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# Co-ordination Chemistry of Higher Oxidation States. Part 41.<sup>1</sup> Synthesis, Spectroscopic and Electrochemical Studies of Cationic Ruthenium(III) Group 15 and 16 Donor Ligand Complexes. Structure of *trans*-[Ru{C<sub>6</sub>F<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o}<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub><sup>†</sup>

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The complexes *trans*-[Ru(L-L)<sub>2</sub>X<sub>2</sub>]BF<sub>4</sub> [X = Cl or Br; L-L = bidentate ligand including C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>-o, C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o, C<sub>6</sub>F<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o, Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, Ph<sub>2</sub>AsCHCHAsPh<sub>2</sub>, C<sub>6</sub>H<sub>4</sub>-(PPh<sub>2</sub>)<sub>2</sub>-o, C<sub>6</sub>F<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>-o, MeSCH<sub>2</sub>CH<sub>2</sub>SMe, PhSCH<sub>2</sub>CH<sub>2</sub>SPh and PhSeCH<sub>2</sub>CH<sub>2</sub>SePh] have been prepared by nitric acid oxidation of the corresponding [Ru(L-L)<sub>2</sub>X<sub>2</sub>] in aqueous HBF<sub>4</sub> and in other ways. The complexes have been characterised by analysis, IR and UV/VIS spectroscopies, and magnetic measurements, and the Ru<sup>II</sup>-Ru<sup>III</sup> redox potentials established by cyclic voltammetry. The crystal structure of *trans*-[Ru{C<sub>6</sub>F<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o}<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> has been determined: monoclinic, space group C2/c, a = 22.080(5), b = 18.064(2), c = 8.576(3) Å,  $\beta = 96.27(3)^\circ$ , R = 0.040 for 2266 reflections [ $F > 3\sigma(F)$ ]; Ru-Br 2.455(1), Ru-As 2.457(1), 2.460(1) Å. Electrochemical studies have provided evidence for the formation of ruthenium(IV) analogues in solution at low temperatures for certain ligands, but these are too unstable to isolate by chemical means. Comparisons with the analogous iron and osmium systems are made.

Ruthenium(II) complexes of the type  $Ru(L-L)_2X_2$  with diphosphine, diarsine or dithioether ligands (L-L) are well known,<sup>2</sup> <sup>7</sup> and are mostly six-co-ordinate neutral complexes, often obtainable with both *cis* or *trans* geometries. If the ligands are bulky as in  $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$  or have longer backbones, five-co-ordinate cationic species of type  $[Ru(L-L)_2X]^+$  are readily formed.<sup>8,9</sup> The corresponding ruthenium(III) complexes have received cursory study,<sup>2,3,5</sup> and we report here some detailed studies of the latter with a variety of Group 15 and 16 donor bidentate ligands. In marked contrast to both iron(IV)<sup>10</sup> and osmium(IV),<sup>1,11</sup> no analogous halogenoruthenium(IV) complexes have been obtained, although *trans*-[Ru(N<sub>4</sub>)X<sub>2</sub>]<sup>2+</sup> cations are known with tetraazamacrocycles (N<sub>4</sub>).<sup>12</sup> We also report a search for these elusive complexes using electrochemical techniques.

#### Experimental

Physical measurements were made as described previously.<sup>13</sup> Electrochemistry at low temperatures <sup>14</sup> was carried out in a jointless cell at a vitreous carbon-disc electrode, using a silver wire as a reference electrode. Cyclic voltammograms were recorded for *ca*.  $0.75 \times 10^{-3}$  mol dm<sup>-3</sup> solutions of selected complexes in acetonitrile at -45 °C and in trifluoroacetic acid at -23 °C. The electrolyte was NBu<sup>n</sup><sub>4</sub>BF<sub>4</sub> in all cases, and the systems were calibrated against ferrocene in separate experiments under the same conditions.

Hydrated 'RuCl<sub>3</sub>•xH<sub>2</sub>O' was obtained from Johnson Matthey and used as supplied. The corresponding bromide was obtained by repeatedly evaporating to dryness a mixture of the trichloride and 48% aqueous HBr.

*Ruthenium*(III) *Complexes.*—Syntheses of ruthenium complexes with methyl-substituted ligands were carried out under a nitrogen atmosphere. The crude ruthenium(II) complexes were prepared mainly by one method, although slight variations were used for some as described below. Ruthenium(III) complexes were then prepared from the ruthenium(II) species.

trans-[Ru{C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o}<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub>. To a deoxygenated solution of RuCl<sub>3</sub>·xH<sub>2</sub>O (0.24 g, 1.0 mmol) in ethanol (50 cm<sup>3</sup>) and water (15 cm<sup>3</sup>), was added C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o (0.70 g, 2.4 mmol) via a syringe. This mixture was refluxed for 1 h under nitrogen, the solution changing from deep blue to yellow and yielding a green-yellow solid upon cooling. This precipitate was filtered off, washed with diethyl ether and dried *in vacuo*. It was suspended in 40% HBF<sub>4</sub> (15 cm<sup>3</sup>), concentrated HNO<sub>3</sub> added dropwise (1 cm<sup>3</sup> in total) and the mixture was stirred for 10 min. The green solid was filtered off, washed with water (10 cm<sup>3</sup>) and then diethyl ether (3 × 10 cm<sup>3</sup>), and dried *in vacuo* (0.21 g, 28%) (Found: C, 28.7; H, 4.0. C<sub>20</sub>H<sub>32</sub>As<sub>4</sub>BCl<sub>2</sub>F<sub>4</sub>Ru requires C, 28.9; H, 3.8%),  $\Lambda$  (MeNO<sub>2</sub>) = 81.5  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>.

The following complexes were prepared analogously: trans-[Ru(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> (65%) (Found: C, 58.3; H, 4.6. C<sub>50</sub>H<sub>44</sub>BCl<sub>2</sub>F<sub>4</sub>P<sub>4</sub>Ru requires C, 58.4; H, 4.3%),  $\Lambda$  (MeNO<sub>2</sub>) = 80  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; trans-[Ru(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> (68%) (Found: C, 59.2; H, 4.2. C<sub>52</sub>H<sub>48</sub>BCl<sub>2</sub>F<sub>4</sub>P<sub>4</sub>Ru requires C, 59.2; H, 4.6%),  $\Lambda$  (MeNO<sub>2</sub>) = 70  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>; trans-[Ru(Ph<sub>2</sub>PCHCHPPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> (62%) (Found: C, 59.2; H, 4.3. C<sub>52</sub>H<sub>44</sub>BCl<sub>2</sub>F<sub>4</sub>P<sub>4</sub>Ru requires C, 59.4; H, 4.2%); trans-[Ru(Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> (48%) (Found: C, 25.7; H, 5.8. C<sub>12</sub>H<sub>32</sub>BCl<sub>2</sub>F<sub>4</sub>P<sub>4</sub>Ru requires C, 25.8; H, 5.8%); trans-[Ru(Ph<sub>2</sub>AsCH<sub>2</sub>CH<sub>2</sub>AsPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> (61%) (Found: C, 50.6; H, 4.1. C<sub>52</sub>H<sub>48</sub>As<sub>4</sub>BCl<sub>2</sub>F<sub>4</sub>Ru requires C, 50.7; H, 3.9%); trans-[Ru{C<sub>6</sub>F<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o<sup>2</sup><sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> (26%) (Found: C, 24.7; H, 2.4. C<sub>20</sub>H<sub>24</sub>As<sub>4</sub>BCl<sub>2</sub>F<sub>12</sub>Ru requires C, 24.6; H, 2.5%),  $\mu$  = 1.91; trans-[Ru(Ph<sub>2</sub>AsCHCHAsPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> (85%) (Found: C, 50.9; H, 3.6%).

The complex *trans*-[Ru(PhSeCH<sub>2</sub>CH<sub>2</sub>SePh)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> was prepared similarly but hypophosphorous acid (2 cm<sup>3</sup>) was added to the refluxing solution to give the crude, pink ruthenium(II) complex (36%) (Found: C, 36.2; H, 3.3.  $C_{28}H_{28}$ -BCl<sub>2</sub>F<sub>4</sub>RuSe<sub>4</sub> requires C, 35.8; H, 3.0%).

The following complexes were prepared similarly, but using RuBr<sub>3</sub>·xH<sub>2</sub>O as the starting material: *trans*-[Ru(Ph<sub>2</sub>PCH<sub>2</sub>-

<sup>†</sup> Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1992, Issue 1, pp. xx-xxv.

**Table 1** Atomic coordinates for *trans*- $[Ru{C_6F_4(AsMe_2)_2-o}_2-Br_2]BF_4$ 

Atom	x	у	Ζ
Ru	0.2500	0.750 0	0.0000
Br	0.257 99(4)	0.641 95(5)	0.174 63(10)
As(1)	0.216 07(4)	0.827 45(5)	0.209 43(9)
As(2)	0.353 46(4)	0.787 78(5)	0.105 53(9)
F(1)	0.230 0(2)	0.939 4(3)	0.487 9(6)
F(2)	0.329 5(3)	0.990 2(3)	0.654 1(6)
F(3)	0.440 8(3)	0.952 5(4)	0.582 1(7)
F(4)	0.452 7(2)	0.861 0(4)	0.339 0(7)
C(1)	0.165 7(4)	0.913 1(5)	0.154 2(11)
C(2)	0.176 7(4)	0.779 4(5)	0.374 2(11)
C(3)	0.288 9(4)	0.869 8(5)	0.326 9(8)
C(4)	0.284 9(4)	0.917 9(4)	0.449 2(9)
C(5)	0.335 0(5)	0.945 3(5)	0.537 3(10)
C(6)	0.390 8(5)	0.927 0(5)	0.500 1(10)
C(7)	0.396 3(4)	0.877 8(6)	0.374 8(10)
C(8)	0.346 3(3)	0.849 8(5)	0.287 3(9)
C(9)	0.398 8(4)	0.849 2(6)	-0.0224(11)
C(10)	0.411 4(4)	0.714 3(6)	0.181 4(13)
В	0.0000	0.231 2(20)	0.7500
F(5)	0.040 1(4)	0.190 4(5)	0.677 3(10)
F(6)	0.034 1(5)	0.276 3(7)	0.854 8(16)

CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (81%) (Found: C, 54.7; H, 4.3. C<sub>52</sub>H<sub>48</sub>-BBr<sub>2</sub>F<sub>4</sub>P<sub>4</sub>Ru requires C, 54.6; H, 4.2%),  $\mu = 2.00$ ; trans-[Ru(Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (60%) (Found: C, 21.9; H, 5.1. C<sub>12</sub>H<sub>32</sub>BBr<sub>2</sub>F<sub>4</sub>P<sub>4</sub>Ru requires C, 22.2; H, 5.0%); trans-[Ru{C<sub>6</sub>H<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o}<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (17%) (Found: C, 26.0; H, 3.5. C<sub>20</sub>H<sub>32</sub>As<sub>4</sub>BBr<sub>2</sub>F<sub>4</sub>Ru requires C, 26.1; H, 3.5%); trans-[Ru {C<sub>6</sub>F<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o}<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (23%) (Found: C, 22.6; H, 2.3. C<sub>20</sub>H<sub>24</sub>As<sub>4</sub>BBr<sub>2</sub>F<sub>12</sub>Ru requires C, 22.6; H, 2.3%),  $\mu = 2.02$ .

The complex *trans*-[Ru(PhSeCH<sub>2</sub>CH<sub>2</sub>SePh)<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> was prepared from the ruthenium(II) species, which was prepared by refluxing the analogous ruthenium(II) chloro complex in ethanol overnight, with a large excess of LiBr (Found: C, 32.5; H, 2.9.  $C_{28}H_{28}BBr_2F_4RuSe_4$  requires C, 32.7; H, 2.7%).

The following complexes were prepared similarly from RuX<sub>3</sub>·xH<sub>2</sub>O, but using *N*,*N*-dimethylformamide as solvent, replacing ethanol and water: *trans*-[Ru{C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>-*o*]<sub>2</sub>Cl<sub>2</sub>]-BF<sub>4</sub> (67%) (Found: C, 62.5; H, 4.3. C<sub>60</sub>H<sub>48</sub>BCl<sub>2</sub>F<sub>4</sub>P<sub>4</sub>Ru requires C, 62.6; H, 4.2%); *trans*-[Ru{C<sub>6</sub>F<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>-*o*]<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> (53%) (Found: C, 55.3; H, 3.3. C<sub>60</sub>H<sub>40</sub>BCl<sub>2</sub>F<sub>12</sub>P<sub>4</sub>Ru requires C, 55.6; H, 3.1%); *trans*-[Ru{C<sub>6</sub>H<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>-*o*]<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (51%) (Found: C, 58.0; H, 4.1. C<sub>60</sub>H<sub>48</sub>BBr<sub>2</sub>F<sub>4</sub>P<sub>4</sub>Ru requires C, 58.1; H, 3.9%),  $\Lambda$  (MeNO<sub>2</sub>) = 70  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>,  $\mu$  = 1.86; *trans*-[Ru{C<sub>6</sub>F<sub>4</sub>(PPh<sub>2</sub>)<sub>2</sub>-*o*]<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (57%) (Found: C, 52.1; H, 3.1. C<sub>60</sub>H<sub>40</sub>BBr<sub>2</sub>F<sub>12</sub>P<sub>4</sub>Ru requires C, 52.0; H, 2.9%); *trans*-[Ru{Pu}(Ph<sub>2</sub>AsCHCHAsPh<sub>2</sub>)<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (72%) (Found: C, 46.9; H, 3.0. C<sub>52</sub>H<sub>44</sub>As<sub>4</sub>BBr<sub>2</sub>F<sub>4</sub>Ru requires C, 47.4; H, 3.4%),  $\mu$  = 1.96.

The complex trans- $[Ru{C_6H_4(PMe_2)_2-o}_2Cl_2]BF_4$  was prepared similarly from RuCl<sub>3</sub>•xH<sub>2</sub>O, but using 2-methoxyethanol as the solvent (28%) (Found: C, 36.5; H, 5.0.  $C_{20}H_{32}BCl_2F_4P_4Ru$  requires C, 36.7; H, 4.9%).

trans-[Ru(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub>. To a solution of RuCl<sub>3</sub>·xH<sub>2</sub>O (0.24 g, 1.0 mmol) in 2-methoxyethanol (60 cm<sup>3</sup>) was added MeSCH<sub>2</sub>CH<sub>2</sub>SMe (0.34 g, 2.8 mmol) via a syringe, and the mixture was refluxed for 2 h. The colour changed from dark red to orange-yellow upon addition of hypophosphorous acid (2 cm<sup>3</sup>) after 1 h of reflux. The solvent was removed under vacuum and the crude ruthenium(II) species was extracted into CH<sub>2</sub>Cl<sub>2</sub> and reprecipitated with diethyl ether. The ruthenium(II) complex was prepared by suspending the ruthenium(II) complex in ethanol (30 cm<sup>3</sup>) and 40% HBF<sub>4</sub> (5 cm<sup>3</sup>), and bubbling chlorine gas through the suspension until no further colour change from yellow-orange to red was observed. The reaction mixture was left to stir for 15 min. The red precipitate was filtered off, washed with diethyl ether and dried *in vacuo* (0.21 g, 42%) (Found: C, 19.0; H, 4.1. C<sub>8</sub>H<sub>20</sub>BCl<sub>2</sub>F<sub>4</sub>RuS<sub>4</sub> requires

C, 19.1; H, 4.0%),  $\Lambda$  (MeNO<sub>2</sub>) = 91.1  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>,  $\mu$  = 2.05.

The complex trans-[Ru(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)<sub>2</sub>Cl<sub>2</sub>]BF<sub>4</sub> was prepared analogously (39%) (Found: C, 45.0; H, 3.9.  $C_{28}H_{28}$ -BCl<sub>2</sub>F<sub>4</sub>RuS<sub>4</sub> requires C, 44.7; H, 3.7%).

The complex *trans*-[Ru(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> was prepared similarly from RuBr<sub>3</sub>•*x*H<sub>2</sub>O, except that the crude ruthenium(II) species was suspended in ethanol (30 cm<sup>3</sup>) and 40% HBF<sub>4</sub> (5 cm<sup>3</sup>) and bromine in CCl<sub>4</sub> (*ca.* 5% v/v) were added until a permanent excess of bromine was observed. The reaction mixture was stirred for 15 min. The blue precipitate was filtered off, washed with diethyl ether and dried *in vacuo* (45%) (Found: C, 16.3; H, 3.5. C<sub>8</sub>H<sub>20</sub>BBr<sub>2</sub>F<sub>4</sub>RuS<sub>4</sub> requires C, 16.2; H, 3.4%).

The following compounds were prepared similarly: trans-[Ru(PhSCH<sub>2</sub>CH<sub>2</sub>SPh)<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (44%) (Found: C, 40.0; H, 3.4. C<sub>28</sub>H<sub>28</sub>BBr<sub>2</sub>F<sub>4</sub>RuS<sub>4</sub> requires C, 40.0; H, 3.3%); trans-[Ru(Me-SeCH<sub>2</sub>CH<sub>2</sub>SeMe)<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> (Found: C, 12.4; H, 2.7. C<sub>8</sub>H<sub>20</sub>-BBr<sub>2</sub>F<sub>4</sub>RuSe<sub>4</sub> requires C, 12.3; H, 2.6%).

X-Ray Structure Determination.—Air-stable green crystals of  $[Ru{C_6F_4(AsMe_2)_2-o}_2Br_2]BF_4$  were grown by vapour diffusion of diethyl ether into acetonitrile solutions and sealed in glass capillaries. Preliminary photographic X-ray examination established the crystal system and approximate cell dimensions. Density measured by flotation (CCl<sub>4</sub>-C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>).

Crystal data.  $C_{20}H_{24}As_4BBr_2F_{12}Ru$ , M = 1063.78, monoclinic, space group C2/c, a = 22.080(5), b = 18.064(2), c = 8.576(3) Å,  $\beta = 96.27(3)^{\circ}$ , U = 3400.1 Å<sup>3</sup>, Z = 4,  $D_m = 2.13(2)$ ,  $D_c = 2.079$  g cm<sup>-3</sup>, F(000) = 2012,  $\lambda(Mo-K\alpha) = 0.710$  69 Å,  $\mu = 66.7$  cm<sup>-1</sup>.

Data collection. Using a CAD-4 diffractometer equipped with graphite monochromator and Mo-K $\alpha$  radiation, 3247 reflections ( $\theta = 1.5-25^{\circ}$ ;  $h \ 0-26$ ,  $k \ 0-21$ ,  $l \ -10$  to 10) were measured from a room-temperature crystal (0.45  $\times$  0.40  $\times$  0.4 mm). Two intensity check reflections showed no decay and a  $\psi$ -scan empirical absorption correction based on three reflections was applied (transmission: maximum 99.8, minimum 82.5%). The systematic absences indicated the space group Cc or C2/c of which the latter was confirmed by the structure solution. After data reduction there remained 2990 unique reflections ( $R_{int} = 0.010$ ) of which 2266 with  $F > 3\sigma(F)$  were used in the refinement.

Structure solution. The positions of the Ru, As and Br atoms were determined by direct methods available in SHELXS 86<sup>15</sup> and subsequent structure-factor and electron-density syntheses located the remaining non-H atoms. Hydrogen atoms were introduced into the model at a later stage in calculated positions [d(C-H) = 0.95 Å]. Full-matrix least-squares refinement<sup>16</sup> minimising  $\sum w\Delta^2$  converged to R = 0.040 {196 parameters, 2266 reflections, anisotropic (Ru, As, Br, F, C, B) and isotropic (H) atoms,  $w = 1/[\sigma^2(F) + 0.0005F^2]$ , R' = 0.058,  $\Delta/\sigma =$ 0.14}. The final difference electron-density synthesis showed all features in the range 0.96 to -0.61 e Å<sup>-3</sup>. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 17 (Ru, As) and SHELX 76<sup>16</sup> (Br, F, C, B, H). All calculations were carried out on an IBM 3090 computer using the programs SHELXS 86,15 SHELX 76,16 ORTEP II 18 and PARST.<sup>19</sup> The atomic coordinates are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## **Results and Discussion**

The reduction of 'RuX<sub>3</sub>· $nH_2O$ '\* (X = Cl or Br) with diphosphines, diarsines, dithioethers or diselencethers in

<sup>\*</sup> Despite the name, hydrated ruthenium trichloride and tribromide mostly contain Ru<sup>IV</sup>, the 'trihalide' referring to the 1:3 Ru:X ratio.<sup>20</sup>

Table 2 Selected spectroscopic data for the trans ruthenium(III) complexes

		$v(Ru-X)^{a}/$	
Compound	Colour	cm <sup>-1</sup>	Ultraviolet-visible $E_{max}^{b}/10^{3} \text{ cm}^{-1} (\epsilon/\text{dm}^{3} \text{ mol}^{-1} \text{ cm}^{-1})$
[Ru(Ph,PCH,PPh,),Cl,]BF <sub>4</sub>	Dark green	346	14.2 (420), 21.4 (530), 25.0 (550)
[Ru(Ph,PCH,CH,PPh,),Cl,]BF4	Red-brown	345	13.9 (690), 21.3 (680), 23.8 (670), 25.8 (670)
$[Ru{C_6H_4(PMe_2)_2-o}_2Cl_2]BF_4$	Blue-green	330	14.7 (735), 17.3 (120) (sh), 26.7 (1070)
$[Ru{C_{6}H_{4}(PPh_{2})_{2}-o]_{2}Cl_{2}]BF_{4}$	Red-brown	347	13.6 (1360), 16.6 (400), 20.4 (1470), 24.9 (1230)
$[Ru{C_6F_4(PPh_2)_2-o}_2Cl_2]BF_4$	Dark red	357	13.2 (1140), 16.9 (625), 19.6 (1280), 25.1 (1040), 32.9 (45 560)
[Ru(Ph <sub>2</sub> PCHCHPPh <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]BF <sub>4</sub>	Dark brown	346	13.8 (1070), 20.4 (970), 24.4 (800)
$[Ru(Me_2PCH_2CH_2PMe_2)_2Cl_2]BF_4$	Blue-green	329	14.7 (1420), 16.6 (380) (sh), 27.2 (2580)
[Ru(Ph <sub>2</sub> AsCH <sub>2</sub> CH <sub>2</sub> AsPh <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]BF <sub>4</sub>	Green	340	14.0 (860), 16.2 (260) (sh), 22.7 (900), 33.1 (37 810)
$[Ru{C_6H_4(AsMe_2)_2-o}_2Cl_2]BF_4$	Blue-green	342	15.2 (1400), 17.0 (340) (sh), 27.3 (1630)
$[Ru{C_6F_4(AsMe_2)_2-o}_2Cl_2]BF_4$	Blue	340	15.6 (735), 17.5 (225) (sh), 21.3 (340), 26.5 (880)
[Ru(Ph <sub>2</sub> AsCHCHAsPh <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]BF <sub>4</sub>	Dark green	346	14.2 (1280), 16.6 (390), 22.6 (1290), 26.5 (1460)
$[Ru(MeSCH_2CH_2SMe)_2Cl_2]BF_4$	Dark red	348	17.2 (780), 23.2 (2665) in MeCN
[Ru(PhSCH <sub>2</sub> CH <sub>2</sub> SPh) <sub>2</sub> Cl <sub>2</sub> ]BF <sub>4</sub>	Dark brown	354	17.1 (340), 22.4 (1310), 32.8 (16 440)
$[Ru(PhSeCH_2CH_2SePh)_2Cl_2]BF_4$	Green	344	15.6 (450), 23.6 (1570), 32.4 (20 860)
$[Ru(Me_2NCH_2CH_2NMe_2)_2Cl_2]ClO_4$			27.2 (3100), 32.5 (1540) <sup>c</sup> in 0.1 mol dm <sup>-3</sup> HCl
[Ru(Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> ) <sub>2</sub> Br <sub>2</sub> ]BF <sub>4</sub>	Purple-brown	268	13.1 (5050), 18.7 (1360), 23.4 (1440)
$[Ru{C_6H_4(PMe_2)_2-o}_2Br_2]BF_4$	Green	268	13.4 (3615), 15.4 (530) (sh), 22.5 (1480), 23.8 (1385) (sh)
$[\operatorname{Ru}{C_6H_4(\operatorname{PPh}_2)_2-o}_2\operatorname{Br}_2]BF_4$	Dark blue	271	12.6 (3050), 15.0 (780), 17.4 (960), 23.2 (910), 32.3 (11 210) (sh)
$[Ru{C_6F_4(PPh_2)_2-o}_2Br_2]BF_4$	Blue-green	284	12.5 (3100), 14.9 (900), 16.6 (870), 22.8 (810), 32.1 (25 670)
$[Ru(Me_2PCH_2CH_2PMe_2)_2Br_2]BF_4$	Green	272	13.5 (4925), 23.15 (2500)
$[Ru{C_6H_4(AsMe_2)_2-o}_2Br_2]BF_4$	Green	283	13.9 (3380), 15.0 (500) (sh), 23.1 (1130), 24.7 (1290)
$[\operatorname{Ru}{C_6F_4}(\operatorname{AsMe}_2)_2 - o]_2\operatorname{Br}_2]\operatorname{BF}_4$	Green	271	12.1 (sh), 14.0 (5480), 15.6 (840) (sh), 22.5 (1110) (sh), 24.3 (1440)
[Ru(Ph <sub>2</sub> AsCHCHAsPh <sub>2</sub> ) <sub>2</sub> Br <sub>2</sub> ]BF <sub>4</sub>	Blue-black	268	13.1 (4190), 15.2 (785), 18.8 (1080), 22.5 (1130), 32.0 (21 220) (sh)
$[Ru(MeSCH_2CH_2SMe)_2Br_2]BF_4$	Dark blue	287	17.4 (3990), 21.1 (620), 27.9 (465) in MeCN
[Ru(PhSCH <sub>2</sub> CH <sub>2</sub> SPh) <sub>2</sub> Br <sub>2</sub> ]BF <sub>4</sub>	Grey-blue	260	15.3 (sh), 17.8 ( $-$ ), 23.5 ( $-$ ) <sup><i>d</i></sup> in HCONMe <sub>2</sub>
$[Ru(MeSeCH_2CH_2SeMe)_2Br_2]BF_4$	Dark blue	n.a.	17.4 (3910), 21.6 (580), 28.5 (460) in MeCN
$[Ru(PhSeCH_2CH_2SePh)_2Br_2]BF_4$	Blue	n.a.	15.3 (750), 18.8 (720) (sh), 22.9 (910) (sh), 31.6 (16 470)
$[Ru(Me_2NCH_2CH_2NMe_2)_2Br_2]ClO_4$			21.2 (4280), 27.0 (480) <sup>c</sup> in MeCN
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<sup>a</sup> Nujol mull, n.a. = not assigned. <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub> solution unless indicated otherwise. <sup>c</sup> Data from ref. 21. <sup>d</sup> Complex decomposes slowly in solution,  $\varepsilon_{mol}$  not cited.



Fig. 1 The UV/VIS spectra of *trans*-[ $Ru{C_6H_4(PMe_2)_2-o}_2X_2$ ]BF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub>: X = Cl (---) or Br (----)

refluxing alcohols results in the production of yellow or orange ruthenium(II) complexes, *trans*-[Ru(L-L)<sub>2</sub>X<sub>2</sub>].<sup>2-7</sup> In a few cases the reductions were completed by addition of H<sub>3</sub>PO<sub>2</sub> (see Experimental section). The crude ruthenium(II) complexes suspended in 40% aqueous HBF<sub>4</sub> are easily oxidised to the deeply coloured [Ru(L-L)<sub>2</sub>X<sub>2</sub>]BF<sub>4</sub> (Table 2) by dropwise addition of concentrated HNO<sub>3</sub>. The dithioether complexes tend to dissolve in this acid mixture from which they cannot be recovered. The ruthenium(III) dithioether complexes are better obtained by halogen oxidation of the ruthenium(II) analogues in EtOH-HBF<sub>4</sub> suspension. The new diselencether complexes *trans*-[Ru(RSeCH<sub>2</sub>CH<sub>2</sub>SeR)<sub>2</sub>X<sub>2</sub>]BF<sub>4</sub> (R = Ph, X = Cl or Br; R = Me, X = Br) were easily made, but repeated attempts to obtain a pure sample of *trans*-[Ru(MeSeCH<sub>2</sub>CH<sub>2</sub>SeMe)<sub>2</sub>-Cl<sub>2</sub>]BF<sub>4</sub> have been unsuccessful.

The trans- $[Ru(L-L)_2X_2]BF_4$  complexes are deeply coloured, air-stable solids, soluble in a wide range of organic solvents, in which they are 1:1 electrolytes. The diphosphine and diarsine complexes are stable in solution but the dithioether complexes,

especially those of  $PhSCH_2CH_2SPh$ , decompose in strong donor solvents such as dimethyl sulfoxide or *N*,*N*-dimethyl-formamide. The diselencether complexes appear more stable than the dithioethers, although all are reduced to  $Ru^{II}$  on boiling in alcohols.

The assignment of *trans* geometry to the ruthenium(II) precursors is based upon the characteristic UV/VIS spectra which in local  $D_{4h}$  symmetry exhibit two d-d transitions  ${}^{1}A_{1g} \longrightarrow {}^{1}E_{g}$  and  ${}^{1}A_{1g} \longrightarrow {}^{1}A_{2g}$ , and for each of the diphosphine complexes a single  ${}^{31}P$  NMR resonance.<sup>7,22,23</sup> The outersphere oxidation of the inert  $t_{2g}{}^{6}$  complexes would be expected to occur with retention of configuration. Confirmation that the ruthenium(III) complexes have *trans* geometries comes from the single IR-active v(Ru-X) vibrations, and the very similar UV/VIS spectra (Table 2) to those of the *trans*- $[Os(L-L)_2X_2]^+$  analogues.<sup>1</sup> Definitive evidence was provided by the X-ray study of *trans*- $[Ru\{C_6F_4(AsMe_2)_2-o\}_2Br_2]BF_4$  (below). The ruthenium(III) complexes are paramagnetic with  $\mu$  ca. 1.7-1.9 consistent with 4d  $t_{2g}{}^5$  ground states,<sup>24</sup> which precludes the use of NMR spectroscopy to establish the stereochemistry.

UV/VIS Spectra.—The assignment of the UV/VIS spectra (Table 2, Fig. 1) of the diphosphine and diarsine complexes follows from those of the iron(III)<sup>25</sup> and osmium(III)<sup>1</sup> analogues. For these low-spin d<sup>5</sup> ions in a  $D_{4h}$  field the d-orbital configuration is  $b_2^2 < e^3 < a_1^0 < b_1^0$  and the strong bands of the [Ru(L-L)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complexes at 14 000–16 000 and 24 000– 27 000 cm<sup>-1</sup> are the  $\sigma(P,As) \longrightarrow e(Ru)$  and  $\sigma(P,As) \longrightarrow$  $a_1(Ru)$  charge-transfer (c.t.) transitions. For the bromides the corresponding features lie at 2000–3000 cm<sup>-1</sup> lower in energy. The reported spectra<sup>21</sup> of *trans*-[Ru(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-X<sub>2</sub>]<sup>+</sup> provide the approximate energies expected for the transitions  $\pi(X) \longrightarrow e(Ru)$  [the  $\sigma(N) \longrightarrow e(Ru)$  transitions are in the UV region], which lie at *ca.* 27 000 (X = Cl) and 22 000 cm<sup>-1</sup> (X = Br). Unfortunately for *trans*-[Ru(L-L)<sub>2</sub>-Cl<sub>2</sub>]BF<sub>4</sub> the  $\pi(Cl) \longrightarrow e(Ru)$  c.t. bands lie in the same region as



**Fig. 2** The UV/VIS spectra of *trans*-[Ru(MeSCH<sub>2</sub>CH<sub>2</sub>SMe)<sub>2</sub>X<sub>2</sub>]BF<sub>4</sub> in MeCN: X = Cl(--) or Br (----)



Fig. 3 View of the cation of  $trans-[Ru{C_6F_4(AsMe_2)_2-o}_2Br_2]BF_4$  showing the atom-labelling scheme. The thermal ellipsoids are drawn with boundary surfaces at the 50% level

Table 3 Selected bond lengths (Å) and angles (°) for trans-[Ru{ $C_6F_4(AsMe_2)_2 - o$ }\_2Br\_2]BF<sub>4</sub>

Ru-As(1) Ru-As(2)	2.457(1) 2.460(1)	Ru–Br	2.455(1)
As–C C–C	1.918(9)–1.958(8) 1.35(1)–1.41(1)	C-F 1.31	(1)-1.35(1)
B-F(5) B-F(6)	1.36(2) 1.38(2)	$\begin{array}{c} \operatorname{As}(1)\cdots\operatorname{As}(2)\\ \operatorname{Br}\cdots\operatorname{As}\end{array}$	3.332(1) 3.449(1) (minimum)
As(1)-Ru- Br-Ru-As Ru-As(1)- Ru-As(1)- Ru-As(1)- Ru-As(1)- C-As-C As-C-C	$\begin{array}{ccc} -As(2) & 85.3(1) \\ s(1) & 90.8(1) \\ -C(1) & 119.3(3) \\ -C(2) & 118.3(3) \\ -C(3) & 107.4(2) \\ 102.0(4)-104.2(4) \\ 119.4(6)-121.6(6) \end{array}$	Br-Ru-As(2) Ru-As(2)-C(8) Ru-As(2)-C(9) Ru-As(2)-C(10) C-C-C 118.3( F-C-C 117.1( F-B-F 106.5(	89.7(1) 107.6(2) 118.2(3) 119.6(3) 8)–122.5(8) 7)–121.3(8) 6)–114.0(9)

the  $\sigma(P,As) \longrightarrow a_1(Ru)$  and as argued elsewhere <sup>1</sup> are rarely seen due to the high intensity of the latter. However for the bromides the  $\pi(Br) \longrightarrow e(Ru)$  are often evident at ca. 22 000 cm<sup>-1</sup>. Medium-intensity features are also seen at ca. 20 000 cm<sup>-1</sup> in the spectra of the aryl-substituted ligand complexes, but these are weak or not observed with alkyl-substituted ligands. Examination of several samples of the same complexes showed these features to have constant relative intensities to the c.t. bands, eliminating the possibility that they are due to impurities, and they are assigned as metal-centred (d-d) transitions which 'borrow' intensity from the nearby chargetransfer bands. Such borrowing is known to be much less in alkyl-substituted ligand systems.<sup>26</sup> It is notable that the energies of the lowest  $\sigma(P,As) \longrightarrow Ru$  c.t. transitions are *ca.* 3000 cm<sup>-1</sup> to lower energies than those of the corresponding osmium(III) complexes,<sup>1</sup> reflecting the greater oxidising ability of the ruthenium(III) complexes, and paralleling the trends in RuII-Ru<sup>III</sup> and Os<sup>II</sup>-Os<sup>III</sup> redox potentials (below).

The UV/VIS spectra of the Group 16 donor ligand complexes (Table 2, Fig. 2) are less readily interpreted since  $\pi(S,Se) \longrightarrow$ Ru c.t. bands are expected at similar energies to those of the  $\pi(Cl,Br) \longrightarrow Ru$  bands. For the chlorides *trans*-[Ru(L-L)<sub>2</sub>-Cl<sub>2</sub>]<sup>+</sup> (L-L = RSCH<sub>2</sub>CH<sub>2</sub>SR or RSeCH<sub>2</sub>CH<sub>2</sub>SR) the intense features at 22 000–24 000 cm<sup>-1</sup> as well as the weaker lowerenergy absorptions are probably  $\pi(S,Se) \longrightarrow e(Ru)$ , consistent with the optical electronegativities of  $\sigma(P,As) < \pi(S,Se) < \pi(Cl)$ .<sup>27</sup> For the bromo-complexes the corresponding main absorption lies at *ca*. 17 000 cm<sup>-1</sup> with weaker ill-defined features to higher energy. Both  $\pi(Br) \longrightarrow e(Ru)$  and  $\pi(S,Se) \longrightarrow e(Ru)$  are expected in this region, and a definite assignment of the individual bands is not possible.

X-Ray Structure of trans-[Ru{C<sub>6</sub>F<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o}<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub>.— The structure consists of discrete anions and cations with the ruthenium atom located on a centre of symmetry (Fig. 3). The diarsine ligand has been structurally characterised in the nickel complex <sup>28</sup> [Ni{C<sub>6</sub>F<sub>4</sub>(AsMe<sub>2</sub>)<sub>2</sub>-o}<sub>2</sub>Br<sub>2</sub>]BF<sub>4</sub> and the present geometry is in accord with it. Good comparator molecules are rare and although a number of Ru–Br and Ru–As distances have been reported <sup>29</sup> these are usually for ruthenium(II) compounds and chemically rather different from the present example. The Ru–Br distance [2.455(1) Å] (Table 3) may be compared with 2.552(2) Å reported <sup>30</sup> for Ru<sup>III</sup>–Br (*trans* to P) in a porphyrin complex and 2.540(1) Å for Ru–Br (*trans* to Br) in the ruthenium(II) complex [Ru(Me<sub>2</sub>SO)<sub>4</sub>Br<sub>2</sub>].<sup>31</sup> The Ru–As distances [2.457(1) and 2.460(1) Å] may be compared with 2.404(1) and 2.455(1) Å found <sup>32</sup> in [Ru{C<sub>6</sub>H<sub>4</sub>(AsMePh)<sub>2</sub>-o}-(CO)<sub>2</sub>Cl<sub>2</sub>] and the range of values 2.308(5)–2.472(5) Å reported <sup>33</sup> in [Ru{As[C<sub>6</sub>H<sub>4</sub>(AsPh<sub>2</sub>)-o]<sub>3</sub>}Br<sub>2</sub>].

Many trans octahedral bis(chelate) complexes adopt a 'stepped' structure<sup>28</sup> but in the present example the angle between the RuAs<sub>4</sub> and  $C_6As_2$  planes is very small (1.7°). The As atoms are displaced by ca. 0.1 Å (average) from the  $C_6$  plane but on opposite sides and as expected the benzene ring is planar. The B atom of the tetrahedral BF<sub>4</sub><sup>-</sup> anion is on a two-fold axis and the ion is not apparently disordered although there are large values for the thermal parameters of B and F. Although this material crystallises in the same space group as that of the analogous nickel compound<sup>28</sup> in which the Ni is also on a centre of symmetry, the two materials are not isomorphous although they are isostructural.

*Electrochemistry.*—Cyclic voltammetry was used to determine the formal potentials of the  $Ru^{II}$ – $Ru^{III}$  couples. Voltammograms were recorded at potential scan rates over the range 0.05–0.2 V s<sup>-1</sup>, at a polished, vitreous carbon-disc electrode for 0.5 × 10<sup>-3</sup> mol dm<sup>-3</sup> solutions of the ruthenium(III) complexes in MeCN, containing 0.1 mol dm<sup>-3</sup> NBu<sup>n</sup><sub>4</sub>BF<sub>4</sub>. The results are listed in Table 4 and Fig. 4 shows a typical example.

The complexes gave electrochemically reversible  $Ru^{II}-Ru^{III}$  couples, except for *trans*-[ $Ru\{C_6H_4(PPh_2)_2-o\}_2Cl_2$ ]BF<sub>4</sub> and *trans*-[ $Ru\{C_6H_4(PPh_2)_2-o\}_2Br_2$ ]BF<sub>4</sub> which gave irreversible  $Ru^{II}-Ru^{III}$  couples, but this is almost certainly due to the insolubility of the corresponding ruthenium(II) complexes in MeCN.

Reversible Ru<sup>II</sup>–Ru<sup>III</sup> couples were found over the range 0.3–0.8 V as shown in Table 4. The effect of varying the halide ligands, the substituents on the donor atom, and the backbone of the bidentate ligand are similar to those previously observed for the iron and osmium analogues.<sup>1,10</sup> The Ru<sup>II</sup>–Ru<sup>III</sup> couples were seen at *ca*. 0.3 V more positive than the Os<sup>II</sup>–Os<sup>III</sup> couples for corresponding diphosphine or diarsine ligand complexes.<sup>1</sup> The Ru<sup>II</sup>–Ru<sup>III</sup> couple for the corresponding *trans*-

The Ru<sup>II</sup>-Ru<sup>III</sup> couple for the corresponding *trans*-[Ru(Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complex has been observed at -0.2 V [relative to the saturated calomel electrode (SCE), after correction for differing reference electrodes] which is *ca*. 0.5 V less positive than for the diphosphine and diarsine complexes. The Ru<sup>II</sup>-Ru<sup>III</sup> couples for corresponding tertiary amine macrocycle complexes are seen at similar potentials.<sup>12,21</sup>

Table 4	Electrochemical	data, J	$E_e^\circ$	$ \mathbf{V} $	vs.	SCE
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Compound	Ru <sup>11</sup> –Ru <sup>111 a</sup>	Ru <sup>III</sup> Ru <sup>IV a.</sup>
[Ru(Ph,PCH,PPh,),Cl,]BF4	+ 0.55	+ 1.68
[Ru(Ph,PCH,CH,PPh,),Cl,]BF4	+0.54	+1.68
$[Ru C_6H_4(PMe_2)_2 - o]_2Cl_2]BF_4$	+0.50	+1.59
$[\operatorname{Ru} \{C_6H_4(\operatorname{PPh}_2)_2 - o\}_2 Cl_2]BF_4$	$(+0.62)^{b}$	+1.72
$[\operatorname{Ru}{C_6F_4(\operatorname{PPh}_2)_2-o}_2\operatorname{Cl}_2]BF_4$	+0.80	+2.04
[Ru(Ph <sub>2</sub> PCHCHPPh <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]BF <sub>4</sub>	+0.62	+1.73
$[Ru(Me_2PCH_2CH_2PMe_2)_2Cl_2]BF_4$	+0.33	+ 1.47
[Ru(Ph <sub>2</sub> AsCH <sub>2</sub> CH <sub>2</sub> AsPh <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]BF <sub>4</sub>	+0.54	+1.80
$[\operatorname{Ru}\{\operatorname{C}_{6}\operatorname{H}_{4}(\operatorname{AsMe}_{2})_{2}\text{-}o\}_{2}\operatorname{Cl}_{2}]\operatorname{BF}_{4}$	+0.40	+ 1.58
$[\operatorname{Ru}{C_6F_4(AsMe_2)_2-o}_2Cl_2]BF_4$	+0.75	+ 1.93
[Ru(Ph <sub>2</sub> AsCHCHAsPh <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]BF <sub>4</sub>	+0.63	+1.91
$[Ru(MeSCH_2CH_2SMe)_2Cl_2]BF_4$	+0.55	d
[Ru(PhSCH <sub>2</sub> CH <sub>2</sub> SPh) <sub>2</sub> Cl <sub>2</sub> ]BF <sub>4</sub>	+0.65	d
$[Ru(PhSeCH_2CH_2SePh)_2Cl_2]BF_4$	+0.57	d
$[Ru(Ph_2PCH_2CH_2PPh_2)_2Br_2]BF_4$	+0.55	+1.65
$[Ru{C_6H_4(PMe_2)_2-o}_2Br_2]BF_4$	+0.55	+1.43
$[Ru{C_6H_4(PPh_2)_2-o}_2Br_2]BF_4$	$(+0.65)^{b}$	+ 1.86
$[\operatorname{Ru}{C_6F_4(\operatorname{PPh}_2)_2}-o]_2\operatorname{Br}_2]\operatorname{BF}_4$	+0.79	+1.87
$[Ru(Me_2PCH_2CH_2PMe_2)_2Br_2]BF_4$	+0.43	+1.52
$[Ru{C_6H_4(AsMe_2)_2-o}_2Br_2]BF_4$	+0.41	+1.56
$[\operatorname{Ru}\{\operatorname{C}_{6}\operatorname{F}_{4}(\operatorname{AsMe}_{2})_{2}-o\}_{2}\operatorname{Br}_{2}]\operatorname{BF}_{4}$	+0.79	+ 1.91
$[Ru(Ph_2AsCHCHAsPh_2)_2Br_2]BF_4$	+0.64	d
$[Ru(MeSCH_2CH_2SMe)_2Br_2]BF_4$	+0.57	d
$[Ru(PhSCH_2CH_2SPh)_2Br_2]BF_4$	+0.70°	d
$[Ru(PhSeCH_2CH_2SePh)_2Br_2]BF_4$	+0.59	d
$[Ru(MeSeCH_2CH_2SeMe)_2Br_2]BF_4$	+0.56	d

" In MeCN solution containing 0.1 mol dm<sup>-3</sup> NBu<sup>n</sup><sub>4</sub>BF<sub>4</sub>;  $\Delta E_p$  were between 60 and 100 mV. The [Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]/[Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup> couple is at 0.41 V. <sup>6</sup> Irreversible couple. <sup>c</sup> Data obtained from the ruthenium(ii) complex due to instability of the  $Ru^{III}$  in solution. <sup>4</sup> Several irreversible waves observed.



Fig. 4 Cyclic voltammograms for  $[Ru{C_6H_4(PMe_2)_2-o}_2Cl_2]BF_4$  in MeCN containing 0.1 mol dm<sup>-3</sup> NBu<sup>n</sup><sub>4</sub>BF<sub>4</sub>, at potential scan rates of 0.05, 0.1 and 0.2 V s<sup>-1</sup>

Ruthenium(IV) Complexes.—The complexes trans-[Os(L-L)2- $X_{2}[ClO_{4}]$ , were prepared by concentrated nitric acid oxidation of the osmium(III) analogues,<sup>1</sup> but corresponding treatment of the ruthenium(III) complexes either with HNO3 or HNO<sub>3</sub> in CF<sub>3</sub>CO<sub>2</sub>H solution resulted in decomposition, although for a few complexes including those of  $C_6H_4$ - $(AsMe_2)_2$ -o and  $C_6H_4(PMe_2)_2$ -o fleeting dark colours were noted which disappeared in seconds. Cyclic voltammetry revealed that, for most of the complexes in either CH<sub>2</sub>Cl<sub>2</sub> or MeCN solution at room temperature, completely irreversible oxidation was observed at highly positive potentials (Table 4). The electrochemical behaviour of the ruthenium(III) complexes of  $C_6H_4(PMe_2)_2$ -o and  $C_6H_4(AsMe_2)_2$ -o was also examined at low temperatures in MeCN (-45 °C) and CF<sub>3</sub>CO<sub>2</sub>H  $(-23 \ ^{\circ}C)$ , but again only completely irreversible oxidations were observed at scan rates  $\leq 0.5$  V s<sup>-1</sup>. The irreversible  $Ru^{III} - Ru^{IV}$  oxidations show a similar dependence upon the ligands to those reported previously for the (reversible) Os<sup>III</sup>- $Os^{IV}$  couples, but occur at *ca.* 0.3 V more positive values. Ruthenium(IV) complexes of tertiary amine macrocycles have been generated electrochemically in MeCN solution<sup>12</sup> with Ru<sup>III</sup>-Ru<sup>IV</sup> potentials of ca. 1.5-1.6 V, which are only slightly less positive than the potentials of the Group 15 ligands in the present work. However, the macrocycles clearly provide some kinetic stabilisation of the Ru<sup>IV</sup>. The high potentials coupled with the very short lifetimes of the ruthenium(IV) species produced in the present work would seem to preclude their isolation.

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