Rhodium– and Iridium–Perfluorobenzenethiolato Complexes, $[(C_5Me_5)Ir(SC_6F_5)_2]$, $[(C_5Me_5)Ir(SC_6F_4H\text{-}p)_2]$ and $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]$: Syntheses, Crystal Structures and Solution Behaviour*

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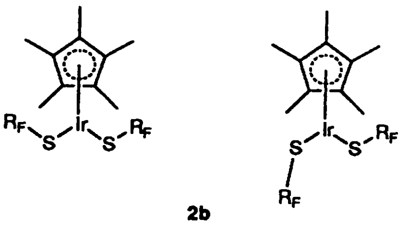
Reaction of $[(C_5Me_5)_2M_2(\mu\text{-}Cl)_2Cl_2]$ (M = Rh **1a** or Ir **1b**) with $Pb(SR_F)_2$ gave $[(C_5Me_5)Ir(SR_F)_2]$ **2b** ($R_F = C_6F_5$ or $C_6F_4H\text{-}p$) containing five-co-ordinate Ir^{III}, or ionic $[(C_5Me_5)_2Rh_2(\mu\text{-}SR_F)_3][(C_5Me_5)Rh(SR_F)_3]$ **3a** ($R_F = C_6F_5$ or $C_6F_4H\text{-}p$) containing six-co-ordinate Rh^{III} in both the anion and cation. Complexes **2b** and **3a** ($R_F = C_6F_5$) were characterised by single-crystal X-ray determinations; the structures of **2b** ($R_F = C_6F_5$ or $C_6F_4H\text{-}p$) are very similar, but in the former the SC_6F_5 ligands are related by a plane of symmetry. The NMR spectra of **2b** in solution are consistent with the mirror-symmetric solid-state structure. However, those of the rhodium complexes **3a**, while consistent with the ionic solid-state structures in methanol, show quite different features in less-polar solvents, indicating that they participate in the equilibrium $[(C_5Me_5)_2Rh_2(\mu\text{-}SR_F)_3][(C_5Me_5)Rh(SR_F)_3] \rightleftharpoons 3[(C_5Me_5)Rh(SR_F)_2]$ where $[(C_5Me_5)Rh(SR_F)_2]$ has a similar structure to that of **2b** ($R_F = C_6F_5$). Complexes **1a** and **1b** reacted with $Pb(SC_6H_4F\text{-}p)_2$ to give salts formulated as the triply bridged $[(C_5Me_5)_2M_2(\mu\text{-}SC_6H_4F\text{-}p)_3]Cl\cdot H_2O$ (M = Rh **4a** or Ir **4b**), while **1b** reacted with $Ag(SCF_3)$ to afford the diiridium complexes $[(C_5Me_5)_2Ir_2(\mu\text{-}SCF_3)_2(SCF_3)_2]$ **5b** and $[(C_5Me_5)_2Ir_2(\mu\text{-}SCF_3)_3]Cl\cdot H_2O$ **6b**.

The structural chemistry and the reactions of transition-metal complexes with sulfur ligands, especially thiolates,[1] continue to attract much attention. In continuation of our interest in the chemistry of half-sandwich complexes of rhodium and iridium,[2,3] particularly in combination with thiolates,[4,5] we have developed the further chemistry of pentamethylcyclopentadienyl-rhodium and -iridium perfluorothiolate complexes. These pseudo-halides of pentamethylcyclopentadienyl-rhodium and -iridium can also increase our understanding of the basic chemistry of the halides $[\{(\eta^5\text{-}C_5Me_5)MX_2\}_2]$, where one major difficulty is the absence of a readily available spectroscopic probe. The ^{19}F NMR spectra of the perfluorothiolates, by contrast, provide a very useful probe for examining such behaviour.

We describe details of the preparation, properties and crystal structures of $[(C_5Me_5)Ir(SC_6F_4H\text{-}p)_2]$, $[(C_5Me_5)Ir(SC_6F_5)_2]$ and $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]$ and the evidence for novel equilibria in solution, as well as for some related complexes with the ligands $SC_6H_4F\text{-}p$ and SCF_3. A part of this work has been the subject of a preliminary communication.[6]

Results

Syntheses of $[\{(C_5Me_5)M(SR_F)_2\}_n]$.—The reaction of 2 equivalents of the bis(perfluorobenzenethiolato)lead salts with the chloro-complexes **1a** (M = Rh) or **1b** (M = Ir) in chloroform solution afforded complexes with the empirical formula '$(C_5Me_5)M(SR_F)_2$' and lead chloride, which precipitated, according to equation (1). The desired complex was usually



2b

$R_F = C_6F_5$ $C_6F_4H\text{-}p$

$$\tfrac{1}{2}[\{(C_5Me_5)MCl_2\}_2] + Pb(SR_F)_2 \longrightarrow [(C_5Me_5)M(SR_F)_2] + PbCl_2 \quad (1)$$

(**1** under the first reactant; **2** under the product)

purified by chromatography and crystallisation; yields of 85–90% of the green (iridium) or brown (rhodium) complexes were generally obtained. The structures adopted by the various $[\{(C_5Me_5)M(SR_F)_2\}_n]$ complexes depend on (*i*) the metal, (*ii*) the medium, and (*iii*) the precise nature of R_F. Thus they were characterised with the aid of three crystal structure determinations and by NMR spectroscopy in solution.

Crystal Structures of $[(C_5Me_5)Ir(SR_F)_2]$ **2b** ($R_F = C_6F_5$ *or* $C_6F_4H\text{-}p$).—The two structures are very similar, but differ in the relative orientations adopted by the SR_F ligands. Both complexes are mononuclear with an (effectively) five-co-ordinate iridium(III) centre, which is η^5-bonded to its C_5Me_5 ring (average Ir–C 2.157 Å for $R_F = C_6F_5$ and 2.187 Å for $C_6F_4H\text{-}p$) on the one side and *S*-bonded to two SR_F ligands on the other [Ir–S 2.292(4) Å for $R_F = C_6F_5$ and 2.323(4) and 2.274(4) Å for $C_6F_4H\text{-}p$]. The sulfur–perfluorophenyl bond lengths are also very similar [S–C 1.764(13) Å for $R_F = C_6F_5$

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

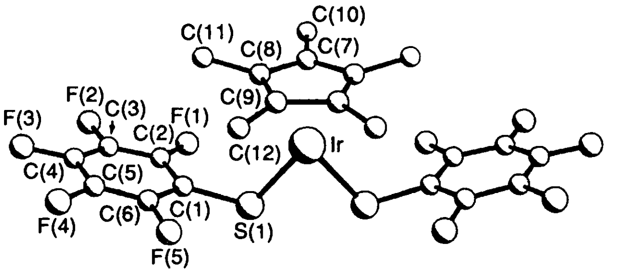


Fig. 1 View of the crystal structure of $[(C_5Me_5)Ir(SC_6F_5)_2]$ ($R_F = C_6F_5$)

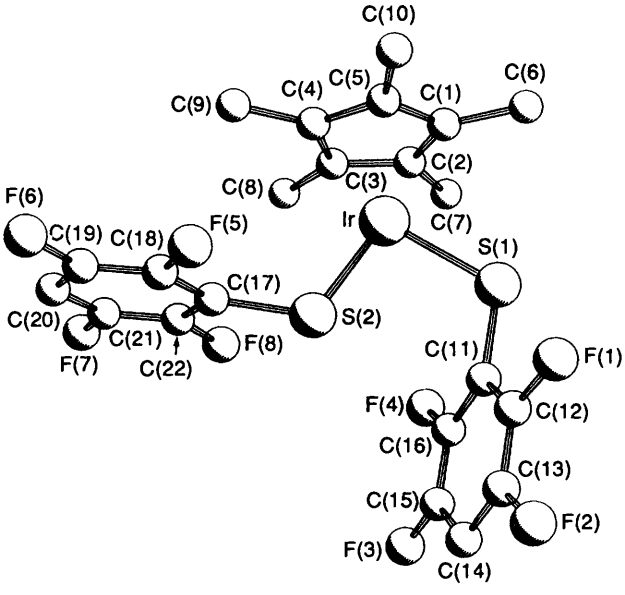
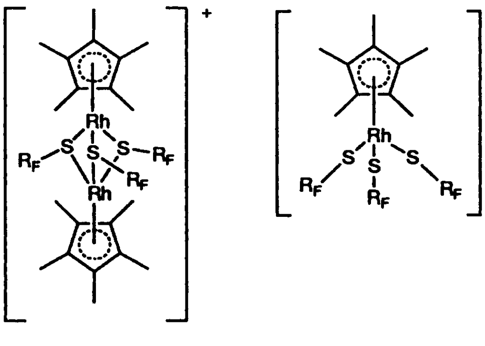


Fig. 2 View of the crystal structure of $[(C_5Me_5)Ir(SC_6F_4H\text{-}p)_2]$ ($R_F = C_6F_4H\text{-}p$)

and 1.773(13) and 1.769(15) Å for C_6F_4H-*p*], as are the Ir–S–C angles [111.1(4), and 112.7(5), 112.9(4)° respectively]. The major difference between the two structures is that the SC_6F_5 complex has a plane of symmetry through the iridium, C(7), C(10), and the midpoint of C(9)–C(9′) of the ring; this symmetry is absent in **2b** ($R_F = C_6F_4H$-*p*). The differences can be seen in the angle S–Ir–S, 78.9(2)° for $R_F = C_6F_5$, but which opens out to 90.8(1)° for C_6F_4H, and graphically in the figures: thus the perfluorophenylthio rings have a symmetrical 'gull-wing' appearance in **2b** ($R_F = C_6F_5$) (Fig. 1); one has the same conformation in **2b** ($R_F = C_6F_4H$-*p*), while the other points down, away from the metal centre (Fig. 2). There is also a difference in the dihedral angles between the planes containing Ir, S, and C for each; it is 9.3° in **2b** ($R_F = C_6F_4H$-*p*) and 2.8° in **2b** ($R_F = C_6F_5$). We suggest that crystal packing forces are responsible for these differences.

The crystal structure of $[(C_5Me_5)Ir(SH)_2(PMe_3)]$[7] shows similar Ir–S bond lengths [average 2.375(2) Å] and a similar S–Ir–S bond angle, 88.74(7)°, to those found here.

Crystal Structure of $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]$ **3a** ($R_F = C_6F_5$).—By contrast to the very simple structures adopted by the iridium complexes, the rhodium analogue showed an ionic structure (Fig. 3), made up of a dinuclear cation with three bridging pentafluorobenzenethiolates, and a mononuclear anion with three terminal pentafluorobenzenethiolates. In both ions the SR_F ligands adopt a very approximate C_3 symmetry with respect to the rhodiums. The quality of the X-ray data was more limited than for the iridium complexes and detailed comparisons are thus inappropriate.



3a $R_F = C_6F_5$ or C_6F_4H-*p*

However, The Rh(3)–S distances in the anion [2.410(15), 2.407(17) and 2.425(13) Å] are similar, and quite significantly longer than the Ir–S bonds in **2b** ($R_F = C_6F_5$). The six bridging Rh–S bonds in the dinuclear cation [2.402(13), 2.486(12), 2.425(14), 2.410(15), 2.407(17) and 2.425(13) Å] are of similar length to those in the anion. Experimentally it has been found that Rh–X and Ir–X bond lengths are generally very similar in isostructural pentamethylcyclopentadienyl complexes.[2] The increase in length over the iridium complexes is therefore probably a result of *three* SR_F ligands co-ordinating to the metal centres in the rhodium complex, while only two are bound to the iridiums; the extra steric constraints caused by the extra ligand are then eased by a longer M–S bond. The estimated standard deviations (e.s.d.s) on the S–C bonds are too large to allow meaningful comparisons, but again they tend to be longer than in **2b** ($R_F = C_6F_5$).

As might be anticipated, the S–Rh–S angles in the mononuclear anion are all much larger [91.8(5), 93.8(5) and 94.7(5)°] than those in the bridging SC_6F_5 ligands [76.7(4), 76.8(4), 77.6(4), 78.1(4), 78.4(4) and 79.4(4)°]. The Rh–S–Rh angles in the cation are quite acute [85.7(4), 87.5(4), 87.7(4)°], but the angles Rh–S–C_6F_5 cannot meaningfully be differentiated in the two situations.

A closely related structure, containing the cation $[(C_5Me_5)_2Rh_2(\mu\text{-}SMe)_3]^+$, is known,[8] with average Rh–S bond lengths of 2.372(9) Å and angles S–Rh–S of 78.6(3) and Rh–S–Rh of 85.8(3)°. The bond angles are virtually identical to those in the cation of **3a** ($R_F = C_6F_5$), and while the Rh–S bonds lengths in the μ-SMe complex are slightly shorter, this is only at the edge of significance. However the angle Rh–S–Rh in $[(C_5Me_5)_2Rh_2(\mu\text{-}SMe)_3]^+$ is again significantly smaller than in $[(C_5Me_5)_2Rh_2(\mu\text{-}SMe)_2Cl_2]$[8] where only two ligands span the two metals.

It may also be noted that while the other dimensions are very similar to those in the analogous dirhodium complexes, the angles Ru–S–Ru in the Ru^{III}_2 cation $[(C_5Me_5)_2Ru_2(\mu\text{-}SR)_3]^+Cl^-$ [R = aryl, average 68.2(1)°][9] and in the neutral $Ru^{II}Ru^{III}$ compound $[(C_5Me_5)_2Ru_2(\mu\text{-}SPr^i)_3]$ [average 76.8(1)°][10] are both very much more acute. This may be indicative of the presence of some M–M bonding in these two complexes holding the metals together more firmly. A similar situation appears to apply in the diiridium complexes $[(cod)_2Ir_2(\mu\text{-}SPh)_2]$ and $[(cod)_2Ir_2(\mu\text{-}SPh)Cl_2]$ (cod = cycloocta-1,5-diene),[11] where in the first, Ir^I_2, the angle Ir–S–Ir is 85.40(8)°, while in the second, Ir^IIr^{II}, the angle is only 72.94(4)°.

Solution Behaviour of $[\{C_5Me_5)Ir(SC_6F_5)_2]$, $[(C_5Me_5)Ir(SC_6F_4H\text{-}p)_2]$ *and* $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]$.—The ^{19}F NMR spectrum of the iridium complex **2b** ($R_F = C_6F_5$) in $(CD_3)_2CO$ solution shows just three signals at δ −132.6 (m, *o*-F), −159.4 (t, *p*-F) and −164.0 (m, *m*-F), corresponding to a single set of *o*-, *p*- and *m*-F. The spectrum is the same in toluene, acetone and nitromethane

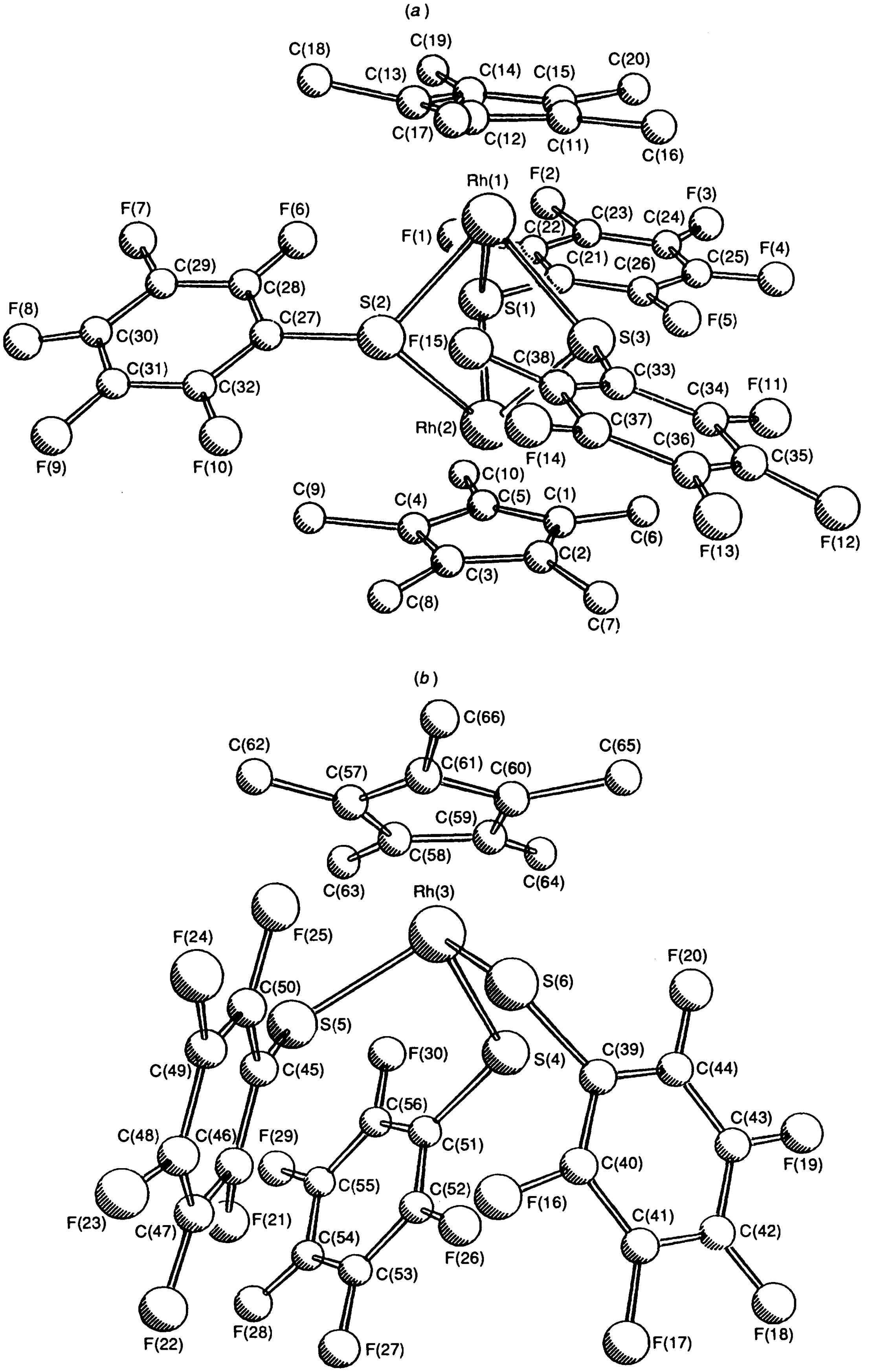


Fig. 3 View of the crystal structure of $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][C_5Me_5)Rh(SC_6F_5)_3]$ **3a** ($R_F = C_6F_5$) (*a*) the cation, and (*b*) the anion

solution, and is fully consistent with the solid-state structure (Fig. 1); in particular the observation of a single set of signals agrees with the symmetrical relationship of the two pentafluorophenyls. The complex is also essentially non-conducting in acetone solution (15 ohm^{-1} cm^2 mol^{-1}), in agreement with a non-ionic structure.

The deep green complex [$(C_5Me_5)Ir(SC_6F_4H$-*p*$)_2$] **2b** ($R_F = C_6F_4H$-*p*) is also essentially non-conducting in acetone solutions (12 ohm^{-1} cm^2 mol^{-1}), and the ^{19}F NMR spectra show just two bands, at δ −131.4 and −140.0 (in toluene, acetone or nitromethane), corresponding to a single set of *o*- and *m*-F. This spectrum indicates a covalent structure in which both tetrafluorophenyls are equivalent, in other words one such as **2b** ($R_F = C_6F_5$). This suggests that the less symmetrical structure shown by the X-ray determination of **2b** ($R_F = C_6F_4H$-*p*) must be easily converted into the symmetrical gull-wing structure of **2b** ($R_F = C_6F_5$), presumably by a low-energy rotation around the Ir–S(1) bond. Attempts to observe this by low-temperature ^{19}F NMR spectroscopy were only partially successful; some broadening became detectable only at −80 °C (the effective limit in toluene solution).

The NMR behaviour of the deep green ionic complex, [$(C_6Me_5)_2Rh_2(\mu$-$SC_6F_5)_3$][$(C_5Me_5)Rh(SC_6F_5)_3$] **3a** ($R_F = C_6F_5$) is much more complex and depends strongly on the solvent. In a polar solvent such as CD_3OD the ^{19}F NMR spectrum is consistent with the crystal structure, and shows resonances for the *o*-, *m*- and *p*-F as pairs of multiplets of approximately equal intensity at δ −128.0, −132.75 (*o*-F), −161.6, −166.0 (*m*-F) and −153.3, −161.6 (*p*-F), indicating two sets of C_6F_5. The spectrum in toluene, in sharp contrast, shows just three resonances at δ −134.2 (*o*-F), −167.0 (*m*-F) and −161.8 (*p*-F), and is almost identical to that of the iridium complex **2b** ($R_F = C_6F_5$) which has the 'covalent' five-co-ordinate structure. The ^{19}F NMR spectra of **3a** ($R_F = C_6F_5$) in solvents of intermediate polarity such as acetone show resonances which are consistent with mixtures of both the 'covalent' and the 'ionic' forms, in a ratio 60:40.

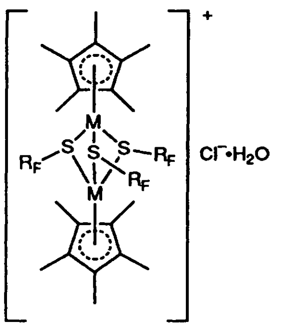
A solution of complex **3a** ($R_F = C_6F_5$) shows appreciable conductivity (90 ohm^{-1} cm^2 mol^{-1} at infinite dilution). This value is lower than that normally found for 1:1 electrolytes (100–140 ohm^{-1} cm^2 mol^{-1}),[12] probably because of the low mobility associated with the large ions. Similar values were found for the other ionic complexes (see below).

We therefore conclude that while the rhodium complex **3a** ($R_F = C_6F_5$) adopts the ionic form [$(C_5Me_5)_2Rh_2(\mu$-$SC_6F_5)_3$][$(C_5Me_5)Rh(SC_6F_5)_3$] both in the solid state and in very polar solvents, it rearranges to a 'covalent' monomeric form, akin to that shown by [$(C_5Me_5)Ir(SC_6F_5)_2$] **2b** ($R_F = C_6F_5$), when it is dissolved in a non-polar solvent such as toluene. In solvents of intermediate polarity both forms co-exist, pointing to a slow equilibrium (2).

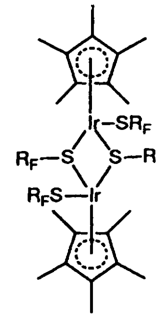
$$[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3] \rightleftharpoons 3[(C_5Me_5)Rh(SC_6F_5)_2] \quad (2)$$

The rhodium complex **3a** ($R_F = C_6F_4H$-*p*), prepared from **1a** and $Pb(SC_6F_4H$-*p*$)_2$, shows significant conductivity (91 ohm^{-1} cm^2 mol^{-1}, close to that expected for a 1:1 electrolyte), and exactly the same NMR behaviour as that of **3a** ($R_F = C_6F_5$). The ^{19}F NMR spectrum in toluene shows just two signals [δ −130.0 (*o*-F) and −140.1 (*m*-F)], almost identical to that of the iridium complex **2b** ($R_F = C_6F_4H$-*p*), to which the 'covalent' structure has been assigned. In solvents of intermediate polarity such as acetone, resonances for **3a** ($R_F = C_6F_4H$-*p*) are observed which are characteristic of the co-existence of both the 'covalent' and the 'ionic' forms [multiplets at δ −128.5, −133.0 (*o*-F) and −138.5, −142.0 (*m*-F)]. The spectrum in methanol shows only the last four multiplets.

Complexes of Other Fluorothiolate Ligands.—Reaction of complexes **1a** and **1b** with 2 equivalents per metal of [$Pb(SC_6H_4F$-*p*$)_2$] afforded a complex which we have identified by analysis and spectroscopically as the triply bridged ionic [$(C_5Me_5)_2M_2(\mu$-SC_6H_4F-*p*$)_3$]$Cl\cdot H_2O$ (M = Rh **4a** or Ir **4b**). The same complexes were obtained when a large excess of [$Pb(SC_6H_4F$-*p*$)_2$] was used; the last remaining chloride could not be replaced by SC_6H_4F-*p*. Both complexes show high conductivity (98 for **4a**, 107 ohm^{-1} cm^2 mol^{-1} for **4b**), in agreement with the proposed 1:1 ionic structure. Only one signal was observed in the ^{19}F NMR spectra [**4a**, δ −115.85 (tt), in $CDCl_3$; **4b**, δ −114.5 (m) in $(CD_3)_2CO$], which did not change in solvents of different polarity.



	M	R_F
4a	Rh	C_6H_4F–*p*
4b	Ir	C_6H_4F–*p*
6b	Ir	CF_3



5b $R_F = CF_3$

Treatment of the iridium chloride complex **1b** with 4 equivalents of $Ag(SCF_3)$ gave a mixture of two complexes, identified as [$(C_5Me_5)_2Ir_2(\mu$-$SCF_3)_2(SCF_3)_2$] **5b** (4% yield) and [$(C_5Me_5)_2Ir_2(\mu$-$SCF_3)_3$]$Cl\cdot H_2O$ **6b** (32% yield). With 8 equivalents of $Ag(SCF_3)$ the same products [but with somewhat more **5b** (6%)] were obtained. Thus replacement of the last chloride by $Ag(SCF_3)$ is also difficult.

The ^{19}F NMR spectrum of complex **5b** showed two singlets (δ −36.0 and −38.7), assigned to the bridging and terminal SCF_3 groups respectively, while the ^1H NMR spectrum showed one singlet (δ 1.8), indicating only one type of C_5Me_5. The conductivity determination (10 ohm^{-1} cm^2 mol^{-1}) was consistent with a non-electrolyte. By contrast, compound **6b** had a conductivity (92 ohm^{-1} cm^2 mol^{-1}) very near to the value normally associated with a 1:1 electrolyte. This complex also shows just one singlet (δ −33.6, due to the bridging SCF_3 group) in the ^{19}F NMR spectrum, and also one signal (δ 1.8) in the ^1H NMR. These data, taken together with the micro-analyses, indicated the structures proposed.

Discussion

We have shown in this work that reaction of [$(C_5Me_5)_2M_2$-$(\mu$-$Cl)_2Cl_2$] (M = Rh **1a** or Ir **1b**) with $Pb(SR_F)_2$ gives [$(C_5Me_5)Ir(SR_F)_2$] **2b** ($R_F = C_6F_5$ or C_6F_4H-*p*) and [$(C_5Me_5)_2Rh_2(\mu$-$SR_F)_3$][$(C_5Me_5)Rh(SR_F)_3$] **3a** ($R_F = C_6F_5$ or C_6F_4-H-*p*). The crystal structures of **2b** ($R_F = C_6F_5$ or C_6F_4H-*p*) are very similar; both complexes contain five-co-ordinate Ir^{III}, but in the former the SC_6F_5 ligands are related by a plane of symmetry, which is absent in the latter. However, their NMR spectra in solution are both consistent with the mirror-symmetric solid-state structure. This implies that either the ^{19}F NMR chemical shifts are accidentally coincident for the two SC_6F_4H-*p* ligands in **2b** ($R_F = C_6F_4H$-*p*) or that this complex undergoes a low-energy dynamic process which makes them equivalent. Low-temperature NMR spectroscopy could not resolve the question, but a broadening of the resonances was observed at the lowest accessible temperature. This is consistent with a dynamic process.

The analogous rhodium complexes showed an ionic structure in the solid state, **3a** ($R_F = C_6F_5$ or C_6F_4H-*p*) containing six-co-ordinate Rh^{III} in both the anion and cation. The solution NMR spectra were consistent with this formulation in polar solvents such as methanol, but were very similar to those of the iridium complexes **2b** in toluene. The spectra in solvents of intermediate polarity (such as acetone) showed the presence of both the ionic and the covalent forms, indicating that they participate in an equilibrium of type (2) where $[(C_5Me_5)Rh(SR_F)_2]$ has a similar structure to that of **2b** ($R_F = C_6F_5$).

We conclude that, within this series of pentamethylcyclopentadienyl complexes of perfluorobenzenethiolate ligands, those of iridium are rather inert (apart from some motions involving rotation about Ir–S bonds or inversion at S), and appear always to prefer the covalent five-co-ordinate to the ionic six-co-ordinate geometry. By contrast, the related complexes of rhodium show substantial lability in solution, and the precise state of the molecule depends very much on the solvent. Qualitative observations on the halides $[(C_5Me_5)_2M_2(\mu\text{-}X)_2X_2]$, for example, show that the rhodium chloro-complex **1a** forms the cationic $[(C_5Me_5)_2M_2(\mu\text{-}Cl)_3]^+$ more easily than the analogous iridium complex,[13] indicating that this may be a general phenomenon.

While the precise form of the equilibrium (2) for the rhodium perfluorobenzenethiolate complexes appears unprecedented, perfluorobenzenethiolates of other metals have been shown to participate in dynamic behaviour. Thus, for example, the complex $[(C_5H_5)W(CO)(SC_6F_5)_3]$ has two isomeric forms at low temperatures which interconvert by rotation about the W–S bonds, or inversion at S.[14]

We also have evidence indicating the complexity of the relationships between structure, metal and ligand: thus complexes which are obtained from the reaction of **1** with other fluorothiolates show quite different structures. For example, the triply bridged ionic species $[(C_5Me_5)_2M_2(\mu\text{-}SR_F)_3]^+Cl^-$ are the only products of the reaction of **1a** and **1b** with $Pb(SC_6H_4F\text{-}p)_2$, and the main product of the reaction of **1b**, even with an excess of $Ag(SCF_3)$. This suggests that neither SCF_3^- nor $SC_6H_4F\text{-}p^-$ is as good a nucleophile as $SC_6F_4H\text{-}p^-$ or $SC_6F_5^-$ towards these pentamethylcyclopentadienyl-rhodium and -iridium complexes.

Experimental

All operations were carried out under dry nitrogen using standard Schlenk techniques. Solvents were purified and then distilled under nitrogen prior to use. Microanalyses were performed by the University of Sheffield Microanalysis Service and by Galbraith Laboratories, USA. Infrared spectra were recorded on a Perkin Elmer 1330 spectrometer with Data Station 1300 over the 4000–200 cm^{-1} range as CsI pellets, NMR spectra (in $CDCl_3$, at 25 °C, unless otherwise specified) on Varian VXR-300S and Bruker AM-250 (^1H), Varian VXR-300S and Bruker WP-80SY (^{19}F) and Varian VXR-300S (^{13}C) spectrometers. Conductivities were measured with a YSI-32 digital conductimeter, in acetone in the concentration range 0.1–10 mmol dm^{-3} and extrapolated to infinite dilution. The compounds $[(C_5Me_5)_2Rh_2Cl_4]$[15] and $Ag(SCF_3)$[16] were prepared by literature methods. The salts $Pb(SR_F)_2$ ($R_F = C_6F_5$ or C_6F_4H-*p*) and $Pb(SC_6H_4F\text{-}p)_2$ were prepared from $Pb(O_2CMe)_2$ and C_6F_5SH, *p*-HC_6F_4SH and *p*-FC_6H_4SH purchased from Aldrich.

$[(C_5Me_5)Ir(SC_6F_5)_2]$ **2b** ($R_F = C_6F_5$).—The salt $Pb(SC_6F_5)_2$ (1.52 g, 2.51 mmol) was added to a solution of complex $[(C_6Me_5)_2Ir_2(\mu\text{-}Cl)_2Cl_2]$ **1b** (1.0 g, 1.255 mmol) dissolved in chloroform (30 cm^3) and stirred (25 °C, 24 h) giving a cloudy deep green solution. The reaction mixture was filtered and evaporated *in vacuo*, giving a deep green residue which was chromatographed on silica gel. Elution with chloroform gave a deep green solid, **2b** ($R_F = C_6F_5$) (1.63 g, 90%) (Found: C, 36.1; H, 2.1; S, 8.8. $C_{22}H_{15}F_{10}IrS_2$ requires C, 36.4; H, 2.0; S, 8.8%). Conductivity 15 ohm^{-1} cm^2 mol^{-1}. NMR: ^1H, δ 1.50 (s, C_5Me_5); $^{13}C\text{-}\{^1H\}$, δ 8.6 (s, C_5Me_5), 91.4 (s, C_5Me_5), 113.8 (br, CS), 137.35 [d, *J*(F–C) 252, *m*-C], 139.4 (d, *J* 253, *p*-C) and 147.5 (d, *J* 241, *o*-C); ^{19}F ($C_6D_5CD_3$), δ −131.92 [d, *J*(F–F) 23, *o*-F], − 158.09 [t, *J*(F–F) 21 Hz, *p*-F] and −164.0 (m, *m*-F).

$[(C_5Me_5)Ir(SC_6F_4H\text{-}p)_2]$ **2b** ($R_F = C_6F_4H$-*p*).—This complex (0.88 g, 85%) was prepared analogously from **1b** (0.60 g, 0.97 mmol) (Found: C, 36.2; H, 2.3; S, 9.2. $C_{22}H_{17}F_8IrS_2$ requires C, 38.3; H, 2.5; S, 9.3%). Conductivity 12 ohm^{-1} cm^2 mol^{-1}. NMR: ^1H, δ 1.53 (s, C_5Me_5) and 6.82 [tt, 2 H, *J*($H\text{–}F_m$) 10.5, *J*($H\text{–}F_p$) 7.5 Hz, SC_6F_4H-*p*]; ^{19}F, δ −131.4 (m, *o*-F) and −140.0 (m, *m*-F).

$[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]$ **3a** ($R_F = C_6F_5$).—This complex (1.85 g, 90%) was obtained analogously, as a deep brown solid from **1a** (1.0 g, 1.62 mmol) (Found: C, 42.1; H, 2.5; S, 10.0. $C_{66}H_{45}F_{30}Rh_3S_6$ requires C, 41.5; H, 2.4; S, 10.0%). Conductivity 90 ohm^{-1} cm^2 mol^{-1}. NMR: ^1H, δ 1.57 (s, C_5Me_5; δ 1.37 in $C_6D_5CD_3$); $^{13}C\text{-}\{^1H\}$, δ 8.65 ($C_5\mathit{Me}_5$), 98.1 [d, *J*(Rh–C) 7, C_5Me_5], 99.0 [d, *J*(Rh–C) 7, C_5Me_5], 114.6 (m, CS, SC_6F_5), 137.4 [d, *J*(F–C) 248, *m*-C], 138.5 [d, *J*(F–C) 248, *p*-Cl] and 147.9 [d, *J*(F–C) 237 Hz, *o*-C]; ^{19}F [$(CD_3)_2CO$], δ −128.0 (m, *o*-F), −131.5 (m, *o*-F), −132.4 (m, *o*-F), −153.7 (t, *p*-F), −160.8 (t, *p*-F), −161.7 (m, *m*-F), −165.5 (m, *m*-F), −169.6 (m, *m*-F), −169.6 (m, *p*-F); ($C_6D_5CD_3$), δ −134.2 (m, *o*-F), −161.8 (t, *p*-F) and −167.0 (m, *m*-F).

$[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_4H\text{-}p)_3][(C_5Me_5)Rh(SC_6F_4H\text{-}p)_3]$ **3a** ($R_F = C_6F_4H$-*p*).—This complex (1.72 g, 89%) was obtained analogously, as a deep brown solid from **1a** (1.0 g, 1.62 mmol) (Found: C, 44.4; H, 2.9; S, 10.5. $C_{66}H_{51}F_{24}Rh_3S_6$ requires C, 44.0; H, 2.85; S, 10.6%). Conductivity 91 ohm^{-1} cm^2 mol^{-1}. NMR: ^1H, δ 1.41, 1.51 (ss, 2 × C_5Me_5) and 6.73 [tt, *J*(F–H) 9.1, *m*-F; *J*(F–H) 7.2, *o*-F; SC_6F_4H-*p*]; $^{13}C\text{-}\{^1H\}$, δ 8.55 (s, $C_5\mathit{Me}_5$), 97.2 [d, *J*(Rh–C) 7, C_5Me_5], 97.9 [d, *J*(Rh–C) 7, C_5Me_5], 121.9 (m, CS, SC_6F_4H), 144.6 [d, *J*(F–C) 246, *m*-C] and 146.7 [d, *J*(F–C) 236 Hz, *o*-C]; ^{19}F [$(CD_3)_2CO$], δ −128.5 (m, *o*-F), −133.0 (m, *o*-F), −138.5 (m, *m*-F), −142.0 (m, *m*-F); ($C_6D_5CD_3$), δ −130.0 (m, *o*-F) and −140.1 (m, *m*-F).

$[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6H_4F\text{-}p)_3]Cl\cdot H_2O$ **4a**.—This complex (1.28 g, 87%) was obtained analogously, as an orange solid from **1a** (1.0 g, 1.62 mmol) (Found: C, 49.9; H, 4.9; Cl, 3.7. $C_{38}H_{44}ClF_3ORh_2S_3$ requires C, 50.0; H, 4.8; Cl, 3.9%). Conductivity 98 ohm^{-1} cm^2 mol^{-1}. NMR: ^1H, δ 1.35 (s, 30 H, C_5Me_5), 2.33 (s, 2 H, H_2O), 7.04 [t, 6 H, *J*(H–H) = *J*(H–F) = 8, *m*-H; SC_6H_4F-*p*] and 7.74 [dd, 6 H, *J*(H–F) 6, *o*-H]; $^{13}C\text{-}\{^1H\}$, δ 8.7 (s, $C_5\mathit{Me}_5$), 97.8 [d, *J*(Rh–C) 7, C_5Me_5], 115.9 [d, *J*(F–C) 22, *m*-C], 127.2 [d, ^2J(F–C) 3, CS, SC_6H_4F-*p*], 134.6 [d, *J*(C–F) 8, *o*-C] and 163.0 [d, *J*(F–C) 250, *p*-C); ^{19}F, δ −115.85 [tt, *J*($F\text{–}H_m$), 8, *J*($F\text{–}H_o$) 6 Hz; SC_6H_4F-*p*]; ^{19}F [$(CD_3)_2CO$], δ −113.7 (tt, *p*-F).

$[(C_5Me_5)_2Ir_2(\mu\text{-}SC_6H_4F\text{-}p)_3]Cl\cdot H_2O$ **4b**.—This complex (0.57 g, 70%) was obtained analogously, as a yellow solid from **1b** (0.6 g, 0.75 mmol) (Found: C, 41.7; H, 3.9; Cl, 3.2. $C_{38}H_{44}ClF_3Ir_2OS_3$ requires C, 41.9; H, 4.1; Cl, 3.25%). Conductivity 107 ohm^{-1} cm^2 mol^{-1}. ^1H NMR: δ 1.40 (s, 30 H, C_5Me_5), 1.75 (s, 2 H, H_2O) and 7.07 [t, *J*(H–F) 5 Hz, *o*-H, SC_6H_4F-*p*].

$[(C_5Me_5)_2Ir_2(\mu\text{-}SCF_3)_2(SCF_3)_2]$ **5b** and $[(C_5Me_5)_2Ir_2(\mu\text{-}SCF_3)_3]Cl\cdot H_2O$ **6b**.—The salt $Ag(SCF_3)$ (0.68 g, 3.28 mmol) was added to complex **1b** (0.65 g, 0.82 mmol) dissolved in chloroform (25 cm^3) and stirred (25 °C, 48 h) in the absence of light. The cloudy yellow reaction mixture was filtered and evaporated to dryness *in vacuo* giving a yellow residue which was chromatographed on silica gel. Elution with chloroform gave a yellow fraction, **5b**, and elution with chloroform–acetone (1:1 v/v) gave another yellow fraction, **6b**. Both solids were dried (25 °C, 24 h) in vacuum. Complex **5b** (0.017 g, 4%) (Found: C, 27.0; H, 3.0; S, 11.9. $C_{24}H_{30}F_{12}Ir_2S_4$ requires C, 27.2; H, 2.85; S, 12.1%). Conductivity 10 ohm^{-1} cm^2 mol^{-1}. NMR: ^1H, δ 1.80 (s, C_5Me_5); ^{19}F, δ −36.0 (s, 6 F, bridging SCF_3) and −38.7 (s, 6 F, terminal SCF_3). Complex **6b** (0.13 g, 32%) (Found: C, 27.3; H, 3.1; Cl, 3.5. $C_{23}H_{32}ClF_9Ir_2OS_3$ requires C, 27.3; H, 3.2;

Table 1 Fractional coordinates ($\times 10^4$) of atoms with standard deviations for complex **2b** ($R_F = C_6F_5$)

Atom	*x*	*y*	*z*
Ir	992(1)	2304(1)	2500
S(1)	813(5)	4759(5)	3135(2)
F(1)	2540(8)	4687(16)	3889(4)
F(2)	2665(8)	3837(19)	5010(5)
F(3)	1138(9)	2534(16)	5595(4)
F(4)	−519(10)	2213(16)	5063(5)
F(5)	−697(8)	3278(15)	3937(5)
C(1)	906(13)	3997(17)	3864(5)
C(2)	1746(14)	4073(21)	4152(7)
C(3)	1824(12)	3662(22)	4731(9)
C(4)	1070(17)	2950(24)	5039(7)
C(5)	248(14)	2848(22)	4763(7)
C(6)	149(11)	3339(21)	4195(7)
C(7)	1969(17)	46(25)	2500
C(8)	1410(12)	−143(18)	3000(6)
C(9)	482(12)	−357(17)	2819(6)
C(10)	3016(23)	283(42)	2500
C(11)	1755(15)	−375(24)	3612(7)
C(12)	−394(15)	−646(26)	3183(9)

Table 2 Selected bond lengths (Å) and angles (°) with standard deviations for complex **2b** ($R_F = C_6F_5$)

Ir–C(7)	2.125(21)	Ir–S(1)	2.292(4)
Ir–C(8)	2.172(13)	S(1)–C(1)	1.764(13)
Ir–C(9)	2.159(13)		
S(1)–Ir–S(1)[a]	78.9(2)	Ir–S(1)–C(1)	111.1(4)

Table 3 Fractional coordinates ($\times 10^4$) of atoms with standard deviations for complex **2b** ($R_F = C_6F_4H$-*p*)

Atom	*x*	*y*	*z*
Ir	855(1)	232(1)	2303(1)
S(1)	1720(4)	2527(3)	2721(3)
S(2)	−1897(4)	136(3)	2481(3)
C(1)	3331(15)	174(12)	1879(10)
C(2)	3176(15)	−112(13)	2797(9)
C(3)	1680(17)	−1315(13)	2611(10)
C(4)	966(16)	−1794(11)	1563(10)
C(5)	1915(16)	−852(12)	1116(9)
C(6)	4676(16)	1267(13)	1696(10)
C(7)	4330(18)	699(16)	3800(10)
C(8)	1151(20)	−1954(16)	3382(12)
C(9)	−529(20)	−3053(14)	1006(13)
C(10)	1613(20)	−951(17)	35(10)
C(11)	103(15)	3187(12)	3154(10)
C(12)	−621(16)	3818(12)	2623(10)
C(13)	−1846(18)	4336(14)	2970(12)
C(14)	−2418(18)	4321(13)	3866(12)
C(15)	−1698(18)	3685(12)	4398(10)
C(16)	−453(17)	3160(13)	4055(11)
C(17)	−3283(15)	−1495(12)	2304(11)
C(18)	−4386(18)	−2292(15)	1418(14)
C(19)	−5566(22)	−3499(17)	1299(18)
C(20)	−5735(22)	−3979(19)	2099(21)
C(21)	−4662(26)	−3231(19)	2972(19)
C(22)	−3482(18)	−2012(14)	3088(12)
F(1)	−104(12)	3927(9)	1765(6)
F(2)	−2541(13)	4935(10)	2417(8)
F(3)	−2208(13)	3634(9)	5273(7)
F(4)	206(12)	2598(8)	4634(7)
F(5)	−4278(14)	−1868(11)	608(8)
F(6)	−6595(17)	−4236(12)	414(12)
F(7)	−4768(18)	−3658(13)	3776(11)
F(8)	−2461(14)	−1267(10)	4003(7)

Table 4 Selected bond lengths (Å) and angles (°) with standard deviations for complex **2b** ($R_F = C_6F_4H$-*p*)

Ir–C(1)	2.179(13)	Ir–S(1)	2.323(4)
Ir–C(2)	2.178(14)	Ir–S(2)	2.274(4)
Ir–C(3)	2.190(17)	S(1)–C(11)	1.769(15)
Ir–C(4)	2.228(13)	S(2)–C(17)	1.773(13)
Ir–C(5)	2.161(14)		
S(1)–Ir–S(2)	90.8(1)	Ir–S(1)–C(11)	112.9(4)
Ir–S(2)–C(17)	112.7(5)		

Cl, 3.5%). Conductivity 92 ohm^{-1} cm^2 mol^{-1}. NMR: ^{1}H, δ 1.80 (s, C_5Me_5); ^{19}F, δ − 33.6 (s, SCF_3).

Crystal Structure of $[(C_5Me_5)Ir(SC_6F_5)_2]$ **2b** ($R_F = C_6F_5$).—*Crystal data.* $C_{22}H_{15}F_{10}IrS_2$, *M* = 725.66, crystallised from chloroform as very dark red needles, crystal dimensions 0.70 × 0.11 × 0.05 mm, orthorhombic, space group *Pnam* (a non-standard setting of *Pnma*, D_{2h}^{16}, no. 62), *a* = 14.200(20), *b* = 7.132(2), *c* = 22.952(32) Å, *U* = 2324(5) Å^3, D_c = 2.074 g cm^{-3}, *Z* = 4, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 59.82 cm^{-1}, *F*(000) = 1383.71.

Three-dimensional, room-temperature X-ray data were collected in the range 6.5 < 2θ < 50° on a Stoe Stadi-2 two-circle diffractometer by the ω-scan method. The 1260 independent reflections (of 2379 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by Gaussian integration methods (minimum and maximum transmission coefficients 0.488 and 0.741). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom, and refined in riding mode. Refinement converged at a final *R* 0.0454 (*R'* 0.0445, 163 parameters; mean and maximum shift/e.s.d. 0.003 and 0.014 respectively), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed minimum and maximum values of − 1.38 and + 1.52 e Å^{-3} adjacent to the iridium atom. Complex scattering factors were taken from ref. 17 and from the program package SHELXTL[18] as implemented on a Data General DG30 computer, which was used for structure solution and refinement. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.000\ 83(F)^2]$ was used in the latter stages of refinement. Atomic coordinates are in Table 1, selected bond lengths and angles in Table 2.

Crystal Structure of $[(C_5Me_5)Ir(SC_6F_4H\text{-}p)_2]$ **2b** ($R_F = C_6F_4H$-*p*).—*Crystal data.* $C_{22}H_{17}F_8IrS_2$, *M* = 689.69, crystallised from hexane as dark red blocks, crystal dimensions 0.45 × 0.30 × 0.20 mm, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), *a* = 8.248(6), *b* = 11.213(12), *c* = 14.203(20) Å, α = 107.63(9), β = 93.65(9), γ = 107.51(7)°, *U* = 1176(2) Å^3, D_c = 1.948 g cm^{-3}, *Z* = 2, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 58.92 cm^{-1}, *F*(000) = 659.85.

Three-dimensional room-temperature X-ray data were collected in the range 3.5 < 2θ < 50° on a Nicolet R3 four-circle diffractometer by the ω-scan method. The 3471 independent reflections (of 4152 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of eight azimuthal scans (minimum and maximum transmission coefficients 0.065 and 0.111). The structure was solved and refined as above. Refinement converged at a final *R* 0.0521 (298 parameters; maximum shift/e.s.d. 0.103), with allowance for the thermal anisotropy of all non-hydrogen atoms. A final difference electron-density synthesis showed peaks of −2.62 and +2.03 e Å^{-3} adjacent to the iridium atom. Complex scattering factors were taken from ref. 17 and from the program package SHELXTL[18] as implemented on a Data General Nova 3 computer. Unit weights were used throughout the refinement. Atomic positional parameters with estimated standard

Table 5 Fractional coordinates (× 10^4) of atoms with standard deviations for complex **3a** ($R_F = C_6F_5$)

Atom	*x*	*y*	*z*
Rh(1)	2163(2)	2719(2)	4620(1)
Rh(2)	271(2)	2377(2)	4260(1)
Rh(3)	4060(2)	7848(2)	2053(2)
S(1)	1031(7)	3605(7)	4429(4)
S(2)	1274(7)	2012(7)	5040(4)
S(3)	1341(6)	1996(7)	3901(4)
S(4)	4484(7)	6517(9)	2404(5)
S(5)	4686(7)	7673(9)	1358(5)
S(6)	2836(7)	7356(8)	1553(5)
F(1)	973(13)	5347(10)	4543(5)
F(2)	913(13)	6594(10)	3863(5)
F(3)	931(13)	6263(10)	2873(5)
F(4)	844(13)	4682(10)	2541(5)
F(5)	997(13)	3438(10)	3232(5)
C(21)	978(13)	4374(10)	3897(5)
C(22)	975(13)	5188(10)	4062(5)
C(23)	921(13)	5829(10)	3708(5)
C(24)	919(13)	5658(10)	3196(5)
C(25)	925(13)	4844(10)	3032(5)
C(26)	972(13)	4203(10)	3385(5)
F(6)	1478(12)	3774(10)	5573(7)
F(7)	1251(12)	4175(10)	6508(7)
F(8)	621(12)	3061(10)	7038(7)
F(9)	406(12)	1490(10)	6698(7)
F(10)	690(12)	1072(10)	5781(7)
C(27)	1097(12)	2414(10)	5665(7)
C(28)	1254(12)	3210(10)	5857(7)
C(29)	1124(12)	3420(10)	6335(7)
C(30)	824(12)	2839(10)	6617(7)
C(31)	692(12)	2036(10)	6434(7)
C(32)	829(12)	1823(10)	5958(7)
F(11)	1032(13)	1152(10)	2923(5)
F(12)	1044(13)	−468(10)	2698(5)
F(13)	1446(13)	−1586(10)	3466(5)
F(14)	1880(13)	−1076(10)	4456(5)
F(15)	1831(13)	542(10)	4683(5)
C(33)	1415(13)	872(10)	3807(5)
C(34)	1195(13)	609(10)	3297(5)
C(35)	1209(13)	−226(10)	3180(5)
C(36)	1452(13)	−798(10)	3574(5)
C(37)	1673(13)	−536(10)	4084(5)
C(38)	1638(13)	297(10)	4202(5)
F(16)	2624(11)	5976(13)	826(6)
F(17)	2394(11)	4364(13)	992(6)
F(18)	2376(11)	3834(13)	1949(6)
F(19)	2618(11)	4910(13)	2743(6)
F(20)	2775(11)	6535(13)	2567(6)
C(39)	2713(11)	6279(13)	1696(6)
C(40)	2591(11)	5724(13)	1286(6)
C(41)	2493(11)	4889(13)	1374(6)
C(42)	2500(11)	4613(13)	1870(6)
C(43)	2591(11)	5174(13)	2275(6)
C(44)	2714(11)	6004(13)	2190(6)
F(21)	4744(13)	6390(14)	562(9)
F(22)	3882(13)	6241(14)	−411(9)
F(23)	2833(13)	7412(14)	−802(9)
F(24)	2522(13)	8616(14)	−183(9)
F(25)	3357(13)	8740(14)	798(9)
C(45)	4066(13)	7569(14)	695(9)
C(46)	4211(13)	6934(14)	380(9)
C(47)	3773(13)	6863(14)	−124(9)
C(48)	3199(13)	7436(14)	−316(9)
C(49)	3044(13)	8061(14)	3(9)
C(50)	3477(13)	8127(14)	508(9)
F(26)	4278(8)	5410(15)	1496(9)
F(27)	5336(8)	4689(15)	1070(9)
F(28)	6839(8)	5008(15)	1449(9)
F(29)	7284(8)	6053(15)	2252(9)
F(30)	6229(8)	6741(15)	2695(9)
C(51)	5239(8)	6063(15)	2114(9)
C(52)	5008(8)	5543(15)	1691(9)
C(53)	5554(8)	5165(15)	1474(9)
C(54)	6328(8)	5340(15)	1665(9)
C(55)	6559(8)	5861(15)	2087(9)
C(56)	6014(8)	6224(15)	2312(9)
C(1)	−758(9)	2458(10)	3646(6)
C(2)	−670(9)	1618(10)	3795(6)
C(3)	−701(9)	1564(10)	4320(6)
C(4)	−826(9)	2368(10)	4492(6)
C(5)	−863(9)	2920(10)	4075(6)
C(6)	−806(9)	2785(10)	3099(6)
C(7)	−592(9)	881(10)	3449(6)
C(8)	−629(9)	778(10)	4650(6)
C(9)	−904(9)	2613(10)	5034(6)
C(10)	−995(9)	3855(10)	4079(6)
C(11)	3246(13)	2496(14)	4410(8)
C(12)	3324(13)	2240(14)	4928(8)
C(13)	3187(13)	2933(14)	5217(8)
C(14)	3056(13)	3624(14)	4883(8)
C(15)	3093(13)	3354(14)	4384(8)
C(16)	3341(13)	1976(14)	3947(8)
C(17)	3545(13)	1360(14)	5121(8)
C(18)	3260(13)	2916(14)	5803(8)
C(19)	2918(13)	4503(14)	5057(8)
C(20)	2994(13)	3928(14)	3913(8)
C(57)	4333(16)	9189(16)	2134(10)
C(58)	4796(16)	8716(16)	2536(10)
C(59)	4314(16)	8370(16)	2832(10)
C(60)	3547(16)	8586(16)	2592(10)
C(61)	3560(16)	9103(16)	2167(10)
C(62)	4578(16)	9695(16)	1712(10)
C(63)	5674(16)	8677(16)	2637(10)
C(64)	4616(16)	7882(16)	3333(10)
C(65)	2860(16)	8358(16)	2816(10)
C(66)	2837(16)	9482(16)	1817(10)
C(67)	5000(43)	−681(39)	338(26)
C(68)	4861(43)	−1010(39)	−158(26)
C(69)	4776(43)	−490(39)	−582(26)
C(70)	4830(43)	360(39)	−511(26)
C(71)	4969(43)	690(39)	−16(26)
C(72)	5054(43)	169(39)	409(26)
C(73)	5202(43)	523(39)	941(26)

Atoms C(67)–C(73), and their associated hydrogen atoms, comprise a half-occupancy toluene of crystallisation.

deviations are in Table 3, selected bond lengths and angles in Table 4.

Crystal Structure of $[(C_5Me_5)_2Rh_2(\mu\text{-}SC_6F_5)_3][(C_5Me_5)Rh(SC_6F_5)_3]\cdot0.5C_6H_5Me$ **3a** ($R_F = C_6F_5$).—*Crystal data.* $C_{69.5}H_{49}F_{30}Rh_3S_6$, $M = 1955.20$, crystallised from toluene as red blocks, crystal dimensions 0.60 × 0.30 × 0.15 mm, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 18.00(6)$, $b = 16.256(25)$, $c = 26.73(7)$ Å, $\beta = 103.68(22)°$, $U = 7600(32)$ Å^3; $D_c = 1.709$ g cm^{-3}, $Z = 4$, Mo-Kα radiation ($\lambda = 0.710\ 69$ Å), μ(Mo-Kα) = 9.03 cm^{-1}, $F(000) = 3867.65$.

Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 40°$ on a Nicolet R3 four-circle diffractometer by the ω-scan method. The 3359 independent reflections (of 7769 measured) for which $|F|/\sigma(|F|) > 3.0$ were corrected as for **2b** ($R_F = C_6F_4H$) (minimum and maximum transmission coefficients 0.532 and 0.612). The structure was also solved and refined in the same way. In view of the limited quality of the X-ray data it was found necessary to apply extensive geometric constraints during refinement. Each pentamethylcyclopentadienyl ring was optimised, initially as two idealised pentagons, which were loosely coupled to maintain realistic C–Me lengths and external ring angles. The pentafluorophenyl fragments were also optimised in order to maintain D_{6h} symmetry for the skeleton, and identical C–F lengths and external ring angles. The half-occupancy of the

Table 6 Selected bond lengths (Å) and angles (°) with standard deviations for complex **3a** ($R_F = C_6F_5$)

Rh(1)–S(1)	2.447(13)	Rh(2)–C(1)	2.169(15)
Rh(1)–S(2)	2.450(15)	Rh(2)–C(2)	2.222(16)
Rh(1)–S(3)	2.432(12)	Rh(2)–C(3)	2.228(17)
Rh(2)–S(1)	2.402(13)	Rh(2)–C(4)	2.205(18)
Rh(2)–S(2)	2.486(12)	Rh(2)–C(5)	2.171(17)
Rh(2)–S(3)	2.425(14)	Rh(1)–C(11)	2.183(25)
Rh(3)–S(4)	2.410(15)	Rh(1)–C(12)	2.200(22)
Rh(3)–S(5)	2.407(17)	Rh(1)–C(13)	2.163(20)
Rh(3)–S(6)	2.425(13)	Rh(1)–C(14)	2.171(23)
S(1)–C(21)	1.879(19)	Rh(1)–C(15)	2.183(25)
S(2)–C(27)	1.889(23)	Rh(3)–C(57)	2.234(27)
S(3)–C(33)	1.854(20)	Rh(3)–C(58)	2.146(26)
S(4)–C(51)	1.869(25)	Rh(3)–C(59)	2.194(27)
S(5)–C(45)	1.866(26)	Rh(3)–C(60)	2.236(30)
S(6)–C(39)	1.817(25)	Rh(3)–C(61)	2.280(28)
S(1)–Rh(1)–S(2)	76.7(4)	S(1)–Rh(1)–S(3)	78.4(4)
S(2)–Rh(1)–S(3)	78.1(4)	S(1)–Rh(2)–S(2)	76.8(4)
S(1)–Rh(2)–S(3)	79.4(4)	S(2)–Rh(2)–S(3)	77.6(4)
Rh(1)–S(1)–Rh(2)	87.7(4)	S(4)–Rh(3)–S(5)	91.8(5)
Rh(1)–S(2)–Rh(2)	85.7(4)	S(4)–Rh(3)–S(6)	94.7(5)
Rh(1)–S(3)–Rh(2)	87.5(4)	S(5)–Rh(3)–S(6)	93.8(5)
Rh(1)–S(1)–C(21)	116.1(9)	Rh(3)–S(4)–C(51)	112.8(10)
Rh(1)–S(2)–C(27)	120.5(8)	Rh(3)–S(5)–C(45)	117.4(10)
Rh(1)–S(3)–C(33)	122.3(7)	Rh(3)–S(6)–C(39)	110.0(8)
Rh(2)–S(1)–C(21)	119.1(7)	Rh(2)–S(2)–C(27)	114.8(8)
Rh(2)–S(3)–C(33)	113.2(9)		

toluene of solvation, which is situated near to a crystallographic inversion centre, was also refined with constrained D_{6h} geometry for the ring, with a riding methyl substituent. Hydrogen atoms were included in calculated positions, with isotropic thermal parameters related to those of the supporting atom. After optimisation all these fragments were refined in the final cycles as rigid groups. Refinement converged at a final R 0.1330 (389 parameters; maximum shift/e.s.d. 0.083), with allowance for the thermal anisotropy of rhodium, sulfur, and fluorine atoms only. A final difference electron-density synthesis showed peaks of -1.05 and $+1.08$ e Å^{-3}. Sources of scattering factors and unit weights as for **2b** ($R_F = C_6F_4H$-*p*). Atomic positional parameters with estimated standard deviations are in Table 5, selected bond lengths and angles in Table 6.

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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