Synthesis of New η^4-Hexafluorobenzene Complexes of Ruthenium and Osmium from Atoms of the Metals: Crystal Structure of $[Ru(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta^4\text{-}C_6F_6)]$†

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Condensation of ruthenium or osmium atoms with mixtures of hexafluorobenzene and a second arene at −196 °C has given the novel compounds $[M(\eta^6\text{-arene})(\eta^4\text{-}C_6F_6)]$ (M = Ru or Os; arene = $C_6H_3Me_3$-1,3,5, $C_6H_4Me_2$-1,3 or C_6H_6), these being further examples of compounds with a partially co-ordinated hexafluorobenzene ligand. The hapticity of the arene rings was determined from their proton and fluorine NMR spectra. This was confirmed for the specific case of $[Ru(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta^4\text{-}C_6F_6)]$ by an X-ray crystallographic study. The bis(hexafluorobenzene) compounds could not be prepared.

This work represents an extension of the chemistry of hexafluorobenzene from the previously described reactions of molybdenum and tungsten atoms,[1] to include the Group 8 metals ruthenium and osmium. No hexafluorobenzene complexes of these elements have previously been reported, indeed very few accounts of the reactions of ruthenium and osmium atoms are to be found in the lierature, these being limited to the preparation of the compounds $[Ru(\eta^4\text{-}C_4H_6)_2L]$ (L = CO, PF_3 or Bu^tNC),[2] $[Ru(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)]$[3] and $[Os(\eta^6\text{-}C_6H_6)(\eta^4\text{-}C_6H_6)]$[4] and C–H oxidative-addition products from the reactions between osmium atoms and alkylbenzenes or mixtures of benzene and an alkane.[4]

Results

Ruthenium atoms (prepared by electron-bombardment heating of a pellet of metallic ruthenium under high vacuum) and an excess of mesitylene–hexafluorobenzene (1 : 1) were cocondensed at −196 °C onto the liquid-nitrogen-cooled walls of a metal-atom reactor arranged for upwards evaporation of metal and ligand. After 1 h, evaporation of both metal and ligand was halted, and the reactor allowed to warm to room temperature. The excess of ligand was recovered, and the reactor walls washed down with acetone, yielding a yellow-brown solution. This was pumped to dryness and repeatedly extracted with pentane, from which an orange-brown microcrystalline solid, identified as $[Ru(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(\eta^4\text{-}C_6F_6)]$ **1** was isolated in < 5% yield based on metal evaporated. Characterisation was by mass spectrometry and ^1H and ^{19}F NMR spectroscopy (see Table 1 for comparative data). Orange-brown crystals suitable for X-ray crystallography were obtained by slowly cooling a saturated solution of **1** in pentane.

Complex **1** crystallises in the monoclinic system, with space group $P2_1/c$. The mesitylene ligand is η^6 co-ordinated and essentially planar, and the hexafluorobenzene ligand η^4 co-ordinated, with atoms C(1)–C(4) bonded to Ru as a pseudo-butadiene fragment (see Fig. 1). The non-co-ordinated part of this ligand is bent away substantially from the ruthenium atom. The average Ru–C and C–C bond lengths (see Table 2) for the mesitylene are 2.258(5) and 1.408(7) Å respectively, and are similar to the values of 2.25 and 1.41 Å reported for the η^6-hexamethylbenzene ring of $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]$.[5] The Ru–C bonds of the η^4-C_6F_6 ligand of **1** are all approximately equal in length at *ca.* 2.09 Å in contrast to the analogous bonds of the η^4-C_6Me_6 ligand of $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]$, in which the Ru–C(1) and Ru–C(4) bonds (*ca.* 2.18 Å) are 0.1 Å longer than Ru–C(2) and Ru–(3) (*ca.* 2.08 Å). Substantial distortion of the C_6F_6 ring is evident compared with the free molecule or η^6-bound analogues. The unco-ordinated C=C double bond is notably shorted to 1.297(9) Å, *cf.* 1.29(3) Å reported for the unco-ordinated C=C bond of the η^4-C_6F_6 ligand in $[Ir(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_6F_6)]$.[6] The bending of the C_6F_6 in **1** about the C(1)–C(4) axis results in a dihedral angle of 137° between the C(1)–C(4) and C(1), C(4)–C(6) planes, close to the values reported for the η^4-C_6F_6 ring of $[Ir(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_6F_6)]$ and the η^4-C_6Me_6 ring of $[Ru(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_6)]$ (135.5 and 137° respectively). The butadiene-like fragment of the η^4 ligand of **1** makes an angle of 11.5° to the plane of the mesitylene ligand [see Fig. 2(*a*)]. This compares to values of 5.2 and 12.9° respectively for the appropriate angles in the

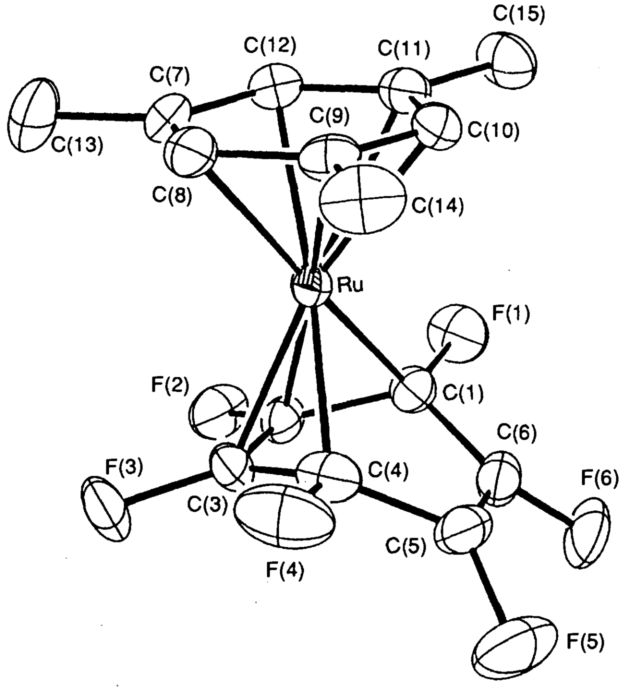

Fig. 1 Molecular structure of complex **1** showing the labelling scheme. Displacement ellipsoids are drawn to enclose 50% probability density

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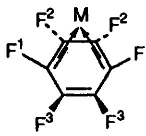
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Proton and ^{19}F chemical shift data (δ); comparison with known η^4-C$_6$F$_6$ complexes



	^{19}F			
Compound	F^1	F^2	F^3	^{1}H
[Ir(η^5-C$_5$Me$_5$)(η^4-C$_6$F$_6$)]^6	−202.9	−187.2	−141.6	—
[Ir(η^5-C$_5$H$_5$)(η^4-C$_6$F$_6$)]^6	−189.1	−181.7	−141.9	—
[Ru(η^6-C$_6$H$_3$Me$_3$-1,3,5)(η^4-C$_6$F$_6$)] **1**	−201.1	−183.6	−135.2	4.92 (s, 3 H, C$_6$*H*$_3$Me$_3$), 1.92 (s, 9 H, C$_6$H$_3$*Me*$_3$)
[Ru(η^6-C$_6$H$_4$Me$_2$-1,3)(η^4-C$_6$F$_6$)] **2**	−200.3	−183.6	−136.8	4.90 (s, 1 H), 4.89 (t, 1 H, $^2J_{\mathrm{HH}}$ = 6.2 Hz), 4.66 (d, 2 H, C$_6$*H*$_4$Me$_2$), 1.65 (s, 6 H, C$_6$H$_4$*Me*$_2$)
[Ru(η^6-C$_6$H$_6$)(η^4-C$_6$F$_6$)] **3**	−193.0	−180.4	−135.3	4.90 (s, C$_6$H$_6$)
[Os(η^6-C$_6$H$_3$Me$_3$-1,3,5)(η^4-C$_6$F$_6$)] **4**	−202.1	−183.6	−143.4	4.65 (s, 3 H, C$_6$*H*$_3$Me$_3$), 1.83 (s, 9 H, C$_6$H$_3$*Me*$_3$)
[Os(η^6-C$_6$H$_6$)(η^4-C$_6$F$_6$)] **5**	−190.2	−179.6	−141.1	4.60 (s, C$_6$H$_6$)

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Ru–C(1)	2.104(5)	C(1)–C(2)	1.433(7)
Ru–C(2)	2.089(5)	C(1)–C(6)	1.450(7)
Ru–C(3)	2.072(5)	C(2)–C(3)	1.394(8)
Ru–C(4)	2.097(5)	C(3)–C(4)	1.442(8)
Ru–C(7)	2.271(5)	C(4)–C(5)	1.497(8)
Ru–C(8)	2.253(5)	C(5)–C(6)	1.297(9)
Ru–C(9)	2.248(5)	C(7)–C(8)	1.418(8)
Ru–C(10)	2.233(5)	C(7)–C(12)	1.410(7)
Ru–C(11)	2.264(5)	C(7)–C(13)	1.491(8)
Ru–C(12)	2.278(5)	C(8)–C(9)	1.411(7)
F(1)–C(1)	1.374(6)	C(9)–C(10)	1.401(7)
F(2)–C(2)	1.348(6)	C(9)–C(14)	1.516(7)
F(3)–C(3)	1.358(6)	C(10)–C(11)	1.406(7)
F(4)–C(4)	1.370(6)	C(11)–C(12)	1.407(7)
F(5)–C(5)	1.357(7)	C(11)–C(15)	1.516(8)
F(6)–C(6)	1.350(6)		
F(1)–C(1)–C(2)	116.6(4)	F(1)–C(1)–C(6)	114.8(4)
C(2)–C(1)–C(6)	117.7(4)	F(2)–C(2)–C(1)	124.3(4)
F(2)–C(2)–C(3)	123.1(4)	C(1)–C(2)–C(3)	112.6(4)
F(3)–C(3)–C(2)	121.4(5)	F(3)–C(3)–C(4)	125.4(5)
C(2)–C(3)–C(4)	113.1(4)	F(4)–C(4)–C(3)	117.5(5)
F(4)–C(4)–C(5)	115.9(5)	C(3)–C(4)–C(5)	116.3(5)
F(5)–C(5)–C(4)	118.7(5)	F(5)–C(5)–C(6)	125.1(5)
C(4)–C(5)–C(6)	114.2(5)	F(6)–C(6)–C(1)	121.1(5)
F(6)–C(6)–C(5)	122.4(5)	C(1)–C(6)–C(5)	114.4(5)
C(8)–C(7)–C(12)	117.9(4)	C(8)–C(7)–C(13)	120.6(5)
C(12)–C(7)–C(13)	121.4(5)	C(7)–C(8)–C(9)	121.3(5)
C(8)–C(9)–C(10)	119.1(4)	C(8)–C(9)–C(14)	119.7(5)
C(10)–C(9)–C(14)	121.1(5)	C(9)–C(10)–C(11)	120.9(4)
C(10)–C(11)–C(12)	119.2(4)	C(10)–C(11)–C(15)	121.3(4)
C(12)–C(11)–C(15)	119.5(4)	C(7)–C(12)–C(11)	121.5(4)

compounds [Ru(η^6-C$_6$Me$_6$)(η^4-C$_6$Me$_6$)] and [Ir(η^5-C$_5$H$_5$)(η^4-C$_6$F$_6$)]. Interestingly, the mesitylene ligand in **1** adopts a staggered configuration with respect to the η^4 ring [see Fig. 2(*b*)]. Thus the C–C bond to one of the mesitylene methyl carbons lies nearly perpendicular to the C(2)–C(3) bond of the η^4-C$_6$F$_6$ ligand. In all previously reported structures of bis(arene)metal complexes the two rings have been eclipsed.

Cocondensation of ruthenium atoms, hexafluorobenzene and 1,3-dimethylbenzene gave the product [Ru(η^6-C$_6$H$_4$Me$_2$-1,3)-(η^4-C$_6$F$_6$)] **2** in 3% yield based on metal evaporated, after washing out the reactor with methylcyclohexane, pumping the yellow-brown solution obtained to dryness and extracting the solid residue with pentane. The structure was again confirmed by ^{1}H and ^{19}F NMR and mass spectrometry.

After cocondensing ruthenium atoms, benzene and hexafluorobenzene a thermally unstable product was obtained. However, by washing the reactor with tetrahydrofuran whilst maintaning its temperature below −40 °C, it was possible to recover the product without decomposition. The solution was evaporated to dryness at −30 °C and extracted with pentane, giving an orange solution. This too was pumped to dryness at −30 °C, yielding an orange solid. It was dissolved in [^{2}H$_8$]toluene, sealed in an NMR tube and stored in liquid nitrogen until required. From the similarity of the ^{1}H and ^{19}F NMR spectra to those previously described, the product was identified as [Ru(η^6-C$_6$H$_6$)(η^4-C$_6$F$_6$)] **3**. Thermal decomposition of the product was observed above 0 °C, yielding a buff coloured solid.

Osmium atoms were also prepared by electron bombardment of the bulk metal, and allowed to react with mesitylene–hexafluorobenzene (1 : 1). Washing the reactor out with methylcyclohexane gave a yellow-brown solution. Red-brown microcrystalline [Os(η^6-C$_6$H$_3$Me$_3$-1,3,5)(η^4-C$_6$F$_6$)] **4** was isolated in 6% yield based on metal evaporated after pumping this solution to dryness and extracting with pentane. The product was characterised by mass, ^{1}H and ^{19}F NMR spectroscopy.

Following a similar procedure, osmium atoms were also allowed to react with benzene–hexafluorobenzene (1 : 1). Washing the reactor out with methylcyclohexane and pumping to dryness gave a dark brown product in < 5% yield based on metal evaporated. This was identified, by its mass and ^{1}H and ^{19}F NMR spectra, as [Os(η^6-C$_6$H$_6$)(η^4-C$_6$F$_6$)] **5**.

No molecular products were identified after the cocondensation of ruthenium or osmium atoms and neat hexafluorobenzene.

Discussion

The η^6,η^4 formulation of these compounds has some precedent in the arene chemistry of Group 8 metals, since both [Ru(η^6-C$_6$H$_6$)(η^4-C$_6$H$_6$)],[3] which is thermally unstable decomposing above −30 °C, and thermally stable [Os(η^6-C$_6$H$_6$)(η^4-C$_6$H$_6$)][4] have previously been prepared directly from the metal atoms and benzene. Thermally stable [Ru(η^6-C$_6$Me$_6$)(η^4-C$_6$Me$_6$)] has also been reported, being prepared *via* the two-electron reduction of [Ru(η^6-C$_6$Me$_6$)$_2$]$^{2+}$.[7] Only two compounds containing η^4-hexafluorobenzene ligands have previously been reported, these being the iridium complexes [Ir(η^5-C$_5$R$_5$)-(η^4-C$_6$F$_6$)] (R = H or Me).[6]

The identification of hexafluorobenzene as the η^4-bound ligand in this work was achieved primarily by ^{1}H and ^{19}F NMR spectroscopy. In all cases the ^{1}H NMR spectra were consistent with η^6 co-ordination of the arene and rapid rotation about the metal–arene axis. Thus a sharp singlet for C$_6$H$_6$ and C$_6$H$_3$-Me$_3$-1,3,5 and a singlet, a doublet and a triplet with integration

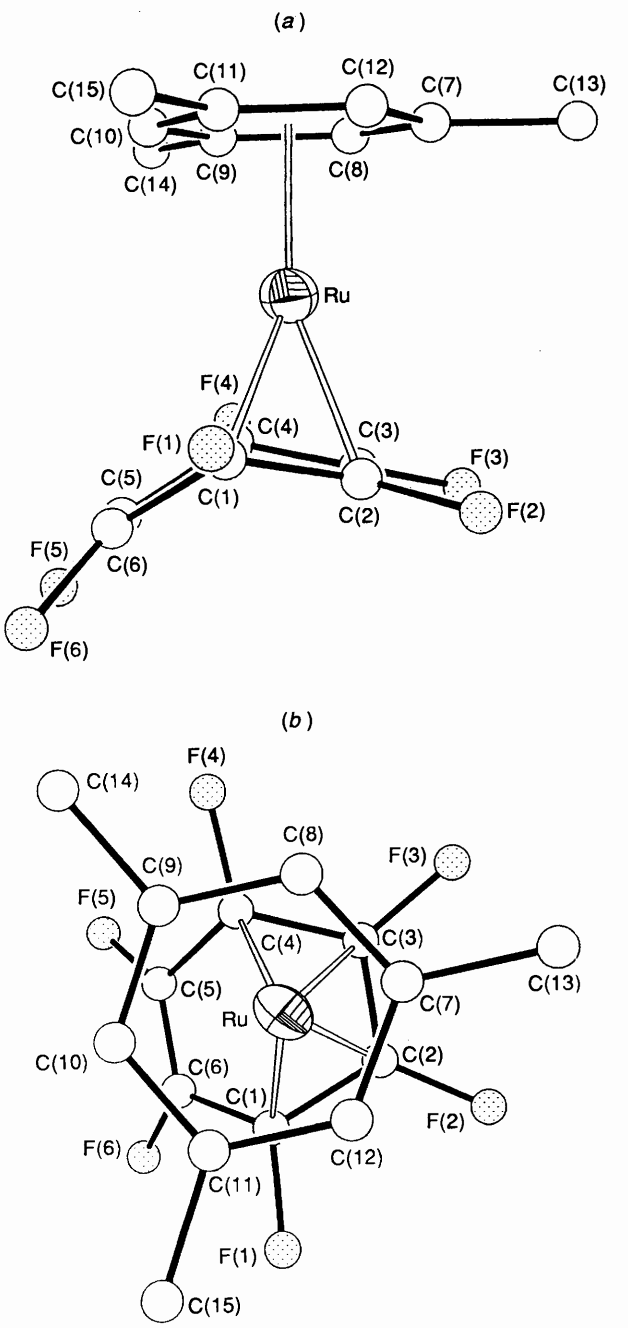


Fig. 2 Alternative views of the molecular structure of complex **1** viewed (*a*) perpendicular to and (*b*) parallel to the molecular mirror plane

1:2:1 for $C_6H_4Me_2$-1,3 were observed in the region normally associated with the aromatic protons of an arene η^6 co-ordinated to a metal(0) centre. Sharp singlets from the methyl protons of the methylated ligands were also observed. Having established the η^6 co-ordination of the more electron-rich arene in these compounds, the 18-electron rule implied that the hexafluorobenzene ligand was η^4 co-ordinated. The ^{19}F NMR spectra revealed this to be the case, showing three multiplets of equal intensity and with chemical shifts consistent with the spectral data previously reported for the η^4-co-ordinated hexafluorobenzene complexes [Ir(η^5-C_5R_5)(η^4-C_6F_6)] (R = H or Me)[6] (see Table 1). Final confirmation was obtained from the crystal structure of **1**.

As with previously reported reactions of Group 6 metal atoms with hexafluorobenzene,[1] the yields of these reactions were low, being in the range 3–6% based on the metal evaporated. The compounds described were, without exception, the only organometallic product isolated from the various reactions. No compounds containing just the more electron-rich arene ligand were observed. On the basis of an extensive study of metal atom–arene reactions,[8] we attribute this fact to destructive oxidative addition of C_6F_6 to the intermediate arene–metal half-sandwich species formed between metal atoms and the electron-rich arene. We believe that our products were formed by an initial interaction between metal atoms and hexafluorobenzene and subsequent addition of the more electron-rich arene.

All compounds exhibit a parent ion in their mass spectrum. In most cases, the primary breakdown involves loss of the partially co-ordinated C_6F_6 ring. However, the spectrum of **5** deviated from this behaviour; both OsF_4^+ and $P - C_6F_5^+$ ions, arising from fluorine abstraction, were observed together with an ion $Os(C_6F_6)^+$ which could easily be an osmium fluoride species such as $OsF(C_6F_5)^+$.

There was some evidence for the formation of η^6-hexafluorobenzene complexes [Ru(η^6-C_6F_6)(η^4-diene)] on co-condensation of Ru atoms, hexafluorobenzene and butadiene, cyclohexa-1,3-diene or cycloocta-1,5-diene, but these products were contaminated by varying amounts of polymeric impurities from which separation was impossible.

Using the metal-atom technique, we have been able to demonstrate a new range of ruthenium(0) and osmium(0) hexafluorobenzene compounds. It is hoped that this work will stimulate others to devise more conventional larger-scale routes to compounds of this type. This would allow exploitation of the organometallic chemistry of these and related species. Earlier studies and the work reported here demonstrate that there is no inherent reason why there should not be an extensive organometallic chemistry based on hexafluorobenzene compounds.

Experimental

General Procedures.—Ruthenium or osmium vapour was generated under high vacuum (0.001 Pa) using a Varian Associates magnetically focused electron gun, operating with the hearth at +4.5 kV. Metal and ligand were evaporated vertically upwards and condensed on the liquid-nitrogen-cooled walls of the stainless-steel vacuum chamber (diameter 250 mm). The arene was typically present in an least 10- to 15-fold excess in the matrix. At the end of a 1 h run the unreacted arene was pumped out as a vapour, and the product recovered by washing the reactor walls with an appropriate solvent.

Low- and high-resolution mass spectra were recording using AEI MS902 and VG AutoSpec instruments; ruthenium spectra are based on ^{96}Ru (5.52% abundance), osmium spectra on ^{192}Os (41.0% abundance). Peaks have been scaled accordingly with the most abundant ion normalised to 100%. Note that for high-resolution (mass-matching) mass spectra recorded on the AEI MS902 instrument the ^{96}Ru isotope peak was observed, whereas on theVG AutoSpec machine measurements were made on the ^{102}Ru peak. Both of the spectra of the osmium compounds were recorded on the VG AutoSpec machine, using the ^{192}Os isotope peaks.

Proton NMR spectra were recorded at 270 MHz using a JEOL GX270 spectrometer in sealed tubes in C_6D_6 or $C_6D_5CD_3$ for thermally unstable compounds. Spectra were referenced against characteristic solvent resonances. Fluorine spectra were recorded on a JEOL FX90Q spectrometer at 90 MHz, also in sealed tubes, with an external $CFCl_3$ reference.

Specific Reactions.—Ruthenium, mesitylene and hexafluorobenzene. Ruthenium (0.545 g, 5.4 mmol) was evaporated at 720 W from the magnetically focused gun for 1 h. The vapour was cocondensed at −196 °C with equimolar $C_6H_3Me_3$-1,3,5 (6.5 g) and C_6F_6 (10.0 g) (108 mmol total). The metal-to-ligand ratio was 1:20. The excess of arene was pumped away at the end of the run, the reactor being washed out with acetone (200 cm^3).

Table 3 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Ru	2606(1)	1510(1)	865(1)
F(1)	1122(3)	−201(5)	2145(2)
F(2)	3102(3)	−1768(4)	2146(2)
F(3)	4066(3)	−1813(4)	499(3)
F(4)	2840(4)	−310(5)	−914(2)
F(5)	982(3)	−2214(5)	−796(3)
F(6)	81(2)	−2196(5)	851(3)
C(1)	1595(3)	−490(7)	1362(3)
C(2)	2632(4)	−1151(6)	1409(3)
C(3)	3096(4)	−1163(6)	596(4)
C(4)	2425(5)	−532(7)	−104(3)
C(5)	1344(5)	−1236(7)	−96(4)
C(6)	932(4)	−1210(7)	669(4)
C(7)	3819(4)	3585(7)	1313(3)
C(8)	3677(4)	3734(6)	394(3)
C(9)	2697(4)	4046(6)	13(3)
C(10)	1850(4)	4223(6)	557(3)
C(11)	1970(4)	4125(6)	1472(3)
C(12)	2954(4)	3827(6)	1841(3)
C(13)	4859(5)	3239(10)	1705(5)
C(14)	2575(5)	4184(9)	−973(3)
C(15)	1059(5)	4331(8)	2066(4)

Pumping to dryness and repeated extraction with pentane (6 × 100 cm^3) gave a yellow solution, from which 95 mg (4.3%) of dark brown [Ru(η^6-$C_6H_3Me_3$-1,3,5)(η^4-C_6F_6)] **1** was isolated (Found: C, 44.35; H, 3.10. $C_{15}H_{12}F_6Ru$ requires C, 44.25; H, 2.95%). Mass spectrum: *m/z* 401.9931 (Calc. 401.9919, error 3.0); ^{96}Ru, *m/z* 402 (13, M^+), 216 (100, $M^+ - C_6F_6$), 186 (2, $C_6F_6^+$), 120 (6, $C_6H_3Me_3^+$) and 119 (14%, $C_6H_3Me_3^+$ − H).

Ruthenium, m*-xylene and hexafluorobenzene.* Ruthenium (0.820 g, 8 mmol) was evaporated at 720 W from the magnetically focused gun for 1 h. The vapour was cocondensed at −196 °C with equimolar $C_6H_4Me_2$-1,3 (5.7 g) and C_6F_6 (10.0 g) (107 mmol total). The metal-to-ligand ratio was 1:13. The excess of arene was pumped away at the end of the run, the reactor being washed out with methylcyclohexane (200 cm^3). Pumping to dryness and extraction with pentane (3 × 15 cm^3) gave a yellow solution, from which 98 mg (3%) of yellow-orange [Ru(η^6-$C_6H_4Me_2$-1,3)(η^4-C_6F_6)] **2** was isolated. Mass spectrum: *m/z* 393.974 075 (Calc. 393.973 017, error −2.7); ^{102}Ru, *m/z* 388 (35, M^+), 202 (100, $M^+ - C_6F_6$) and 105 (54%, $C_6H_4Me_2^+$ − H).

Ruthenium, benzene and hexafluorobenzene. Ruthenium (0.293 g, 2.9 mmol) was evaporated at 585 W from the magnetically focused gun for 1 h. The vapour was cocondensed at −196 °C with equimolar C_6H_6 (6.1 g) and C_6F_6 (14.5 g) (156 mmol total). The metal-to-ligand ratio was 1:54. The reactor was washed out with tetrahydrofuran (200 cm^3) whilst at −40 °C. Pumping to dryness and extraction with pentane gave an orange solution, from which an orange solid was obtained. The total yield was 23 mg (2.2%) of thermally unstable [Ru(η^6-C_6H_6)(η^4-C_6F_6)] **3**. This decomposed overnight at room temperature to a buff coloured residue.

Osmium, mesitylene and hexafluorobenzene. Osmium (1.282 g, 5.0 mmol) was evaporated at 900 W from the magnetically focused gun for 1 h. The vapour was cocondensed at −196 °C with equimolar $C_6H_3Me_3$-1,3,5 (6.5 g) and C_6F_6 (10.0 g) (108 mmol total). The metal-to-ligand ratio was 1:20. The excess of arene was pumped away at the end of the run, the reactor being washed out with methylcyclohexane (180 cm^3). Pumping to dryness and extraction with pentane (4 × 20 cm^3) gave a yellow-brown solution, from which 152 mg (5.9%) of red-brown [Os(η^6-$C_6H_3Me_3$-1,3,5)(η^4-C_6F_6)] **4** was isolated. Mass spectrum: *m/z* 498.044 579 (Calc. 498.045 807, error 2.5); ^{192}Os, *m/z* 498 (7, M^+), 331 (11, $M^+ - C_6F_6$), 120 (54, $C_6H_3Me_3^+$) and 119 (100%, $C_6H_3Me_3^+$ − H).

Osmium, benzene and hexafluorobenzene. Osmium (1.282 g, 6.7 mmol) was evaporated at 900 W from the magnetically focused gun for 1 h. The vapour was cocondensed at −196 °C with equimolar C_6H_6 (9.5 g) and C_6F_6 (22.7 g) (244 mmol total). The metal-to-ligand ratio was 1:36. The excess of arene was pumped away at the end of the run, the reactor being washed out with methylcyclohexane (180 cm^3). Pumping to dryness gave 104 mg (3.4%) of dark brown [Os(η^6-C_6H_6)(η^4-C_6F_6)] **5**. Mass spectrum: *m/z* 455.998 100 (Calc. 455.998 857, error 1.7); ^{192}Os, *m/z* 456 (100, M^+), 378 (13, $M - C_6H_6$), 289 (76, $M^+ - C_6F_5$), 268 (73, OsF_4^+), 78 (24, $C_6H_6^+$) and 77 (14%, $C_6H_5^+$).

Crystal Structure Analysis of Complex **1**.—*Crystal data.* $C_{15}H_{12}F_6Ru$, $M = 407.3$, monoclinic, space group $P2_1/c$ (no. 14), $a = 13.029(8)$, $b = 7.201(5)$, $c = 15.289(11)$ Å, $\beta = 91.18(5)°$, $U = 1434.2(17)$ Å^3, $Z = 4$, $D_c = 1.89$ g cm^{-3}, $\bar{\lambda} = 0.710\,73$ Å, $\mu = 1.15$ mm^{-1}, $F(000) = 800$, $T = 295$ K.

Diffraction measurements were made with a Siemens four-circle P3m diffractometer using graphite-monochromated Mo-Kα X-radiation on a single crystal (approximate dimensions 0.6 × 0.3 × 0.3 mm) mounted on a glass fibre in air. Cell dimensions were determined from the setting angle values of 19 centred reflections. A total of 3000 diffracted intensities (including checks) were measured in a unique hemisphere of reciprocal space for $3.0 < 2\theta < 50.0°$ by Wyckoff ω scans. Three check reflections remeasured after every 75 ordinary data showed no decay and *ca.* 3% variation over the period of data collection. Of the non-check intensity data collected, 2526 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences; of these 2074 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 630 azimuthal scan data; maximum and minimum transmission coefficients were 0.843 and 0.655 respectively. Lorentz and polarisation corrections were applied. The structure was solved by heavy-atom (Patterson and Fourier difference) methods, and refined by full-matrix least squares against *F*. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were constrained to idealised geometries (C–H 0.96 Å) and assigned a common refined isotropic displacement parameter. Refinement of the 200 least-squares variables converged smoothly to residual indices $R = 0.036$, $R' = 0.044$, $S = 1.37$ where $R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, $\Delta = F_o - F_c$ and N_o, N_v are the numbers of observations and variables. Weights, *w*, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$ where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0005$ was chosen to minimise the variation in *S* as a function of F_o. Final difference electron-density maps showed no features outside the range +0.9 to −0.75 e Å^{-3}, the largest features being within 1 Å of the metal atoms. Table 3 reports the atomic positional parameters. All calculations were made with programs of the SHELXTL PLUS[9] system as implemented on a Siemens R3m/V structure-determination system. Complex neutral-atom scattering factors were taken from ref. 10.

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

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