Co-ordination Chemistry of Higher Oxidation States. Part 23.[1] Synthesis and Properties of Tetrahalogenoiridium(IV) Complexes, $[IrL_2X_4]$ [X = Cl or Br; L = pyridine, PR_3, AsR_3, SbR_3, SR_2, or SeR_2]. Crystal and Molecular Structure of *trans*-$[Ir(AsEt_3)_2Br_4]$†

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The iridium(III) anions *trans*-$[IrL_2Cl_4]^-$ [L = pyridine (py), PEt_3, PEt_2Ph, $PEtPh_2$, $AsEt_3$, $AsMe_2Ph$, SMe_2, or $SeMe_2$] have been prepared and oxidised with chlorine to purple iridium(IV) *trans*-$[IrL_2Cl_4]$. Dark green *trans*-$[IrL_2Br_4]$ (L = py, PEt_3, PMe_2Ph, $AsEt_3$, $AsMe_2Ph$, or SMe_2) were obtained similarly from *trans*-$[IrL_2Br_4]^-$ and Br_2 or HNO_3. The $[IrL_2Cl_4]$ (L = PPh_3, $AsPh_3$, or $SbPh_3$) are made directly from $IrCl_3{\cdot}nH_2O$ + 2L, followed by chlorination of the intermediate $[(IrL_2Cl_3)_n]$ produced; *cis*-$[IrL_2Cl_4]$ (L = py or $SbMe_3$) and *trans*-$[IrL_2X_4]^-$ (L = $TeMe_2$, X = Cl; L = $SeMe_2$, X = Br) are also described. The iridium(IV) complexes have been characterised by analysis, i.r., and u.v.–visible spectroscopy and for the complex $[Ir(AsEt_3)_2Br_4]$ by *X*-ray diffraction. Crystals of *trans*-$[Ir(AsEt_3)_2Br_4]$ are monoclinic, space group $P2_1/n$ with a = 8.442(1), b = 13.933(2), c = 9.617(1) Å, β = 103.85(1)°, Z = 2, and R = 0.041 for 1 826 reflections [$F > 3\sigma(F)$]. Discrete centrosymmetric molecules with Ir–Br 2.455(1), 2.463(1) and Ir–As 2.489(1) Å are present. Assignments are proposed for the u.v.–visible spectra of *trans*-$[IrL_2X_4]$ in terms mainly of $\pi_X, \sigma_X, \sigma_L \longrightarrow Ir\ (t_{2g})$ ligand-to-metal charge-transfer transitions. For most couples, $[IrL_2X_4]$–$[IrL_2X_4]^-$, the electron-transfer reaction is close to reversible and formal potentials, estimated from the cyclic voltammograms, correlate well with spectroscopic data. The voltammograms for four anions (X = Cl, L = $TeMe_2$ and X = Br, L = $SbPh_3$, $SeMe_2$, or dimethyl sulphoxide) show that the corresponding iridium(IV) complexes have half-lives of only a few seconds and this explains the failure to isolate them from chemical syntheses. Cyclic voltammograms for $[RhL_2Cl_4]^-$ (L = PEt_3, SMe_2, $SeMe_2$, or py) show that oxidation occurs at more positive potentials, but the rhodium(IV) complexes are unstable. Neutral iridium(III) complexes $[IrL_3X_3]$ are not oxidised by X_2 or HNO_3, and possible reasons for this and the crucial role of the $[IrL_2X_4]^-$ intermediates in the preparation of $[IrL_2X_4]$ are discussed.

The chemistry of iridium(IV) is not extensive,[2] a reflection of the great stability of the $5d\ t_{2g}{}^6$ configuration of iridium(III) which makes oxidation difficult. A number of complexes of the type $[IrL_2Cl_4]$ [L = *e.g.* pyridine (py) or tertiary phosphine] have been reported but few have been subjected to detailed study.[3–8] The aims of the present investigation were to characterise a series of these complexes with Group 5B and 6B donor ligands and to attempt the preparation of the hitherto unknown‡ bromo complexes. Since these complexes undergo reversible one-electron reductions they are ideal systems in which to study the effects of L and X upon the iridium(III)–iridium(IV) redox potential.

Experimental

Physical measurements were made as described in previous parts of this series. Iridium(III) chloride hydrate was obtained from Johnson Matthey and the corresponding bromide obtained by repeatedly evaporating the chloride with 47% hydrobromic acid, and finally drying the black product *in vacuo*.

Preparations.—Tetrachlorobis(triethylphosphine)iridium(IV), $[Ir(PEt_3)_2Cl_4]$. Iridium trichloride hydrate (0.40 g, 1.1 mmol) was dissolved in a deoxygenated mixture of concentrated hydrochloric acid (4 cm^3) and ethanol (16 cm^3), triethylphosphine (0.53 g, 4.5 mmol) was added, and the mixture refluxed for 2 h. The solvent was removed *in vacuo* and the residue washed with boiling toluene (75 cm^3). The toluene-insoluble product was recrystallised from ethanol–light petroleum (b.p. 60—80 °C) yielding pink plates of the salt $[PEt_3H][Ir(PEt_3)_2Cl_4]$. This salt was dissolved in $CHCl_3$ (10 cm^3) and chlorine was bubbled through the solution which immediately turned dark purple. The solvent was removed *in vacuo* and the product was recrystallised from cyclohexane (0.06 g, 9%) (Found: C, 25.3; H, 5.3. $C_{12}H_{30}Cl_4IrP_2$ requires C, 25.3; H, 5.3%).

Tetrachlorobis(diethylphenylphosphine)iridium(IV), $[Ir(PEt_2Ph)_2Cl_4]$. This complex was made by an analogous method to that for $[Ir(PEt_3)_2Cl_4]$. The initial mixture was refluxed for 5 h, the intermediate iridate(III) salt was recrystallised from ethanol, and the final product was recrystallised from CH_2Cl_2–light petroleum (b.p. 60—80 °C) (10%) (Found: C, 36.5; H, 4.6. $C_{20}H_{30}Cl_4IrP_2$ requires C, 36.0; H, 4.5%).

Tetrachlorobis(triethylarsine)iridium(IV), $[Ir(AsEt_3)_2Cl_4]$. Iridium trichloride hydrate (0.32 g, 0.9 mmol) was dissolved in a deoxygenated mixture of concentrated hydrochloric acid (5 cm^3) and ethanol (20 cm^3). Triethylarsine (0.65 g, 4 mmol) was added and the mixture refluxed for 2 h. The solvent was removed *in vacuo* and the residue washed with boiling toluene (75 cm^3). The insoluble product was dissolved in CH_2Cl_2 (10

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† *trans*-Tetrabromobis(triethylarsine)iridium(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Non-S.I. unit employed: B.M. = 0.927 × 10^{-23} A m^2.

‡ *A brown complex* $[Ir(py)_2Br_4]$ has been described[9] without supporting data. In fact, we find this complex is green (see later).

cm^3) and chlorine was bubbled through the solution which was then filtered and evaporated *in vacuo*. The dark maroon product was recrystallised from light petroleum (b.p. 60—80 °C) (0.065 g, 11%) (Found: C, 21.8; H, 4.5. $C_{12}H_{30}As_2Cl_4Ir$ requires C, 21.9; H, 4.6%).

Tetrachlorobis(dimethylphenylarsine)iridium(IV), $[Ir(AsMe_2Ph)_2Cl_4]$. The same basic method was used as for $[Ir(AsEt_3)_2Cl_4]$. However the reaction mixture was refluxed for 5 h and the dark maroon product was recrystallised from CH_2Cl_2–light petroleum (b.p. 60—80 °C) (8%) (Found: C, 27.3; H, 3.2. $C_{16}H_{22}As_2Cl_4Ir$ requires C, 27.5; H, 3.15%).

Tetrachlorobis(triphenylstibine)iridium(IV), $[Ir(SbPh_3)_2Cl_4]$. Iridium trichloride hydrate (0.50 g, 1.4 mmol) and triphenylstibine (1.77 g, 5.0 mmol) were dissolved in a mixture of ethanol (20 cm^3) and concentrated hydrochloric acid (9 cm^3) and refluxed for 10 min. On cooling, a precipitate formed which was filtered off and extracted with acetone. The acetone was removed *in vacuo* and the solid redissolved in CH_2Cl_2. Excess of a solution of chlorine in CCl_4 was added causing immediate precipitation of a dark mauve solid which was collected on a sinter, washed with acetone, and dried *in vacuo* (0.10 g, 7%) (Found: C, 41.6; H, 3.0. $C_{36}H_{30}Cl_4IrSb_2$ requires C, 41.55; H, 2.9%).

Tetrachlorobis(trimethylstibine)iridium(IV), $[Ir(SbMe_3)_2Cl_4]$. Trimethylstibine, generated from dibromotrimethylstibine (2.7 g, 8.4 mmol) and zinc,[10] was passed into a solution of iridium trichloride hydrate (0.49 g, 1.4 mmol) in ethanol (20 cm^3) and concentrated hydrochloric acid (6 cm^3) and the mixture was refluxed for 2.5 h. The solvent was removed *in vacuo* leaving a gum which, on treatment with ethanol, yielded an orange solution and yellow solid. The solid was filtered off and extracted with acetone which was then removed *in vacuo*. The resultant orange oil was redissolved in CH_2Cl_2 and chlorine was bubbled through the solution causing immediate precipitation of a dark mauve-brown solid which was collected on a sinter, washed with acetone, and dried *in vacuo* (0.18 g, 20%) (Found: C, 11.0; H, 2.8. $C_6H_{18}Cl_4IrSb_2$ requires C, 10.8; H, 2.7%).

Tetrachlorobis(triphenylarsine)iridium(IV), $[Ir(AsPh_3)_2Cl_4]$, *and tetrachlorobis(triphenylphosphine)iridium*(IV), $[Ir(PPh_3)_2Cl_4]$. These were made from $[\{Ir(C_8H_{14})_2Cl\}_2]$ by the literature method[5] (Found: C, 45.7; H, 3.6. $C_{36}H_{30}As_2Cl_4Ir$ requires C, 45.7; H, 3.2) (Found: C, 51.0; H, 3.5. $C_{36}H_{30}Cl_4IrP_2$ requires C, 50.3; H, 3.5%).

Tetrachlorobis(ethyldiphenylphosphine)iridium(IV), $[Ir(PEtPh_2)_2Cl_4]$. Iridium trichloride hydrate (0.33 g, 0.95 mmol) was dissolved in a deoxygenated mixture of ethanol (12 cm^3) and concentrated hydrochloric acid (3 cm^3). Ethyldiphenylphosphine (0.61 g, 2.9 mmol) was added and the mixture refluxed for 2 h. On cooling, the solution was filtered to remove the yellow, insoluble tris complex $[Ir(PEtPh_2)_3Cl_3]$ and the solvent was removed, *in vacuo*. The solid product was extracted into acetone which was then removed *in vacuo*. The product was redissolved in $CHCl_3$ (10 cm^3) and chlorine was bubbled through the solution which immediately turned deep purple. The $CHCl_3$ was removed *in vacuo* and the purple complex was recrystallised from CH_2Cl_2–diethyl ether (0.028 g, 4%) (Found: C, 43.9; H, 4.0. $C_{28}H_{30}Cl_4IrP_2$ requires C, 44.1; H, 3.9%).

Tetrachlorobis(triphenylphosphine)iridium(IV), $[Ir(PPh_3)_2Cl_4]$. Iridium trichloride hydrate (0.37 g, 1.04 mmol) was dissolved in a mixture of water (12 cm^3) and concentrated hydrochloric acid (3 cm^3). Triphenylphosphine (0.55 g, 2.1 mmol) dissolved in ethanol (20 cm^3) was added and the mixture refluxed for 30 min. The yellow precipitate of $[\{Ir(PPh_3)_2Cl_3\}_n]$ was filtered off and dried *in vacuo*. It was then redissolved (0.25 g) in CH_2Cl_2 and chlorine was bubbled through the solution. The purple product was precipitated with cyclohexane, collected on a sinter, and dried *in vacuo* (0.03 g, 12%) (Found: C, 50.0; H, 3.4. $C_{36}H_{30}Cl_4IrP_2$ requires C, 50.3; H, 3.5%).

cis- *and* trans-*Tetrachlorobis(pyridine)iridium*(IV), $[Ir(py)_2Cl_4]$. Iridium trichloride hydrate (0.34 g, 0.95 mmol) was dissolved in a mixture of water (10 cm^3) and concentrated hydrochloric acid (2 cm^3). Pyridine (1 cm^3, 12 mmol) was added and the mixture refluxed for 1 h. The solution was reduced to a small volume and allowed to stand at −10 °C, whereupon buff crystals of [Hpy][*cis*-$Ir(py)_2Cl_4$] precipitated and were collected. Excess of chlorine–water was added to the remaining solution causing immediate precipitation of *trans*-$[Ir(py)_2Cl_4]$ which was collected and dried *in vacuo* (0.21 g, 46%). [Hpy][*cis*-$Ir(py)_2Cl_4$] was oxidised by swirling in chlorine–water then collecting and drying *in vacuo* the resultant, purple, *cis*-$[Ir(py)_2Cl_4]$ (0.03 g, 6.5%) {Found for *cis*-$[Ir(py)_2Cl_4]$: C, 24.6; H, 2.1; N, 5.7. $C_{10}H_{10}Cl_4IrN_2$ requires C, 24.4; H, 2.0; N, 5.7. Found for *trans*-$[Ir(py)_2Cl_4]$: C, 24.5; H, 2.0; N, 5.7%}.

Tetrabromobis(pyridine)iridium(IV), $[Ir(py)_2Br_4]$. Iridium tribromide hydrate (0.42 g, 0.85 mmol) and pyridine (0.8 cm^3, 10 mmol) were dissolved in a mixture of water (10 cm^3) and 47% hydrobromic acid (2 cm^3) and the solution was refluxed for 1 h. The volume was reduced by boiling and excess of bromine–water was added to the cooled solution causing immediate precipitation of the dark grey-green product which was collected on a sinter, washed with water, and dried *in vacuo* (0.13 g, 23%) (Found: C, 18.1; H, 1.6; N, 4.5. $C_{10}H_{10}Br_4IrN_2$ requires C, 17.9; H, 1.5; N, 4.2%).

Tetrabromobis(triethylphosphine)iridium(IV), $[Ir(PEt_3)_2Br_4]$. Iridium tribromide hydrate (0.51 g, 1.04 mmol) was dissolved in a deoxygenated mixture of ethanol (15 cm^3) and 47% hydrobromic acid (10 cm^3). Triethylphosphine (0.39 g, 3.3 mmol) was added and the mixture refluxed for 30 min. The solvent was removed *in vacuo* leaving an oil which, on treatment with ethanol, yielded a yellow solution. On cooling, yellow-green crystals of $[PEt_3H][Ir(PEt_3)_2Br_4]$ precipitated, which were collected and dried *in vacuo*. The salt was redissolved in CH_2Cl_2 and excess of bromine was added causing an immediate dark green colouration. The solvent was removed *in vacuo* and the product recrystallised from cyclohexane (0.038 g, 5%) (Found: C, 19.2; H, 4.0. $C_{12}H_{30}Br_4IrP_2$ requires C, 19.3; H, 4.0%).

Tetrabromobis(dimethylphenylphosphine)iridium(IV), $[Ir(PMe_2Ph)_2Br_4]$. Iridium tribromide hydrate (0.48 g, 0.99 mmol) was dissolved in a deoxygenated mixture of ethanol (15 cm^3) and 47% hydrobromic acid (10 cm^3). Dimethylphenylphosphine (0.60 g, 4.3 mmol) was added and the mixture refluxed for 30 min. The solvent was removed *in vacuo* and the residue extracted with boiling toluene and recrystallised from ethanol–light petroleum (b.p. 60—80 °C) giving buff crystals of $[PMe_2PhH][Ir(PMe_2Ph)_2Br_4]$. The salt was dissolved in CH_2Cl_2 and excess of a solution of bromine in CCl_4 was added. After cooling, the blue-green solution was filtered and the solvent removed *in vacuo*. The product was recrystallised from CH_2Cl_2–light petroleum (b.p. 60—80 °C) containing a trace of bromine (0.032 g, 4%) (Found: C, 24.3; H, 2.9. $C_{16}H_{22}Br_4IrP_2$ requires C, 24.4; H, 2.8%).

Tetrabromobis(triethylarsine)iridium(IV), $[Ir(AsEt_3)_2Br_4]$. Iridium tribromide hydrate (0.50 g, 1.03 mmol) was dissolved in a deoxygenated mixture of ethanol (15 cm^3) and 47% hydrobromic acid (10 cm^3). Triethylarsine (0.89 g, 5.5 mmol) was added and the mixture refluxed for 5 min. The solvent was removed *in vacuo* and the residue extracted with boiling toluene. The remaining solid was dissolved in ethanol and the solution was filtered to remove impurities. The ethanol was removed *in vacuo* and the resultant oil was dissolved in CH_2Cl_2. Excess of bromine in CCl_4 was added and the solution filtered. The solvents were removed *in vacuo* and the bright green product was recrystallised from cyclohexane (0.08 g, 13%) (Found: C, 17.0; H, 3.5. $C_{12}H_{30}As_2Br_4Ir$ requires C, 17.2; H, 3.6%).

Tetrabromobis(dimethylphenylarsine)iridium(IV), $[Ir(AsMe_2Ph)_2Br_4]$. This compound was made by an analogous method to that for $[Ir(AsEt_3)_2Br_4]$. The initial mixture was refluxed for 30 min and the dark green product was recrystallised from CH_2Cl_2–light petroleum (11%) (Found: C, 21.7; H, 2.6. $C_{16}H_{22}As_2Br_4Ir$ requires C, 21.9; H, 2.5%).

Tetramethylammonium trans-*tetrachlorobis(dimethyl sulphide)iridate*(III), $[NMe_4][Ir(SMe_2)_2Cl_4]$. This was prepared by the literature method[11] (Found: C, 18.0; H, 4.5; N, 2.5. $C_8H_{24}Cl_4IrNS_2$ requires C, 18.0; H, 4.5; N, 2.6%).

Tetrachlorobis(dimethyl sulphide)iridium(IV), $[Ir(SMe_2)_2Cl_4]$. This was also made by the literature method[11] by oxidation of $[NMe_4][Ir(SMe_2)_2Cl_4]$ (Found: C, 10.6; H, 2.6. $C_4H_{12}Cl_4IrS_2$ requires C, 10.5; H, 2.6%).

Tetramethylammonium trans-*tetrachlorobis(dimethyl selenide)iridate*(III), $[NMe_4][Ir(SeMe_2)_2Cl_4]$. Iridium trichloride hydrate (0.49 g, 1.4 mmol) and $[NMe_4]Cl{\cdot}H_2O$ (0.19 g, 1.5 mmol) were dissolved in a mixture of water (10 cm^3) and concentrated hydrochloric acid (2 cm^3). Dimethyl selenide (0.32 g, 2.9 mmol) dissolved in ethanol (10 cm^3) was added and the mixture refluxed for 16 h. The solvent was removed *in vacuo* and the residue was recrystallised from hot acetone (0.09 g, 10%) (Found: C, 15.5; H, 3.9; N, 2.2. $C_8H_{24}Cl_4IrNSe_2$ requires C, 15.3; H, 3.8; N, 2.2%).

Tetramethylammonium trans-*tetrachlorobis(dimethyl telluride)iridate*(III), $[NMe_4][Ir(TeMe_2)_2Cl_4]$. Iridium trichloride hydrate (0.38 g, 1.09 mmol), $[NMe_4]Cl{\cdot}H_2O$ (0.16 g, 1.25 mmol), and dimethyl telluride (0.36 g, 2.3 mmol) were dissolved in a mixture of ethanol (10 cm^3) and concentrated hydrochloric acid (2 cm^3) and refluxed for 30 min. The solvent was removed *in vacuo* and the residue extracted with hot acetone. The resultant solution was concentrated and cooled whereupon the orange product precipitated and was collected and dried *in vacuo* (0.025 g, 3%) (Found: C, 13.2; H, 3.4; N, 2.0. $C_8H_{24}Cl_4IrNTe_2$ requires C, 13.3; H, 3.3; N, 1.9%).

Tetraethylammonium trans-*tetrabromobis(dimethyl sulphide)iridate*(III), $[NEt_4][Ir(SMe_2)_2Br_4]$. Iridium tribromide hydrate (0.47 g, 0.96 mmol) was dissolved in a mixture of water (10 cm^3) and 47% hydrobromic acid (2 cm^3). A solution of $[NEt_4]Br$ (0.23 g, 1.1 mmol) and dimethyl sulphide (0.12 g, 1.94 mmol) in ethanol (10 cm^3) was added and the mixture refluxed for 3 h. The solvent was removed *in vacuo* and the residue was extracted with hot acetone. Buff crystals of the product were precipitated by the addition of ethanol and cooling the solution (0.07 g, 10%) (Found: C, 18.4; H, 4.4; N, 1.6. $C_{12}H_{32}Br_4IrNS_2$ requires C, 18.8; H, 4.2; N, 1.8%).

Tetrabromobis(dimethyl sulphide)iridium(IV), $[Ir(SMe_2)_2Br_4]$. The salt $[NEt_4][Ir(SMe_2)_2Br_4]$ (0.05 g, 0.07 mmol) was suspended in water (5 cm^3) and concentrated nitric acid (5 cm^3) was added. The mixture was stirred vigorously for 5 min, then the dark green product was collected on a sinter, washed with water, and dried *in vacuo* (0.03 g, 72%) (Found: C, 7.8; H, 1.8. $C_4H_{12}Br_4IrS_2$ requires C, 7.5; H, 1.9%).

Tetraethylammonium trans-*tetrabromobis(dimethyl selenide)iridate*(III), $[NEt_4][Ir(SeMe_2)_2Br_4]$. Iridium tribromide hydrate (0.53 g, 1.1 mmol) was dissolved in a mixture of water (10 cm^3) and 47% hydrobromic acid (2 cm^3). A solution of $[NEt_4]Br$ (0.23 g, 1.1 mmol) and dimethyl selenide (0.24 g, 2.2 mmol) in ethanol (10 cm^3) was added and the mixture refluxed for 16 h. The solvent was removed *in vacuo* and the residue extracted with hot acetone. This solution was reduced to a few cm^3 and the product was precipitated as a buff powder by the addition of ethanol (0.21 g, 22%) (Found: C, 16.6; H, 3.1; N, 1.5. $C_{12}H_{32}Br_4IrNSe_2$ requires C, 16.75; H, 3.7; N, 1.6%).

Tetraethylammonium trans-*tetrabromobis(dimethyl sulphoxide)iridate*(III), $[NEt_4][Ir(dmso)_2Br_4]$. This complex was prepared by the method of Antonov *et al.*,[12] substituting $3[NEt_4]Br + IrBr_3$ for $K_3[IrBr_6]$.

Tetraethylammonium trans-*tetrachlorobis(diphenyl selenide)iridate*(III). Iridium trichloride (0.4 g, 1.1 mmol), $[NEt_4]Cl$ (0.19 g, 0.11 mmol), and Ph_2Se (0.53 g, 0.22 mmol) were refluxed together in concentrated hydrochloric acid–water–ethanol (2:12:15, 29 cm^3) for 3 h. The solvent was removed *in vacuo*, ethanol added, and the solution filtered to remove some precipitate. The filtrate was evaporated to dryness, the resulting oil triturated with acetone (10 cm^3), and the pink solid produced filtered off and dried *in vacuo* (Found: C, 41.0; H, 4.2; N, 1.6. $C_{32}H_{40}Cl_4IrN$ requires C, 41.3; H, 4.3; N, 1.5%).

Tetramethylammonium trans-*tetrachlorobis(dimethyl sulphide)rhodate*(III), $[NMe_4][Rh(SMe_2)_2Cl_4]$. Rhodium trichloride hydrate (0.25 g, 0.94 mmol), concentrated HCl (0.17 g), dimethyl sulphide (0.14 g, 2.3 mmol), and $[NMe_4]Cl{\cdot}H_2O$ (0.12 g, 0.94 mmol) were refluxed together in water–2-methoxyethanol (5:30 cm^3) for 2.5 h. The product was evaporated to dryness, treated with CH_2Cl_2 and the red-brown powder produced filtered off, washed with CH_2Cl_2 and dried *in vacuo* (0.15 g, 15%) (Found: C, 21.3; H, 5.6; N, 3.2. $C_8H_{24}Cl_4NRhS_2$ requires C, 21.6; H, 5.4; N, 3.2%).

Tetramethylammonium trans-*tetrachlorobis(dimethyl selenide)rhodate*(III), $[NMe_4][Rh(SeMe_2)_2Cl_4]$. Rhodium trichloride hydrate (0.25 g, 0.94 mmol), concentrated HCl (0.17 g), $SeMe_2$ (0.19 g, 1.74 mmol), and $[NMe_4]Cl{\cdot}H_2O$ (0.12 g, 0.94 mmol) were refluxed in water–2-methoxyethanol (5:30 cm^3) for 3 h. The product was evaporated to dryness, extracted with acetonitrile, and the solution filtered. The filtrate was evaporated to dryness, washed with CH_2Cl_2, and the product dried *in vacuo* (0.18 g, 37%) (Found: C, 18.0; H, 4.5; N, 2.4. $C_8H_{24}Cl_4NRhSe_2$ requires C, 17.9; H, 4.5; N, 2.6%).

Triethylphosphonium trans-*tetrachlorobis(triethylphosphine)rhodate*(III) $[PEt_3H][Rh(PEt_3)_2Cl_4]$. Rhodium trichloride hydrate (0.3 g, 1.1 mmol), concentrated HCl (10 cm^3), and triethylphosphine (0.56 g, 4.7 mmol) were mixed in ethanol (25 cm^3) and refluxed for 30 min. The product was evaporated to dryness, treated with toluene, and the orange powder remaining filtered off, washed with boiling toluene, and dried *in vacuo* (0.12 g, 17%) (Found : C, 36.3; H, 7.9. $C_{18}H_{46}Cl_4P_3Rh$ requires C, 36.0; H, 7.7%).

Pyridinium cis(?)-*tetrachlorobis(pyridine)rhodate*(III), $[Hpy][Rh(py)_2Cl_4]$. Rhodium trichloride hydrate (0.3 g, 1.1 mmol) and pyridine (1.0 cm^3, 13 mmol) were mixed in water (20 cm^3) and concentrated HCl (5 cm^3) and refluxed for 1 h. The product was evaporated to dryness, treated with water, and filtered. The red filtrate was refluxed with pyridine (3 cm^3) until it was orange and then evaporated to dryness. It was treated with water (5 cm^3) and the yellow product filtered off, washed with diethyl ether, and dried *in vacuo* (0.18 g, 32%) (Found: C, 37.1; H, 3.2; N, 8.6. $C_{15}H_{16}Cl_4N_3Rh$ requires C, 37.2; H, 3.3; N, 8.7%).

Crystal-structure Determination.—Green, air-stable crystals of $[Ir(AsEt_3)_2Br_4]$ were obtained from CH_2Cl_2–cyclohexane and mounted in thin-walled glass capillaries. Preliminary photographic *X*-ray examination was undertaken and the crystal density was measured by flotation.

Crystal data. $C_{12}H_{30}As_2Br_4Ir$, $M = 836.0$, monoclinic, space group $P2_1/n$ (no. 14), $a = 8.442(1)$, $b = 13.933(2)$, $c = 9.617(1)$ Å, $\beta = 103.85(1)°$, $U = 1\,098.3$ Å^3, $D_m = 2.44(4)$ g cm^{-3}, $Z = 2$, $D_c = 2.527$ g cm^{-3}, $F(000) = 770$, μ(Mo-K_α) = 161.6 cm^{-1}, $\lambda = 0.710\,7$ Å.

Intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation. Accurate cell dimensions were obtained from 25 high-angle ($\theta > 20°$) reflections and from the same crystal ($0.5 \times 0.5 \times 0.2$ mm) at room temperature 2 388 reflections [$1 < \theta < 26°$; $h(-10$ to $10)$, $k(0$—$17)$, $l(0$—$11)$] were recorded. The check

Table 1. Atomic co-ordinates ($\times 10^4$) for *trans*-$[Ir(AsEt_3)_2Br_4]$

Atom	*X/a*	*Y/b*	*Z/c*
Ir	0	0	0
As	1 209(1)	1 102(1)	2 012(1)
Br(1)	2 630(1)	−839(1)	439(1)
Br(2)	830(1)	1 061(1)	−1 748(1)
C(1)	−347(13)	1 854(7)	2 784(11)
C(2)	−1 343(17)	1 283(9)	3 555(13)
C(3)	2 629(13)	2 097(7)	1 601(11)
C(4)	4 219(15)	1 712(8)	1 290(13)
C(5)	2 531(14)	464(8)	3 672(11)
C(6)	3 308(19)	1 151(10)	4 874(14)

reflection showed some decay (6%) and this was allowed for in the data reduction program as well as the usual Lorentz and polarisation corrections. The systematic absences (*hkl*, none; *h*0*l*, $h + l \neq 2n$; 0*k*0, $k \neq 2n$) established the space group and after the data reduction there remained 2 149 unique reflections of which 323 $[F < 3\sigma(F)]$ were removed leaving 1 826 observations for the analysis and refinement. No absorption correction was applied at this stage (see later) since no suitable reflections were available for the ψ-scan measurements.

Solution and refinement. The iridium atom was located on a special position and the remaining atoms were readily located by repeated structure-factor and electron-density calculations. The absorption correction of Walker and Stuart[13] (DIFABS) was applied following isotropic refinement. The heavy atoms (Ir, Br, As) were given anisotropic thermal parameters, empirical weights were used, and H atoms added in calculated positions with a common refined thermal parameter. Full-matrix least-squares refinement converged to $R = 0.041$ {68 parameters, anisotropic (Ir, As, Br) and isotropic (C, H) atoms, d(C–H) = 0.95 Å, $w = 1/[\sigma^2(F) + 0.001F^2]$, $R' = 0.055$, max. shift/error = 0.16}. A final difference electron-density map showed all features in the range 1.36 to −1.24 e Å^{-3}. The final atomic co-ordinates are given in Table 1. Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX[14] (Br, C, H) and ref. 15 (Ir, As) and all calculations were performed on an ICL2976 computer using the programs SHELX,[14] DIFABS,[13] and PLUTO.[16]

Electrochemistry.—All electrochemical experiments were carried out in a three-electrode, two-compartment cell. A vitreous carbon disc (area 0.07 cm^2) sealed into glass was the working electrode and it was repolished after each series of experiments. The counter electrode was a platinum spiral in the same compartment. The reference electrode was a Radiometer saturated calomel electrode (s.c.e.) type K401, which dipped into a separate compartment connected to the working electrode *via* a Luggin capillary. The solvent–electrolyte was deoxygenated in the cell and prior to experiments with a complex, a background voltammogram was recorded. A weighed sample of the solid complex was then added to the electrolyte and the solution was stirred for several minutes. The instrumentation employed was a Hi-tek potentiostat, model DT 2101, a function generator, type PPR1, and a model 60 000 Gould X-Y recorder.

The MeCN and CH_2Cl_2 were both refluxed over CaH_2 and distilled under N_2 prior to use. The electrolyte, $[NBu^n{}_4]BF_4$, was prepared by precipitation in water and recrystallised from ethanol–water.

Results

Synthesis.—The various routes to $[IrL_2X_4]$ complexes are summarised in equations (1)—(4) and the complexes obtained are listed in Table 2.

$$IrX_3{\cdot}nH_2O + HX + 3\,L \longrightarrow [HL][IrL_2X_4] \xrightarrow{X_2} [IrL_2X_4] \quad (1)$$

(L = PEt_3, PEt_2Ph, $PEtPh_2$, $AsEt_3$, $AsMe_2Ph$, py, or $SbMe_3$, X = Cl; L = PEt_3, $AsEt_3$, PMe_2Ph, $AsMe_2Ph$, or py, X = Br)

$$IrX_3{\cdot}nH_2O + [NR_4]X + HX + 2\,L \longrightarrow [NR_4][IrL_2X_4] \xrightarrow[HNO_3]{X_2\text{ or}} [IrL_2X_4] \quad (2)$$

(L = SMe_2 or $SeMe_2$, X = Cl; L = SMe_2, X = Br; R = Me or Et)

$$[\{Ir(C_8H_{14})_2Cl\}_2] + 6\,L \longrightarrow [IrL_3Cl] \xrightarrow{Cl_2} [IrL_2Cl_4]\ (L = PPh_3\text{ or }AsPh_3) \quad (3)$$

$$IrCl_3{\cdot}nH_2O + 2\,L \longrightarrow [(IrL_2Cl_3)_n] \xrightarrow{Cl_2} [IrL_2Cl_4] \quad (4)$$

(L = PPh_3, $AsPh_3$, or $SbPh_3$)

Neutral iridium(III) phosphine or arsine complexes $[Ir(ER_3)_3X_3]$ (E = As or P) are not oxidised with halogen, or electrochemically, to iridium(IV), and are very inert towards ligand-substitution reactions. Hence the routes to $[IrL_2Cl_4]$ in (1) and (2) depend upon the prior synthesis of $[IrL_2Cl_4]^-$.[2–4] The iridium(III) anions are obtained as the main product in (1) only for L = pyridine (py); for phosphines and arsines the major iridium product is *mer*-$[IrL_3Cl_3]$ with small amounts of *fac*-$[IrL_3Cl_3]$, and $[HL][IrL_2Cl_4]$ is produced in <10% yield.[3,17,18] The yields, especially of the minor products, vary with the sample of 'iridium chloride hydrate' used. The constitution of the latter is unclear, but it is probably a mixture of aqua–halogeno complexes, the relative proportions varying from batch to batch,* accounting for the variable yields. Attempts to obtain amine complexes $[IrL_2Cl_4]^-$ (L = NMe_3, $NHEt_2$, piperidine, or NH_3) by route (1) gave $[HL]_3[IrCl_6]$. Bromo anions $[IrL_2Br_4]^-$ are known for L = py, PMe_3, or $SbPh_3$[9,20,21] and we find that analogues with other PR_3 or AsR_3 are readily obtained [route (1)] although the yields are even poorer than for the corresponding chlorides. Cautious oxidation with Br_2 in CCl_4 converts these into deep green $[IrL_2Br_4]$ (Table 2), none of which has been reported previously. Bromination of $K[Ir(SbPh_3)_2Br_4]$[21] gave an insoluble material of low carbon content, and this reaction with $[Ir(SbMe_3)_2Br_4]^-$ afforded a black oil.

Route (2) was used only for Group 6B donors, the yields decreasing as SMe_2 > $SeMe_2$ and Cl > Br. Only very small yields of the analogues with SPh_2 and $SePh_2$ were isolated. Brown $[NMe_4][Ir(TeMe_2)_2Cl_4]$ and $[NEt_4][Ir(SeMe_2)_2Br_4]$ were produced in small yield, but we have been unable to isolate the iridium(IV) complexes.

Routes (3) and (4) were successful only for the examples listed.[5] Attempts to extend route (3) to L = SPh_2, $SbPh_3$, PEt_3, or PMe_2Ph gave iridium(III) complexes which did not oxidise further, whilst route (4) produces only $[IrL_3Cl_3]$ with smaller and more basic phosphines. The $[Ir(AsPh_3)_2Cl_4]$ samples produced by routes (3) or (4) are spectroscopically identical and only one isomer is present. Route (3), for L = PPh_3, gives some $[Ir(PPh_3)_2Cl_4]$ directly, (**A**), and $[\{Ir(PPh_3)_2Cl_3\}_n]$ which is slowly[5] (*ca.* 2 d) oxidised by chlorine to a purple material of the same analytical composition, (**B**). Route (4) yields a material identical to (**A**). Whilst (**A**) is reasonably stable, (**B**) is very unstable in solution in organic solvents; there are also differences in the i.r. and u.v.–visible spectra of (**A**) and (**B**). The instability of (**B**) in solution prevents a more detailed

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* A recent study[19] of commercial rhodium chloride hydrate by ^{103}Rh n.m.r. spectroscopy found that *mer*- and *fac*-$[Rh(H_2O)_3Cl_3]$ and *cis*- and *trans*-$[Rh(H_2O)_4Cl_2]^+$ were present in relative amounts which varied with the sample.

Table 2. Selected spectroscopic data for $[IrL_2X_4]$ complexes

Complex	ν(Ir–X)/cm^{-1}	$10^{-3}\ \nu_{max.}$/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})[a,b]
cis-$[Ir(py)_2Cl_4]$	346, 328, 272	15.8, 17.9, 19.1, 20.2, 22.0, 26.1, 30.3[c]
trans-$[Ir(py)_2Cl_4]$	330, 317 (sh)	5.6, 15.5, 19.8, 25.4, 32.5[c]
trans-$[Ir(PEt_3)_2Cl_4]$	327	5.7 (58), 9.3 (220), 15.0 (110), 18.7 (2 100), 19.8 (2 400), 27.6 (950)
trans-$[Ir(PEt_2Ph)_2Cl_4]$	323	5.7 (32), 9.4 (110), 14.8 (88), 18.5 (1 200), 19.3 (sh), 28.4 (870), 35.3 (14 000)
trans-$[Ir(PEtPh_2)_2Cl_4]$	330	9.9 (141), 14.5 (sh), 18.3 (2 800), 19.0 (2 000), 22.7 (sh), 28.2 (sh), 34.3 (27 000)
trans-$[Ir(PPh_3)_2Cl_4]$	328	5.7 (–), 10.1 (244), 13.7 (sh), 17.9 (2 000), 19.2 (sh), 32.7 (24 000)
trans-$[Ir(AsEt_3)_2Cl_4]$	322	5.7 (116), 8.9 (360), 15.3 (140), 19.0 (2 800), 20.4 (3 000), 27.4 (sh), 34.2 (19 000)
trans-$[Ir(AsMe_2Ph)_2Cl_4]$	328	5.8 (90), 10.0 (375), 14.7 (160), 18.7 (2 800), 19.6 (2 500), 28.2 (sh), 34.4 (21 000)
trans-$[Ir(AsPh_3)_2Cl_4]$	Not observed	5.7 (78), 10.2 (285), 14.4 (sh), 18.1 (1 700), 18.8 (sh), 31.2 (18 000)
trans-$[Ir(SbPh_3)_2Cl_4]$	326	5.7 (–), 7.6 (–), 14.9 (300), 18.7 (2 500), 19.7 (sh), 24.6 (sh), 28.0 (21 000)
cis(?)-$[Ir(SbMe_3)_2Cl_4]$	355, 341, 314	10.8 (sh), 17.6 (sh), 20.2 (–), 22.6 (–), 29.4 (sh), 32.8 (sh)[d]
trans-$[Ir(SMe_2)_2Cl_4]$	325	15.3 (sh), 19.2 (1 375), 20.7 (1 360), 23.8 (440), 28.6 (460)
trans-$[Ir(SeMe_2)_2Cl_4]$	320	13.2 (338), 14.2 (sh), 18.4 (2 500), 19.6 (2 500), 23.2 (560), 28.4 (sh), 35.7 (21 000)
trans-$[Ir(py)_2Br_4]$	227, 219 (sh)	5.3 (–), 11.2 (310), 13.7 (2 500), 15.5 (3 300), 18.5 (460), 23.1 (sh), 25.0 (sh)[c]
trans-$[Ir(PEt_3)_2Br_4]$	226	5.2 (–), 8.5 (970), 10.0 (sh), 12.9 (3 200), 15.8 (4 100), 24.0 (sh), 25.1 (1 200), 33.3 (sh), 36.0 (17 000)
trans-$[Ir(PMe_2Ph)_2Br_4]$	234	5.1 (195), 9.1 (1 630), 9.5 (sh), 12.6 (3 200), 15.4 (2 800), 18.5 (360), 24.9 (1 000), 33.9 (sh), 35.7 (31 000)
trans-$[Ir(AsEt_3)_2Br_4]$	228	5.1 (224), 7.9 (1 230), 10.4 (265), 13.2 (2 600), 16.1 (3 800), 24.2 (1 300), 31.2 (13 000), 34.6 (13 000)
trans-$[Ir(AsMe_2Ph)_2Br_4]$	230	5.1 (–), 8.9 (–), 9.8 (sh), 12.8 (2 300), 15.7 (2 400), 24.8 (sh), 32.2 (16 000), 36.0 (31 500)
trans-$[Ir(SMe_2)_2Br_4]$	210	9.1 (170), 11.8 (2 100), 13.3 (2 600), 14.4 (sh), 15.9 (sh), 20.4 (440), 24.9 (850), 30.9 (sh)

[a] In CH_2Cl_2 solution unless indicated otherwise. [b] (–) Indicates band too weak to measure ε. [c] Acetone solution. Both pyridine chloro complexes were poorly soluble, ε not determined. [d] Poorly soluble and unstable in solution, ε values unreliable.

characterisation although it is possible that it is (or contains) the *cis* isomer (see also ref. 5). Although we could prepare materials of composition $[(IrL_2Br_3)_n]$ by route (4) (L = PPh_3 or $AsPh_3$) these did not oxidise on treatment with bromine, HNO_3, or NOBr.

For an $[IrL_2X_4]$ composition, two isomers (*cis* and *trans*) are possible but only for L = py, X = Cl were both isolated in good yield and thoroughly characterised. We have some evidence for very small amounts of a second isomer for $[Ir(py)_2Br_4]$ and $[Ir(SMe_2)_2Cl_4]$[11] but these could not be isolated pure. In view of the poor overall yields of many of the $[IrL_2X_4]$ complexes, a minor isomer in less than *ca.* 1 : 10 ratio could easily escape detection.

Four rhodium(III) anions $[RhL_2Cl_4]^-$ (L = py, PEt_3, SMe_2, or $SeMe_2$) were made by analogues of routes (1) and (2) for comparison purposes, but did not oxidise on treatment with chlorine–CCl_4 or HNO_3.

Properties.—The $[IrL_2Cl_4]$ complexes are intensely purple, and the bromides are dark green crystalline solids, highly soluble in most organic solvents. The complexes are reasonably stable solids, but readily decompose in solution, especially in strong light. Reduction to iridium(III) is easily achieved by warming in ethanol solution, and clean reduction to $[IrL_2X_4]^-$ is possible with ascorbic acid in MeCN. The first requirement is to establish the isomer present in the isolated complexes (Table 2). The complexes $[IrL_2X_4]$ are paramagnetic ($\mu_{eff.}$ = 1.6—1.9 B.M.), $5d(t_{2g}{}^5)$[3—5,11] and this precludes the use of n.m.r. spectroscopy to establish stereochemistry. N.m.r. data (^1H, ^{31}P, and ^{77}Se) for selected examples of the diamagnetic iridium(III) analogues are given in Table 3, and confirm that only one isomer is present before oxidation (and after reduction with ascorbic acid). For these inert iridium(III) systems oxidation with retention of configuration would be expected. The isomer present in $[IrL_2X_4]$ can be established by vibrational[4,11,20,22] and e.s.r.[5,23] spectroscopy and *X*-ray diffraction. Crystal structures of *trans*-$[Ir(PMe_2Ph)_2Cl_4]$,[24] *trans*-$[Ir(AsEt_3)_2Br_4]$ (see below), and $[NMe_4]$[*trans*-$Ir(SMe_2)_2Cl_4$][25,*] are available, and based upon these one can use the presence of a single strong ν(Ir–X) i.r. vibration (E_u) at *ca.* 320—330 (X = Cl) and *ca.* 210—230 cm^{-1} (X = Br) as indicative of *trans* geometry (D_{4h}) for most of the isolated complexes (Table 2). Comparison with $[IrL_2X_4]^-$ (Table 3) reveals that oxidation results in a *ca.* 15—30 cm^{-1} high-frequency shift in ν(Ir–X). The minor isomer of $[Ir(py)_2Cl_4]$ and the unstable $[Ir(SbMe_3)_2Cl_4]$ show three ν(Ir–Cl) vibrations which are consistent with *cis* stereochemistry (theory predicts four vibrations $2A_1 + B_1 + B_2$). The complex *cis*-$[Ir(py)_2Cl_4]$ is isomorphous with *cis*-$[Pt(py)_2Cl_4]$.[26] Curiously, whilst $[Ir(SbMe_3)_2Cl_4]$ is *cis*, the phenyl analogue $[Ir(SbPh_3)_2Cl_4]$ is *trans*. We note that the complex $[Pt(SbMe_3)_2Cl_4]$ is also probably a *cis* isomer.[27]

The $[IrL_2X_4]$ complexes have very characteristic u.v.–visible spectra (Table 2), and typical examples are shown in Figure 1(*a*) and (*b*). The assignments of the spectra of $[IrX_6]^{2-}$ have been discussed by numerous authors,[28,29] and previous assignments of the spectra of $[IrL_2Cl_4]$ have used the optical electronegativity model[30] or a simple molecular orbital (m.o.) approach.[8] The $[IrX_6]^{2-}$ spectra are dominated by $\pi(X) \longrightarrow Ir(t_{2g})$ l.m.c.t. (ligand to metal charge transfer) bands with intra-configurational bands in the near-i.r. region,[28,29] and hence the absorptions in the $[IrL_2X_4]$ spectra are assignable to L or X $\longrightarrow$ Ir c.t. bands. In D_{4h} symmetry, to a first approximation, the σ and π Ir–X and σ Ir–L orbitals (for py, SMe_2, and $SeMe_2$ there are π Ir–L orbitals also) are not strongly mixed, and one might predict distinct electron-transfer bands from each set to $Ir(t_{2g})$. Dealing with the phosphine and arsine chloro complexes first, the intense absorption at *ca.* 18 000—20 000 cm^{-1} is relatively independent of the ligand, and by comparison with $[IrCl_6]^{2-}$ can be assigned to $\pi_{Cl} \longrightarrow Ir(t_{2g})$ (strictly speaking in D_{4h}, t_{2g} splits into b_{2g} and e_g with the probable ground state $b_{2g}{}^2e_g{}^3$, see ref. 28), and the band(s) at 28 000—30 000 cm^{-1} similarly to $\sigma_{Cl} \longrightarrow Ir(t_{2g})$, with $\pi_{Cl} \longrightarrow Ir(e_g{}^*)$ at >34 000 cm^{-1}. The weak bands (ε < 500 dm^3 mol^{-1} cm^{-1}) at 8000—10 000 cm^{-1} vary in energy with L (and are absent for Group 6B donors) and are assigned as $\sigma_{P,As} \longrightarrow Ir(t_{2g})$ following Rowe

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[*] The original tentative assignment[11] of *cis* geometry to this material based upon n.m.r. data is in error, as subsequently established by the *X*-ray study.

Table 3. Selected spectroscopic data on iridium(III) and rhodium(III) anions

Complex	$\delta(^{31}P-\{^1H\})$/ p.p.m.[a]	$\delta(^1H)$/p.p.m.[b]	$\nu(M-X)$/ cm^{-1}[c]
$[Ir(PEt_3)_2Cl_4]^-$	-30.6		300
$[Ir(PEt_2Ph)_2Cl_4]^-$	-24.1		305
$[Ir(PPh_3)_2Cl_4]^-$	-19.3		
$[Ir(PEt_3)_2Br_4]^-$	-42.5		
$[Ir(PMe_2Ph)_2Br_4]^-$	-46.0		
$[Ir(SMe_2)_2Cl_4]^-$		2.25 $[(CD_3)_2SO]$	314
$[Ir(SeMe_2)_2Cl_4]^-$	$+140$[d]	1.96 $[(CD_3)_2SO]$	307
$[Ir(SeMe_2)_2Br_4]^-$	$+119$[d]	2.25 $[CD_3CN]$	210
$[Ir(SMe_2)_2Br_4]^-$			208
$[Rh(PEt_3)_2Cl_4]^-$	$+6.7$ $(^1J_{Rh-P}$ 83)		317
$[Rh(SeMe_2)_2Cl_4]^-$	$+168$ $(^1J_{Rh-Se}$ 37)[d]	2.15 $[CD_3CN]$	328
$[Rh(SMe_2)_2Cl_4]^-$		2.70 $[D_2O]$	337

[a] In MeCN relative to 85% H_3PO_4; coupling constants in Hz. The low-frequency ^{31}P resonances are unusual for tertiary phosphine complexes but have been observed for other iridium(III) examples.[18] [b] Methyl resonances only in solvent specified. [c] Nujol mull spectra. [d] $\delta(^{77}Se)$ to high frequency of external (neat) $SeMe_2$. Solvent CH_2Cl_2.

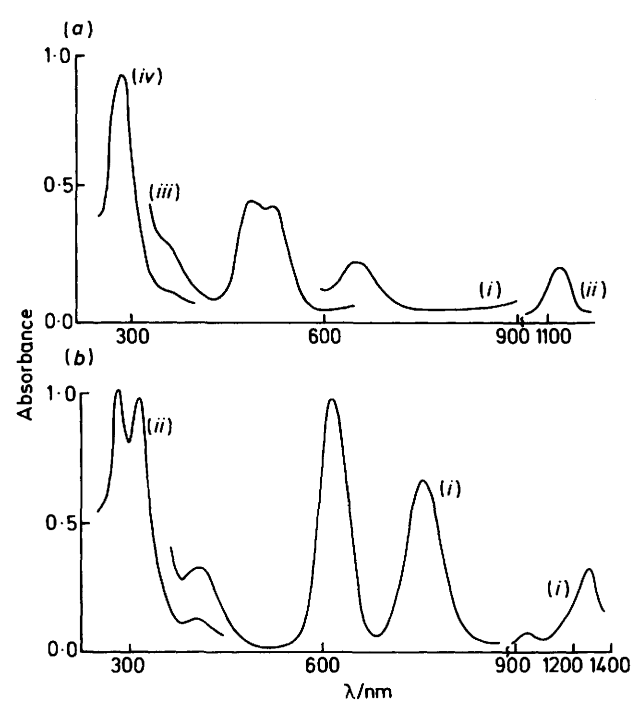

Figure 1. Absorption spectra of dichloromethane solutions of (*a*) $[Ir(AsEt_3)_2Cl_4]$ [(*i*) 1.5 × 10^{-3} mol dm^{-3} = *c*, (*ii*) *c*/3.5, (*iii*) *c*/10, and (*iv*) *c*/30] and (*b*) $[Ir(AsEt_3)_2Br_4]$ [(*i*) 2.6 × 10^{-4} mol dm^{-3} = *c*, (*ii*) *c*/3.3]

et al.[8] In some cases very weak absorptions in the near-i.r. were also found and these are intraconfigurational in origin. The weak bands at 14 000—16 000 cm^{-1} are less certainly assigned; either they are metal centred ('*d–d*'), or related to the parity-forbidden transition $\pi_{t_{1g}(Cl)} \longrightarrow Ir(t_{2g})$ observed in $[IrCl_6]^{2-}$.[28] For $[IrL'_2Cl_4]$ (L′ = SMe_2 or $SeMe_2$) the assignment of the Cl $\longrightarrow$ Ir l.m.c.t. bands is straightforward, but of the L′ $\longrightarrow$ Ir bands is less so. In the spectrum of $[Ir(SeMe_2)_2Cl_4]$ a weak band at 13 200 cm^{-1} with a shoulder at 14 200 cm^{-1} is tentatively assigned to $\pi_{Se} \longrightarrow Ir$, and the 23 200 cm^{-1} band to $\sigma_{Se} \longrightarrow Ir$. For $[Ir(SMe_2)_2Cl_4]$ the 23 800 cm^{-1} absorption may be $\sigma_S \longrightarrow Ir$ but the only candidate for $\pi_S \longrightarrow Ir$ is the broad ill defined shoulder at *ca.* 15 300 cm^{-1} on the much more intense $\pi_{Cl} \longrightarrow Ir$ absorptions. In the spectrum of *trans*-$[Ir(py)_2Cl_4]$ the band at 25 400 cm^{-1} may be $\sigma_{py} \longrightarrow Ir$; in this respect our failure to prepare complexes of saturated aliphatic amines, which would be simpler examples of the N donor type, is unfortunate.

Assignment of the spectra of the bromides can be made on similar grounds by comparison with the corresponding chlorides and with $[IrBr_6]^{2-}$,[29] although the larger splittings, probably a reflection of the much larger spin–orbit coupling constant of bromine, are an added complication. Thus the two intense bands in the range *ca.* 12 000—16 000 cm^{-1} are assigned to $\pi_{Br} \longrightarrow Ir(t_{2g})$, and the rather ill defined absorption at *ca.* 25 000 cm^{-1} to $\sigma_{Br} \longrightarrow Ir(t_{2g})$. The $\sigma_{P,As} \longrightarrow Ir(t_{2g})$ transitions are the moderately intense bands at *ca.* 8 000—10 000 cm^{-1}, and supporting the assignment in $[Ir(SMe_2)_2Cl_4]$, a shoulder at *ca.* 14 400 for $[Ir(SMe_2)_2Br_4]$ may be due to $\pi_S \longrightarrow Ir(t_{2g})$. The $\sigma_{py} \longrightarrow Ir(t_{2g})$ transition may be similarly assigned to the band of $[Ir(py)_2Br_4]$ at *ca.* 25 000 cm^{-1}. The bromides exhibit a weak band or shoulder at *ca.* 9 000—11 000 cm^{-1} possibly the equivalent of that at *ca.* 14 000 cm^{-1} for the chlorides, and similarly unassigned.

Structure of trans-$[Ir(AsEt_3)_2Br_4]$.—Selected bond lengths and angles are given in Table 4, and Figure 2 shows the labelled molecule. The structure consists of centrosymmetric molecules with approximate D_{4h} symmetry. *X*-Ray data on iridium bromo compounds are scarce but the bond lengths in the present case 2.459 Å (av.) can be compared with Ir^{III}–Br(*trans* Br) in $K[Ir(NO)Br_5]$,[31] 2.480 Å (av.), revealing a shortening of *ca.* 0.02 Å (*ca.* 7σ) between Ir^{III} and Ir^{IV}. Comparison of Ir^{IV}–Cl in *trans*-$[Ir(PMe_2Ph)_2Cl_4]$,[24] 2.324(5) Å, with Ir^{III}–Cl(*trans* Cl) in $K[Ir(NO)Cl_5]$, 2.338 (av.),[31] *trans*-$[Ir(SMe_2)_2Cl_4]^-$, 2.354 (av.),[25] and $K_2[Ir(pyz)Cl_5]$ (pyz = pyrazine), 2.351(3) Å,[32] shows a similar trend (*ca.* 0.014—0.025 Å). Only one structure containing triethylarsine has been determined previously,[33] *trans*-$[Pt(AsEt_3)(MeN{=}CHC_6H_4Me\text{-}p)Cl_2]$, and the geometry of the ligand in the present case appears unexceptional. Similarly the only iridium arsine complex structurally characterised appears to be the five-co-ordinate $[Ir\{C_2(CN)_4\}(AsPh_3)_2Cl]$,[34] Ir–As 2.478(2) and 2.481(2) Å.

Electrochemistry.—Cyclic voltammograms (at four potential scan rates, 0.05—0.30 V s^{-1}) were recorded at a vitreous carbon disc electrode for 27 iridium complexes in MeCN or CH_2Cl_2 containing $[NBu^n{}_4]BF_4$ (0.2 mol dm^{-3}). It was intended to prepare solutions of the complexes with a concentration of 1 mmol dm^{-3} in MeCN, but it was clear that several dissolved incompletely. Hence CH_2Cl_2 was also used as a solvent but even then the concentrations were not always known precisely.

Figure 3 shows the sets of cyclic voltammograms obtained for $[Ir(AsMe_2Ph)_2Cl_4]^-$ and $[Ir(AsMe_2Ph)_2Cl_4]$ in MeCN. It can be seen that in both cases the curves have the characteristic shapes for a reversible one-electron process.[7,35] Moreover, quantitative analysis of the curves confirms this conclusion. Thus the peak separation is close to 60 mV, the ratio of the peak currents equal to one, the peak shape factors, $E_p - E_{p/2}$, equal to 60 mV, and the current functions, $I_p/v^{\frac{1}{2}}c$, are independent of the potential scan rate, v. The value of the current function for $[Ir(AsMe_2Ph)_2Cl_4]^-$ leads to a value for the diffusion coefficient of 0.8 × 10^{-5} cm^2 s^{-1}. The same value for the formal electrode potential, 0.91 ± 0.01 V *vs.* s.c.e. (estimated as the average of the two peak potentials), was found from the study of the complexes of Ir^{III} and Ir^{IV}.

The data for the iridium(III)–iridium(IV) couples from these experiments are reported in Table 5 which for the purposes of

Table 4. Bond lengths (Å) and angles (°) for $[Ir(AsEt_3)_2Br_4]$

Ir–Br(1)	2.455(1)	As–C(1)	1.96(1)
Ir–Br(2)	2.463(1)	As–C(3)	1.94(1)
Ir–As	2.489(1)	As–C(5)	1.93(1)
C(1)–C(2)	1.48(2)	Br • • • Br(min.)	3.46
C(3)–C(4)	1.54(1)	Br • • • As(min.)	3.45
C(5)–C(6)	1.52(2)		
As–Ir–Br(1)	88.5(1)	Ir–As–C(5)	114.0(3)
As–Ir–Br(2)	91.7(1)	As–C(1)–C(2)	114.5(8)
As–Ir–Br(1′)	91.5(1)	As–C(3)–C(4)	113.7(7)
As–Ir–Br(2′)	88.3(1)	As–C(5)–C(6)	113.4(8)
Br(1)–Ir–Br(2)	90.6(1)	C(1)–As–C(3)	101.4(4)
Br(1)–Ir–Br(2′)	89.4(1)	C(1)–As–C(5)	103.9(4)
Ir–As–C(1)	115.9(3)	C(3)–As–C(5)	103.6(5)
Ir–As–C(3)	116.2(3)		
Ir–As–C(1)–C(2)	68	Br(1)–Ir–As–C(1)	−163
Ir–As–C(3)–C(4)	−66	Br(1)–Ir–As–C(3)	78
Ir–As–C(5)–C(6)	178	Br(1)–Ir–As–C(5)	−43

Symmetry operation: (′) $-x$, $-y$, $-z$.

comparison also contains data for $[IrCl_6]^{2-}$ and $[Fe(\eta\text{-}C_5H_5)_2]$. The iridium complexes show no further electron-transfer reactions within the potential range investigated, *ca.* +1.5 to −1.2 V. Furthermore, with the $[IrL_2X_4]$ complexes there were no other oxidation or reduction peaks, confirming their high purity. The iridium(III) anions sometimes gave voltammograms which included other small peaks which are probably due to small amounts of other iridium species.

The cyclic voltammetric behaviour of 20 of the complexes in Table 5 are almost completely analogous to that reported for $[Ir(PMe_2Ph)_2Cl_4]$ by Mingos and co-workers[7] and that shown in Figure 3 for $[Ir(AsMe_2Ph)_2Cl_4]$. In other words, the electron-transfer reactions, $[IrL_2X_4] + e^- \rightleftharpoons [IrL_2X_4]^-$, are reversible. Hence the electron transfers must be rapid, standard rate constants above 10^{-2} cm s^{-1}, indicating that the redox reaction leads to no significant reorganisation of the ligands around the central iridium. Moreover, formal potentials may be taken directly from the midpoints between the oxidation and reduction peaks. The absence of any halide oxidation peaks confirms that the halide ions are tightly bound to the iridium.

The deviations from this simple behaviour are of two kinds. First, the peak separations for both *cis*- and *trans*-$[Ir(py)_2Cl_4]$ are substantially larger than 60 mV. Hence although both Ir^{III} and Ir^{IV} are chemically stable, the electron-transfer processes are markedly slower. Secondly, the cyclic voltammograms for the oxidation of $[Ir(TeMe_2)_2Cl_4]^-$, $[Ir(SbPh_3)_2Br_4]^-$, $[Ir(SeMe_2)_2Br_4]^-$, and $[Ir(dmso)_2Br_4]^-$ are different and their behaviour is illustrated by the I *vs.* E curves for the last compound in Figure 4. It may be seen that, while with a scan rate of 0.3 V s^{-1} a well formed cathodic peak is observed, with a potential sweep rate of 0.05 V s^{-1} almost no reverse peak can be detected. Such responses indicate that the iridium(IV) complex is not stable and undergoes a chemical decomposition in MeCN with a half-life of *ca.* 5 s; this is in accord with the failure to isolate the iridium(IV) complexes from the chemical oxidation of these four anions. It may also be noted that the current function, $I_p/v^{\frac{1}{2}}c$, increases as the scan rate is slowed down and this indicates that the oxidation is an e.c.e. process, *i.e.* the chemical decomposition of the Ir^{IV} leads to further oxidation. In keeping with an e.c.e. process the initial electron-transfer product reacts chemically to yield a species whose oxidation will occur at a less positive potential than the initial electron-transfer product.

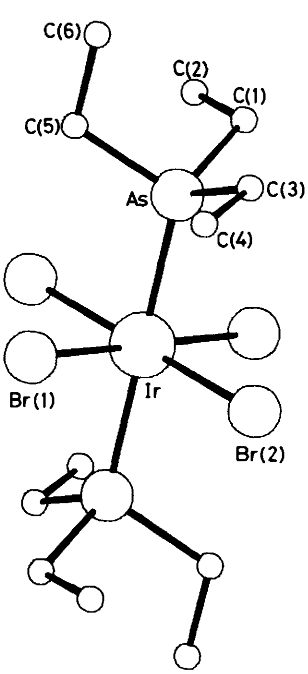

Figure 2. An isolated molecule of $[Ir(AsEt_3)_2Br_4]$ showing the atom-numbering scheme. Primed atoms are related by $\bar{x}$, $\bar{y}$, $\bar{z}$ to unprimed atoms and the atom size is arbitrary

Inspection of the formal potentials of the couples Ir^{III}–Ir^{IV} (Table 5) reveals several trends although one should recognise that the overall range of $E_e^{\ominus}$ is small, *ca.* 400 mV. First, replacement of chloride by bromide, or of arsenic by phosphorus (keeping R constant in ER_3, E = P or As), has little effect upon $E_e^{\ominus}$. These trends have been noted for other high-oxidation-state metal complexes where one-electron redox reactions occur without change of co-ordination number, *e.g.* Ni^{III}–Ni^{IV} (d^7–d^6) or Fe^{II}–Fe^{III}–Fe^{IV} (d^6–d^5–d^4),[36–38] although the studies involved a much more restricted range of ligands, and the systems were less well behaved electrochemically than the present ones. In the $[Ir(EMe_2)_2X_4]^-$–$[Ir(EMe_2)_2X_4]$ (E = S or Se) systems it does seem that selenium is marginally better at stabilising Ir^{IV}, a trend evident in the chemistry, which we have suggested[39] may be due to better donation by the less electronegative selenium.

Generally the effect on $E_e^{\ominus}$ of replacing X^- in $[IrX_6]^{2-}$ by a neutral ligand appears to follow the spectrochemical series, $Cl \approx Br < py < AsR_3 \approx PR_3$, which suggests that strong-field ligands stabilise the t_{2g}^{6} Ir^{III} as expected on ligand-field grounds, and make oxidation consequently more difficult (this also correlates with our inability to prepare $[IrL_3X_3]^+$). However, the $E_e^{\ominus}$ values for the $SbPh_3$ and for the Group 6B ligands deviate from this pattern. Whereas these ligands lie below PR_3 or AsR_3 in the spectrochemical series, the $E_e^{\ominus}$ values are considerably more positive. As the ligands are only moderate donors, it is likely that they will bind poorly to a hard high-oxidation-state metal centre and hence are less able to stabilise it.

If one looks at the Ir^{III}–Ir^{IV} potentials of $[Ir(PR_3)_2X_4]^-$ as a function of the R group, $E_e^{\ominus}$ is found to increase as $P(alkyl)_3 < P(alkyl)_2Ph < PPh_3$* suggesting that for a fixed donor atom, increasing alkyl substitution stabilises the Ir^{IV}. Steric effects are unlikely to be important, and two alternative electronic explanations are possible; either better σ donation

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* This also holds for AsR_3 and for the two examples for SeR_2, Table 5.

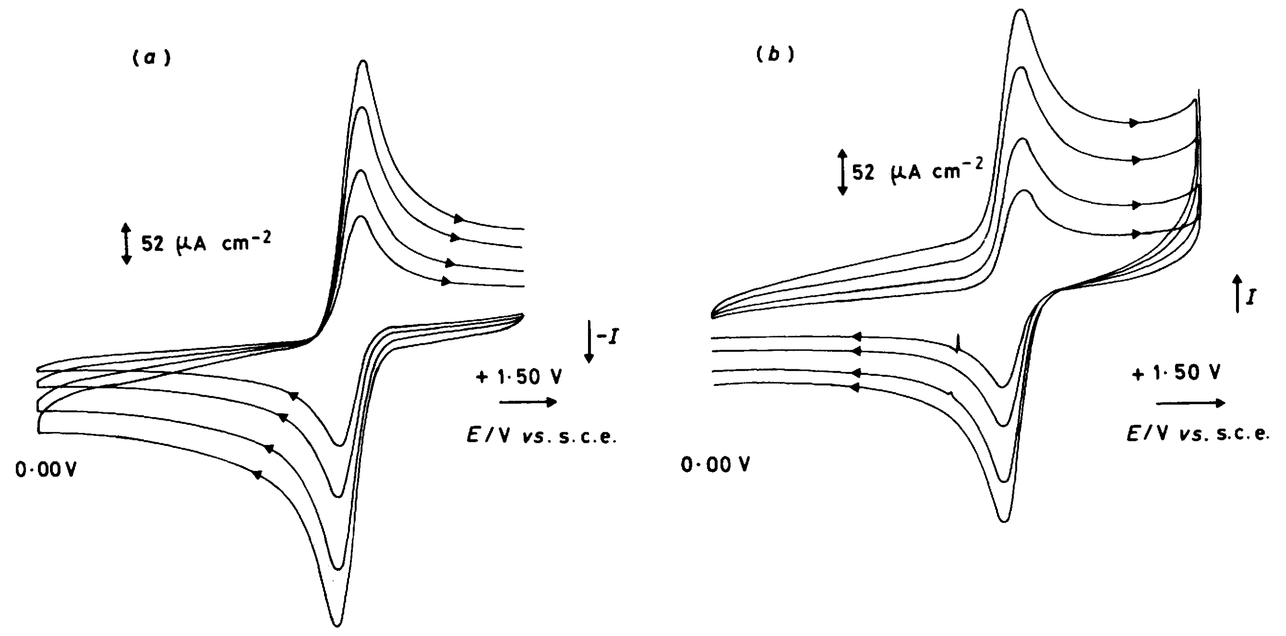

Figure 3. Cyclic voltammograms for (*a*) 1.07 mmol dm^{-3} [Ir(AsMe$_2$Ph)$_2$Cl$_4$] and (*b*) 0.98 mmol dm^{-3} [Ir(AsMe$_2$Ph)$_2$Cl$_4$]$^-$ at a vitreous carbon disc electrode in MeCN–[NBu$^n_4$]BF$_4$. Potential scan rates 0.05, 0.1, 0.2, and 0.3 V s^{-1}

Table 5. Cyclic voltammetric data for the iridium complexes in MeCN (or CH$_2$Cl$_2$), 0.2 mol dm^{-3} [NBu$^n_4$]BF$_4$ at a vitreous carbon electrode

Complex	$E_e^{\ominus}$/V *vs.* s.c.e.	ΔE_p/ mV	$E_p - E_{p/2}$/ mV	I_p^f/I_p^b ^{a}	$I_p^f/v^{\frac{1}{2}}c$ ^{b,c}
[IrCl$_6$]$^{2-}$	0.23^d	120	110	1.0	
trans-[Ir(py)$_2$Cl$_4$]	0.65^d	130	95	1.0	
cis-[Ir(py)$_2$Cl$_4$]	1.08^d	100	90	1.0	
trans-[Ir(PEt$_3$)$_2$Cl$_4$]	0.82^d	65	60	1.0	880
trans-[Ir(PMe$_2$Ph)$_2$Cl$_4$]$^-$	0.99^{e,f}	80	70	1.0	1 075
trans-[Ir(PEt$_2$Ph)$_2$Cl$_4$]	0.86^d	70	60	1.0	
trans-[Ir(PEtPh$_2$)$_2$Cl$_4$]	0.97^{d,f}	80	70	1.0	920
trans-[Ir(PPh$_3$)$_2$Cl$_4$]	0.97^{d,f}	70	65	1.0	
trans-[Ir(AsEt$_3$)$_2$Cl$_4$]	0.76^d	60	60	1.0	900
	0.84^{d,f}	80	70	1.0	
trans-[Ir(AsMe$_2$Ph)$_2$Cl$_4$]	0.90^d	70	60	1.0	625
	0.97^{d,f}	70	65	1.0	
trans-[Ir(AsMe$_2$Ph)$_2$Cl$_4$]$^-$	0.92^e	60	60	1.0	750
trans-[Ir(AsPh$_3$)$_2$Cl$_4$]	0.99^{d,f}	70	65	1.0	630
trans-[Ir(SbPh$_3$)$_2$Cl$_4$]	1.03^{d,f}	60	60	1.0	
trans-[Ir(SMe$_2$)$_2$Cl$_4$]$^-$	1.08^e	80	70	1.0	1 030
trans-[Ir(SeMe$_2$)$_2$Cl$_4$]$^-$	0.97^e	60	60	1.0	1 070
trans-[Ir(SePh$_2$)$_2$Cl$_4$]$^-$	1.09^e	60	60	1.0	830
trans-[Ir(TeMe$_2$)$_2$Cl$_4$]$^-$	1.02^e	80	70	0.8^g	
trans-[Ir(py)$_2$Br$_4$]	0.61^d	75	70	1.0	
trans-[Ir(PEt$_3$)$_2$Br$_4$]	0.90^{d,f}	70	65	1.0	980
trans-[Ir(PMe$_2$Ph)$_2$Br$_4$]$^-$	0.93^e	60	60	1.0	780
trans-[Ir(AsEt$_3$)$_2$Br$_4$]	0.85^d	65	60	1.0	
trans-[Ir(AsMe$_2$Ph)$_2$Br$_4$]	0.91^d	60	60	1.0	
trans-[Ir(AsMe$_2$Ph)$_2$Br$_4$]$^-$	0.93^e	60	60	1.0	750
trans-[Ir(SbPh$_3$)$_2$Br$_4$]$^-$	1.01^e	60	60	0.8^g	
trans-[Ir(SMe$_2$)$_2$Br$_4$]	1.10^d	65	60	1.0	840
trans-[Ir(SeMe$_2$)$_2$Br$_4$]$^-$	0.99^e	60	60	0.7^g	
trans-[Ir(dmso)$_2$Br$_4$]$^-$	1.54^e	90	70	0.75^g	
[Fe(η-C$_5$H$_5$)$_2$]	0.40^e	60	60	1.0	750

^{a} Superscripts f and b indicate forward and back reactions. ^{b} Units are A cm ^{2} V $^{\frac{1}{2}}$ s$^{\frac{1}{2}}$ mol ^{1} cm^3. ^{c} Due to solubility problems, concentrations not always known. ^{d} Forward process is a reduction. ^{e} Forward process is an oxidation; NR$_4^+$ salts. ^{f} Solvent is CH$_2$Cl$_2$. ^{g} At 0.1 V s^{-1}.

(for a fixed donor atom) leads to better binding to Ir^{IV}, or since π-acceptor ability increases as PPh$_3$ > P(alkyl)$_3$ the harder oxidation of [Ir(PR$_3$)$_2$X$_4$]$^-$ could reflect stronger π interaction in the t_{2g}^6 Ir^{III}.

In Figures 5 and 6 the formal potentials of $E_e^{\ominus}$ are plotted *versus* the energies (cm^{-1}) of the charge-transfer transitions in the electronic spectra. For the phosphine and arsine complexes there is good linear correlation of $\sigma_L \longrightarrow \text{Ir}(t_{2g})$ l.m.c.t. energies *versus* $E_e^{\ominus}$ (Figure 5) with substitution of Br for Cl causing a shift in spectral peak energies but not the redox potential, and hence different regressions occur for X = Cl or Br. The only couple not to fit this trend is [Ir(AsEt$_3$)$_2$Br$_4$]$^-$–[Ir(AsEt$_3$)$_2$Br$_4$] but the reason for this is unclear. Figure 6 shows a plot of the average $\pi_{Cl} \longrightarrow \text{Ir}(t_{2g})$ l.m.c.t. energies *versus* $E_e^{\ominus}$ which again shows a good correlation, the $E_e^{\ominus}$ values increasing as the c.t. absorption moves to lower energy, as expected. The Group 6B complexes deviate markedly from the regression for the other compounds and this probably reflects the effect of the free 'lone pair' perturbing the metal t_{2g} orbitals.

In the limit, the Ir^{IV} becomes chemically unstable and this effect is more apparent with the bromo complexes (even though the redox potentials for the chloro and bromo species remain similar). Cyclic voltammograms were also run for some corresponding [RhL$_2$Cl$_4$]$^-$ complexes. Multiple oxidation peaks were observed but they were totally irreversible and at more positive potential.* Hence it was concluded that the oxidation of rhodium(III) to rhodium (IV) is more difficult than of iridium(III) to iridium(IV) and that [RhL$_2$Cl$_4$] are not chemically stable. This is also the experience from attempts to synthesise these species.

Discussion

The complexes of iridium(IV) obtained are all of the type [IrL$_2$X$_4$]; there was no evidence that cationic analogues

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* For [RhL$_2$Cl$_4$]$^-$, E_p^a/V *vs.* s.c.e.: L = SeMe$_2$, 1.55; py, 1.22; SMe$_2$, 1.64; PEt$_3$, 1.26 V. Values are for the first oxidation peak. Due to the total irreversibility and lack of information on the products, no correlations are possible.

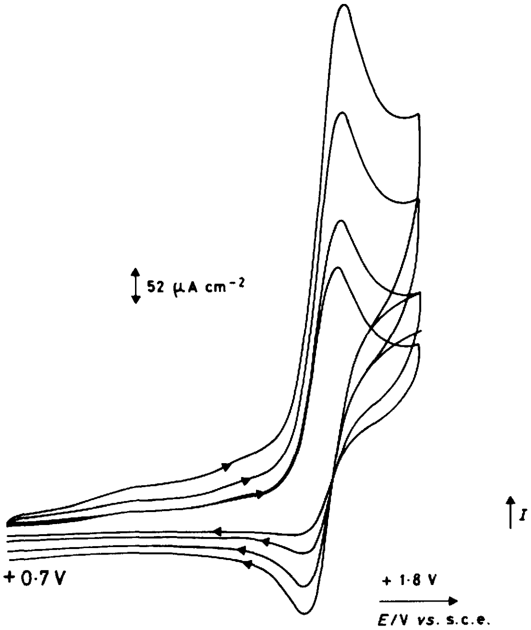

Figure 4. Cyclic voltammograms for the oxidation of $[Ir(dmso)_2Br_4]^-$ in MeCN–$[NBu^n{}_4]BF_4$. Potential scan rates 0.05, 0.1, 0.2, and 0.3 V s^{-1}

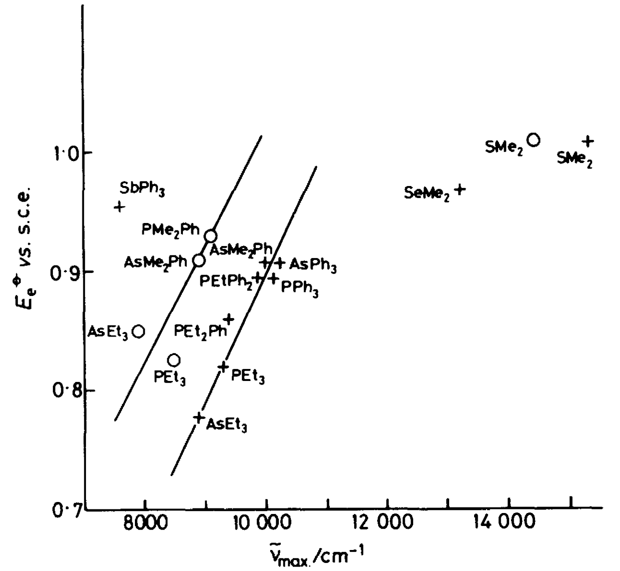

Figure 5. Dependence of the formal electrode potential E_e°, on $\tilde{\nu}_{max.}$, the energy of the $\sigma_L \longrightarrow Ir(t_{2g})$ l.m.c.t. transition. X = Br (○) or Cl (+)

$[IrL_3X_3]^+$ can be produced, a result we have observed previously with dithioether[11] and diselenoether[39] complexes. On the ligand-field model 5*d*, $t_{2g}{}^6$ is a very stable configuration, and replacement of weak-field halide by strong-field donors (PR_3, *etc.*) would be expected to increase this stabilisation, only partly offset by the greater splitting expected with increasing oxidation state. Secondly, the crucial role played by the iridium(III) intermediates $[IrL_2X_4]^-$ in the synthesis of $[IrL_2X_4]$ should be recognised. Thus, whilst the instability of the iridium(IV) complexes of $SbMe_3$ and $TeMe_2$ is no doubt genuine (and not unexpected)[27,40] our failure to prepare $[IrL_2Br_4]$ (L = PPh_3 or $AsPh_3$) is more likely to be due to lack of a viable route, since our data on the other bromides lead us to

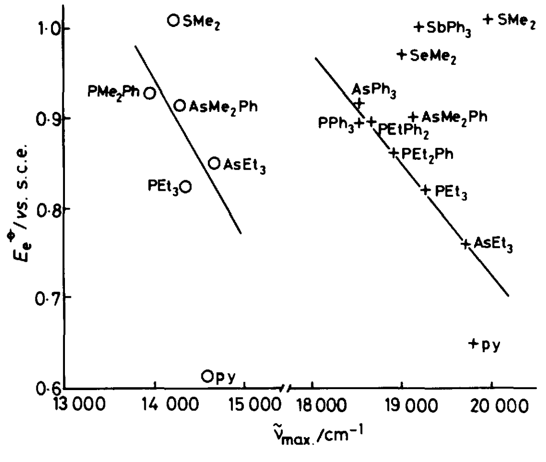

Figure 6. Dependence of E_e° on the energy of the $\pi_X \longrightarrow Ir(t_{2g})$ transition. X = Br (○) or Cl (+)

expect they would be of similar stability. A general conclusion drawn from this work is that the chemistry of iridium(IV) may be quite extensive, and that its presently restricted development possibly reflects the barrier imposed by the kinetic inertness of Ir^{III}, rather than genuine instability.

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