSb_4$ requires C, 49.1; H, 3.4%), Λ_m (10^{-3} mol dm^{-3} MeCN) = 120 ohm^{-1} cm^2 mol^{-1}. X = Br (Found: C, 47.0; H, 3.3. $C_{72}H_{60}BBr_2F_4OsSb_4$ requires C, 46.8; H, 3.2%).

trans-[$Os(py)_4Cl_2$]NO_3.—Powdered [$Os(py)_4Cl_2$] (0.3 g, 0.52 mmol) was suspended in 0.1 mol dm^{-3} hydrochloric acid (10 cm^3) and concentrated nitric acid added dropwise (*ca.* 1 cm^3), with vigorous stirring. The solid rapidly became yellow-brown, and after 15 min was filtered off, rinsed with water (3 × 5 cm^3) and dried *in vacuo* (0.45 g, 70%) (Found: C, 37.8; H, 3.1; N, 10.6. $C_{20}H_{20}Cl_2N_5O_3Os$ requires C, 37.5; H, 3.1; N, 11.0%). The complex *trans*-[$Os(py)_4Br_2$]NO_3 was made similarly (Found: C, 33.4; H, 2.9; N, 9.6. $C_{20}H_{20}Br_2N_5O_3Os$ requires C, 33.0; H, 2.7; N, 9.6%).

Table 5 Atomic coordinates * for *trans*-$[Os(PMe_3)_4Cl_2]BF_4$

Atom	*x*	*y*	*z*
Os	0.1250	0.1250	0.254 70(2)
Cl(1)	0.359 7(5)	0.082 0(1)	0.255 1(1)
P(1)	−0.026 5(6)	0.088 1(1)	0.210 3(1)
P(2)	0.032 0(7)	0.077 2(1)	0.298 2(1)
C(11)	−0.092 7(24)	0.119 4(6)	0.173 6(4)
C(12)	−0.227 0(23)	0.068 9(6)	0.223 7(5)
C(13)	0.066 2(25)	0.042 1(6)	0.191 8(5)
C(21)	−0.169 6(27)	0.086 0(6)	0.316 8(5)
C(22)	0.029 3(28)	0.021 9(5)	0.285 6(5)
C(23)	0.168 1(30)	0.071 7(6)	0.336 0(5)
B	0.6250	0.027 2(9)	0.1250
F(1)	0.525 5(22)	0.003 7(4)	0.106 5(4)
F(2)	0.712 8(28)	0.050 1(4)	0.103 5(4)

* The origin of the atomic coordinates was chosen to be on the centre of symmetry.

cis-$[Os(PMe_2Ph)_4Cl_2]BF_4$.—This complex was prepared in a similar manner to the *trans* isomer, but using 40% HNO_3 at room temperature to effect the oxidation (32%) (Found: C, 42.6; H, 5.0. $C_{32}H_{44}BCl_2F_4OsP_4$ requires C, 42.7; H, 4.9%).

mer-$[Ir(py)_3Cl_3]$.—The salt $Na_3[IrCl_6]$ (1.0 g, 2.1 mmol), concentrated hydrochloric acid (*ca.* 0.1 cm^3) and pyridine (5 cm^3) were heated to reflux in 2-methoxyethanol (20 cm^3) for 2 h and cooled. More pyridine (5 cm^3) was added and the solution refluxed for 1 h and cooled; this procedure was repeated until no solid was observed on cooling the mixture. The solution was concentrated under reduced pressure until precipitation occurred, when the solid was filtered off. This first crop was found to be contaminated with pyridinium salts but further concentration and refrigeration produced a second crop of microcrystals, which were isolated by filtration and shown by spectroscopic measurements to be pure. A third crop of pure *mer*-$[Ir(py)_3Cl_3]$ was also obtained (total pure yield *ca.* 50%) (Found: C, 33.6; H, 3.0; N, 7.7. $C_{15}H_{15}Cl_3IrN_3$ requires C, 33.6; H, 2.8; N, 7.8%).

The complexes *mer*-$[Ir(PEtPh_2)_3Cl_3]$, *mer*-$[Ir(AsMe_2Ph)_3Cl_3]$,[23] *mer*-$[Ir(SMe_2)_3Cl_3]$[25] and *fac*-$[Ir(PEtPh_2)_3Cl_3]$[26] were made by literature routes.

Crystal Structure Determination.—Red air-stable needle crystals of *trans*-$[Os(PMe_3)_4Cl_2]BF_4$ were isolated from EtOH–water, mounted in thin-walled glass capillaries, and examined photographically by X-ray diffraction. The crystals were weak scatterers. Using an Enraf–Nonius CAD4 diffractometer equipped with molybdenum radiation and a graphite monochromator, accurate cell dimensions were obtained from 25 carefully centred reflections, and diffracted intensities (3072) were recorded from a crystal 0.45 × 0.075 × 0.05 mm (ω–2θ scans, $1.5 < \theta < 21°$, *h* 0–8, *k* −32 to 32, *l* 0–38, ambient temperature). The three intensity controls showed no decay during the experiment and after the data reduction there remained 1355 unique reflections ($R_{int} = 0.019$) of which 1040 with $F > 2\sigma(F)$ were used in the analysis and refinement. An empirical ψ-scan absorption correction was applied to the data (transmission: minimum 81.3, maximum 99.9%) along with the usual Lorentz and polarisation corrections. The density was measured by flotation in CCl_4–$C_2H_4Br_2$ mixtures.

Crystal data. $C_{12}H_{36}BCl_2F_4OsP_4$, $M = 652.28$, orthorhombic, space group *Fddd* (no. 70), $a = 8.104(4)$, $b = 32.195(11)$, $c = 38.540(9)$ Å, $U = 10\,055.4$ Å^3, $D_m = 1.74(2)$ g cm^{-3}, $Z = 16$, $D_c = 1.723$ g cm^{-3}, $F(000) = 5104$, Mo-Kα radiation ($\lambda = 0.710\,69$ Å), μ(Mo-Kα) = 55.1 cm^{-1}.

The systematic absences established the space group and the origin was chosen to lie on the centre of symmetry. The structure was solved independently by two means: one involved inspection of the Patterson function and location of the osmium, the second used the direct-methods technique in SHELXS 86.[27] The problem in developing the solution arose from the very small heights of P and Cl in the difference electron-density map phased on the osmium atom. Repeated structure-factor and electron-density syntheses located the remaining non-H atoms. The osmium is located on the 16g position and the boron atom on the 16f position, both with two-fold point symmetry. At the later stages of refinement a number of H atoms were indicated in the difference electron-density synthesis. Hydrogen atoms of the phosphine ligand were introduced into the molecule in calculated positions [d(CH) = 0.95 Å] with a common fixed thermal parameter. Full-matrix least-squares refinement minimising $\Sigma w\Delta^2$ converged to $R = 0.060$ {1040 reflections, 107 parameters, anisotropic (Os, Cl, P, C, F) and isotropic (B, H) atoms, $w^{-1} = [\sigma^2(F) + 0.0007F^2]$, maximum shift/error = 0.09, $S = 1.32$, $R' = 0.053$}. The residual electron density was in the range 1.02 to −1.52 e Å^{-3}. Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX 76[28] (Cl, P, F, B, C, H) and ref. 29 (Os) and all calculations were carried out using the programs SHELX 76,[28] SHELXS 86,[27], ORTEP II,[30] PLUTO[31] and PARST[32] on an IBM 3090 computer. Table 5 gives the atomic coordinates.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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