Iridium–Platinum Perfluorobenzenethiolato Trinuclear Complexes: Crystal Structures of $[\mathrm{Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2}]$ ($\mathrm{R_F = C_6F_5}$ or $\mathrm{C_6F_4H}$-*p*), Syntheses and Solution Behaviour†

Aida Castellanos,[a] Juventino J. García,*[,a] Hugo Torrens,[a] Neil Bailey,[b] Cecilia O. Rodríguez de Barbarin,[b] Atilano Gutierrez[c] and Federico del Río[c]

[a] *Departamento de Química Inorgánica, Facultad de Química, Universidad Nacional Autonoma de México, 04510 México, D. F., México*
[b] *Department of Chemistry, The University of Sheffield, Sheffield S3 7HF, UK*
[c] *Instituto de Química, Universidad Nacional Autónoma de México, 04510 México, D. F., México*

Reaction of $[\mathrm{Ir(C_5Me_5)(SR_F)_2}]$ ($\mathrm{R_F = C_6F_5}$ **1a** or $\mathrm{C_6F_4H}$-*p* **1b**) with $\mathrm{K_2[PtCl_4]}$ gave trinuclear complexes $[\mathrm{Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2}]$ ($\mathrm{R_F = C_6F_5}$ **2a** or $\mathrm{C_6F_4H}$-*p* **2b**). Complexes **2a** and **2b** were characterized by single-crystal X-ray determinations. The structures are very similar and show short contact interactions between the platinum and the *o*-F of the bridging perfluorobenzenethiolate groups. Variable-temperature ^{19}F NMR spectra of solutions of complexes **2a** and **2b** reveal the coexistence of several conformers without the Pt ··· *o*-F short contact found in the solid state.

Transition-metal complexes with sulfur ligands are of significant interest,[1] particularly thiolate complexes containing the $\mathrm{M(C_5Me_5)}$ or $\mathrm{M(C_6H_6)}$ group (M = Ti, V, Fe, Mo, Ru, Rh, Ir or W) have been synthesized and showed unique reactivities.[2] Thiolato complexes of rhodium and iridium have attracted wide interest, especially in connection with their reactivity towards organic substrates.[3] Nevertheless the chemistry of the thiolato-iridium(III) complexes is undeveloped since the first reports of ligand-substitution reactions on pentamethylcyclopentadienyl derivatives.[4]

As part of our studies of the reactivity of complexes with pseudo-halides,[5] we recently reported the synthesis and crystal structures of $[\mathrm{Ir(C_5Me_5)(SR_F)_2}]$ ($\mathrm{R_F = C_6F_5}$ **1a** or $\mathrm{C_6F_4H}$-*p* **1b**) and the corresponding rhodium analogue in solution.[6] In this paper we describe the preparation, properties and crystal structures of the trinuclear complexes $[\mathrm{Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2}]$ ($\mathrm{R_F = C_6F_5}$ **2a** or $\mathrm{C_6F_4H}$-*p* **2b**).

Results and Discussion

Syntheses of $[\mathrm{Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2}]$.—The reaction of the thiolato complex **1a** or **1b** with $\mathrm{K_2[PtCl_4]}$ in equimolecular proportions, in acetone–water (1 : 1 v/v) solutions, afforded the yellow crystalline, trinuclear compounds $[\mathrm{Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2}]$ ($\mathrm{R_F = C_6F_5}$ **2a** or $\mathrm{C_6F_4H}$-*p* **2b**) [equation (1)].

$$\underset{\textbf{1a}\text{ or }\textbf{1b}}{2[\mathrm{Ir(C_5Me_5)(SR_F)_2}]} + \mathrm{K_2[PtCl_4]} \longrightarrow \underset{\textbf{2a}\text{ or }\textbf{2b}}{[\mathrm{Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2}]} + 2\mathrm{KCl} \quad (1)$$

Experimentally the synthesis of **2a** and **2b** was performed with an excess of $\mathrm{K_2[PtCl_4]}$. The desired complex was purified by column chromatography followed by crystallization; yields of 70–80% were obtained. The complexes were characterized through X-ray diffraction crystal-structure determinations and by NMR spectroscopy in solution.

Crystal Structures of $[\mathrm{Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2}]$ ($\mathrm{R_F = C_6F_5}$ **2a** *or* $\mathrm{C_6F_4H}$-*p* **2b**).—The two structures are very similar but differ in the relative orientations adopted by the μ-$\mathrm{SR_F}$ ligands. The complexes are trinuclear with two six-co-ordinate iridium(III) atoms and one platinum(II) centre which is four-co-ordinate. The molecular structure for **2a** with atom labelling is illustrated in Fig. 1. Bond lengths and angles with estimated standard deviations are listed in Table 1.

The molecular structure of complex **2a** is approximately centrosymmetric (approximately C_{2h} across the platinum ion). The co-ordination of the platinum(II) is square planar involving the sulfur atoms of the four perfluorobenzenethiolate, $\mathrm{SR_F}$ substituents, which bridge in pairs, to iridium(III) atoms [Pt–S 2.29–2.34 Å; root-mean-square (r.m.s.) deviation of $\mathrm{S_4}$ plane 0.027 Å, deviations of platinum and two iridiums 0.014, 0.111, −0.029 Å; Ir–S 2.36–2.44 Å]. Each iridium is also η^5 bonded to a $\mathrm{C_5Me_5}$ ring (average Ir–C 2.170 Å, displacements of iridiums from such planes 1.785 and 1.820 Å), and to a chlorine atom (Ir–Cl 2.318 and 2.361 Å). The bridges are slightly asymmetric, in that both S(1) and S(4) form longer bonds to both iridium (by 0.058 Å) and platinum (by 0.041 Å) than do S(2) and S(3). Thus this asymmetry is not consistent with the approximate inversion symmetry of the molecule, but with its approximate C_2 symmetry perpendicular to Ir ··· Pt ··· Ir in the bridge plane. The same compliance with approximate C_2 symmetry is seen in the orientations of the twisted benzenethiolate ligands as shown by their interplanar angles. The S–C bond lengths are very similar (mean 1.798 Å) and the benzenethiolate ring fragments (r.m.s. deviations 0.024, 0.010, 0.011 and 0.006 Å) are inclined at 22.8 and 35.8° between *trans* ligands, and at 72.5 and 123.9° between adjacent *cis* ligands on the platinum ion. The pentamethylcyclopentadienyl groups are approximately parallel (5.1°). The four closest Pt ··· F distances, (2.993–3.075 Å) are less than the anticipated van der Waals distance between Pt and F of approximately 3.30 Å and represents a strong interaction between such atoms, at least in the solid state. Similar M ··· F interactions have been reported before in mononuclear thiolato complexes[7] and in polynuclear perfluorophenylplatinum complexes[8] and apparently add stability to the complexes. The shortest separations between such fluorines on different ligands [for instance F(11) ··· F(6)]

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

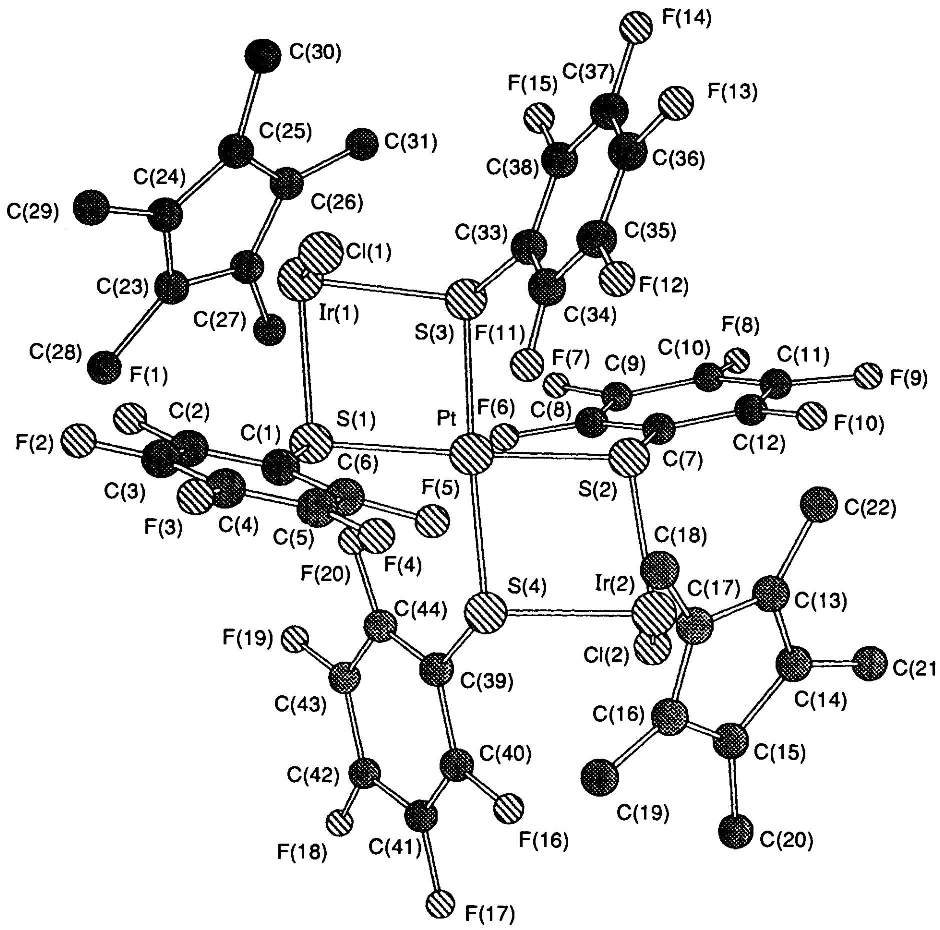

Fig. 1 View of the crystal structure of $[Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2]$ **2a** ($R_F = C_6F_5$)

are 2.67 and 2.72 Å, which would be very close for a van der Waals contact (2.94 Å) between such electronegative atoms. These distances correspond to Pt–S–C–C(F) torsion angles of −11.4, −5.6, −24.4 and −12.4° which serve to minimize these Pt···F and F···F separations. There are short contacts between other *o*-fluorines and methyl carbons on the C_5Me_5 ring (shorter F···C 2.86 Å) which might inhibit major rotations of the ligands about their S–C bonds.

The molecular structure of the trinuclear complex **2b**, with atom labelling is illustrated in Fig. 2. Bond lengths and angles with estimated standard deviations are listed in Table 2. As for the preceding compound, **2b** comprises one centrosymmetric molecule with the platinum(II) on a centre of symmetry at (0,0,0) and a disordered toluene solvent molecule near a different centre $(0,0,\frac{1}{2})$. In contrast, in **2b** the platinum ion is symmetrically bonded to two sulfur atoms of the SC_6F_4H-*p* ligands which bridge in pairs to iridium(III) ions [Pt–S 2.289, 2.291 Å; deviations, necessarily symmetrically, of the two Ir(1) and Ir(1A) from the S_4 plane are −0.225 and +0.225 Å]. Each iridium ion is also η^5 bonded to a C_5Me_5 ring (Ir–C 2.139–2.179 Å; displacements of iridiums from such planes 1.793 Å) and to a chlorine atom (Ir–Cl 2.340 Å). The S–C bond lengths are 1.761 and 1.811 Å, and the benzenethiolate fragments (r.m.s. deviations 0.016, 0.013 Å) are necessarily inclined at 0° between *trans* ligands and 101.6° between adjacent *cis* ligands on the platinum ion. The molecule has approximate C_{2h} symmetry, the nearest Pt···F distances being 2.983 and 3.044 Å; as for structure **2a**, these values are again less than the anticipated van der Waals distance between Pt and F of approximately 3.30 Å. The shortest *o*-F···*o*-F vector of different thiolate ligands is 2.579 Å, again shorter than a van der Waals contact (2.94 Å) between such atoms, and corresponds to Pt–S–C–C(F) torsion angles of −9.1 and −1.1°.

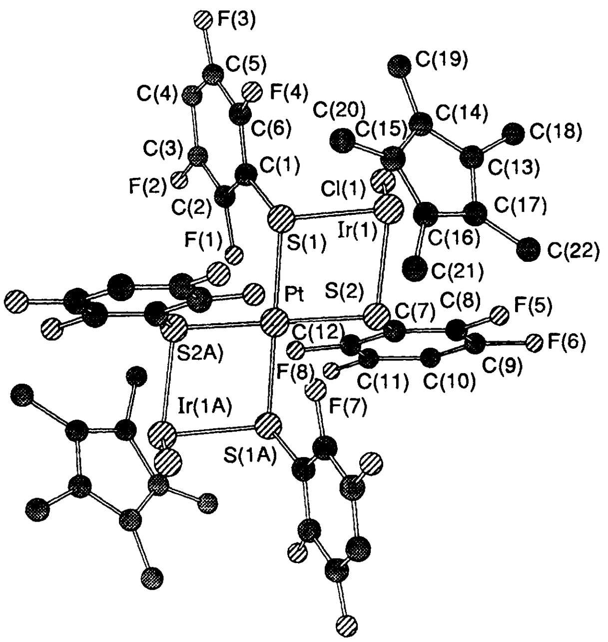

Fig. 2 View of the crystal structure of $[Ir_2Pt(C_5Me_5)(\mu\text{-}SR_F)_4Cl_2]$ **2b** ($R_F = C_6F_4H$-*p*)

Solution Behaviour of Complexes **2a** *and* **2b**.—The ^{19}F NMR spectrum of complex **2a**, in $CDCl_3$ at −40 °C, shows four signals in the *p*-F region at δ −149.5, −150.5, −154.0 and −155.5, with relative intensities 1:4:8:8 respectively, each

Table 1 Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) for complex **2a**

Ir(1)–Cl(1)	2.318(12)	Ir(1)–S(1)	2.443(10)	C(22)–C(13)	1.494(46)	C(28–C(23)	1.481(56)
Ir(1)–S(3)	2.399(16)	Ir(1)–C(23)	2.140(31)	C(29)–C(24)	1.545(65)	C(30)–C(25)	1.524(44)
Ir(1)–C(24)	2.161(33)	Ir(1)–C(25)	2.175(28)	C(31)–C(26)	1.471(71)	C(32)–C(27)	1.560(59)
Ir(1)–C(26)	2.161(27)	Ir(1)–C(27)	2.140(31)	F(1)–C(2)	1.285(36)	F(2)–C(3)	1.268(50)
Ir(2)–Cl(2)	2.361(12)	Ir(2)–S(2)	2.357(10)	F(3)–C(4)	1.321(41)	F(4)–C(5)	1.279(39)
Ir(2)–S(4)	2.429(16)	Ir(2)–C(13)	2.190(31)	F(5)–C(6)	1.337(47)	F(6)–C(8)	1.290(52)
Ir(2)–C(14)	2.197(33)	Ir(2)–C(15)	2.188(29)	F(7)–C(9)	1.306(40)	F(8)–C(10)	1.425(48)
Ir(2)–C(16)	2.174(28)	Ir(2)–C(17)	2.175(31)	F(9)–C(11)	1.356(54)	F(10)–C(12)	1.287(43)
Pt–S(1)	2.335(16)	Pt–S(2)	2.294(15)	F(11)–C(34)	1.254(32)	F(12)–C(35)	1.284(36)
Pt–S(3)	2.293(10)	Pt–S(4)	2.336(11)	F(13)–C(36)	1.341(37)	F(14)–C(37)	1.340(31)
S(1)–C(1)	1.811(29)	S(2)–C(7)	1.800(31)	F(15)–C(38)	1.257(35)	F(16)–C(40)	1.317(32)
S(3)–C(33)	1.746(27)	S(4)–C(39)	1.836(24)	F(17)–C(41)	1.272(35)	F(18)–C(42)	1.314(32)
C(18)–C(17)	1.513(59)	C(19)–C(16)	1.502(57)	F(19)–C(43)	1.300(33)	F(20)–C(44)	1.355(35)
C(20)–C(15)	1.546(41)	C(21)–C(14)	1.489(62)				

Cl(1)–Ir(1)–S(1)	91.4(4)	Cl(1)–Ir(1)–S(3)	91.9(5)	C(14)–C(13)–C(22)	123.9(24)	C(15)–C(14)–C(21)	121.8(16)
S(1)–Ir(1)–S(3)	80.4(4)	Cl(2)–Ir(2)–S(4)	92.2(5)	C(17)–C(13)–C(22)	128.0(24)	C(14)–C(15)–C(20)	125.3(21)
S(2)–Ir(2)–S(4)	80.8(4)	Cl(2)–Ir(2)–S(2)	91.7(4)	C(13)–C(14)–C(21)	130.2(16)	C(17)–C(16)–C(19)	122.3(21)
S(1)–Pt–S(2)	176.9(4)	S(1)–Pt–S(3)	84.9(4)	C(16)–C(15)–C(20)	126.6(21)	C(13)–C(17)–C(18)	121.1(21)
S(2)–Pt–S(3)	92.7(4)	S(1)–Pt–S(4)	98.3(4)	C(15)–C(16)–C(19)	128.9(21)	C(27)–C(23)–C(28)	128.3(27)
S(2)–Pt–S(4)	84.1(4)	S(3)–Pt–S(4)	176.7(5)	C(16)–C(17)–C(18)	130.7(21)	Ir(1)–C(24)–C(25)	71.4(6)
Ir(1)–S(1)–Pt	96.1(4)	Ir(1)–S(1)–C(1)	107.6(9)	C(24)–C(23)–C(28)	123.5(27)	C(23)–C(24)–C(29)	124.1(17)
Pt–S(1)–C(1)	114.5(11)	Ir(2)–S(2)–Pt	98.8(4)	C(25)–C(24)–C(29)	127.8(16)	C(26)–C(25)–C(30)	119.7(24)
Ir(2)–S(2)–C(7)	111.3(10)	Pt–S(2)–C(7)	112.7(12)	C(24)–C(25)–C(30)	132.3(24)	C(25)–C(26)–C(31)	137.8(22)
Ir(1)–S(3)–Pt	98.5(5)	Ir(1)–S(3)–C(33)	111.2(13)	C(27)–C(26)–C(31)	113.9(21)	C(26)–C(27)–C(32)	128.4(22)
Pt–S(3)–C(33)	111.8(9)	Ir(2)–S(4)–Pt	95.6(4)	S(3)–C(33)–C(38)	117.0(8)	C(36)–C(35)–F(12)	121.2(16)
Ir(2)–S(4)–C(39)	109.8(12)	Pt–S(4)–C(39)	112.0(9)	C(35)–C(34)–F(11)	114.9(15)	C(37)–C(36)–F(13)	119.5(15)
S(1)–C(1)–C(2)	117.3(11)	S(1)–C(1)–C(6)	122.6(11)	C(23)–C(27)–C(32)	123.6(22)	C(38)–C(37)–F(14)	119.7(17)
C(1)–C(2)–F(1)	120.1(20)	C(3)–C(2)–F(1)	119.9(20)	S(3)–C(33)–C(34)	123.0(8)	C(37)–C(38)–F(15)	117.6(15)
C(2)–C(3)–F(2)	118.0(18)	C(4)–C(3)–F(2)	121.9(19)	C(33)–C(34)–F(11)	125.1(15)	S(4)–C(39)–C(44)	124.4(8)
C(3)–C(4)–F(3)	117.7(20)	C(5)–C(4)–F(3)	122.2(20)	C(34)–C(35)–F(12)	118.7(16)	C(41)–C(40)–F(16)	118.7(12)
C(4)–C(5)–F(4)	118.8(22)	C(6)–C(5)–F(4)	121.2(22)	C(35)–C(36)–F(13)	120.5(15)	C(42)–C(41)–F(17)	121.5(16)
C(1)–C(6)–F(5)	125.6(14)	C(5)–C(6)–F(5)	114.4(14)	C(36)–C(37)–F(14)	120.3(17)	C(43)–C(42)–F(18)	122.7(15)
S(2)–C(7)–C(8)	121.2(11)	S(2)–C(7)–C(12)	118.8(11)	C(33)–C(38)–F(15)	122.2(15)	C(44)–C(43)–F(19)	120.6(14)
C(7)–C(8)–F(6)	127.3(15)	C(9)–C(8)–F(6)	112.7(15)	S(4)–C(39)–C(40)	115.6(8)	C(43)–C(44)–F(20)	116.5(14)
C(8)–C(9)–F(7)	123.9(24)	C(10)–C(9)–F(7)	116.0(24)	C(39)–C(40)–F(16)	121.3(12)	C(40)–C(41)–F(17)	118.5(16)
C(9)–C(10)–F(8)	121.7(20)	C(11)–C(10)–F(8)	118.1(20)	C(42)–C(43)–F(19)	119.4(14)	C(41)–C(42)–F(18)	117.1(15)
C(10)–C(11)–F(9)	123.2(22)	C(12)–C(11)–F(9)	116.6(22)	C(39)–C(44)–F(20)	123.4(14)		
C(7)–C(12)–F(10)	118.0(24)	C(11)–C(12)–F(10)	122.0(24)				

Table 2 Bond lengths (Å) and angles (°) with e.s.d.s for complex **2b**

Pt–S(1)	2.289(8)	Pt–S(2)	2.291(8)	C(7)–C(8)	1.393(1)	C(7)–C(12)	1.392(1)
Ir(1)–S(1)	2.382(9)	Ir(1)–S(2)	2.413(8)	C(8)–C(9)	1.391(1)	C(9)–C(10)	1.392(1)
Ir(1)–Cl(1)	2.340(10)	Ir(1)–C(13)	2.179(28)	C(10)–C(11)	1.393(1)	C(11)–C(12)	1.390(1)
Ir(1)–C(14)	2.174(31)	Ir(1)–C(15)	2.152(29)	C(13)–C(14)	1.415(1)	C(13)–C(17)	1.413(1)
Ir(1)–C(16)	2.139(28)	Ir(1)–C(17)	2.155(27)	C(13)–C(18)	1.512(52)	C(14)–C(15)	1.415(1)
S(1)–C(1)	1.761(25)	S(2)–C(7)	1.811(23)	C(14)–C(19)	1.389(47)	C(15)–C(16)	1.413(1)
F(1)–C(2)	1.263(35)	F(2)–C(3)	1.301(45)	C(15)–C(20)	1.493(45)	C(16)–C(17)	1.417(1)
F(3)–C(5)	1.277(37)	F(4)–C(6)	1.252(37)	C(16)–C(21)	1.550(60)	C(17)–C(22)	1.390(51)
F(5)–C(8)	1.330(30)	F(6)–C(9)	1.307(31)	C(23)–C(24)	1.385(1)	C(23)–C(28)	1.394(1)
F(7)–C(11)	1.263(33)	F(8)–C(12)	1.245(30)	C(24)–C(25)	1.385(1)	C(25)–C(26)	1.392(1)
C(1)–C(2)	1.390(1)	C(1)–C(6)	1.384(1)	C(26)–C(27)	1.387(1)	C(27)–C(28)	1.385(1)
C(2)–C(3)	1.392(1)	C(3)–C(4)	1.384(1)	C(27)–C(29)	1.537(1)		
C(4)–C(5)	1.390(1)	C(5)–C(6)	1.392(1)				

S(1)–Pt–S(2)	84.6(3)	S(1)–Pt–S(2A)	95.4(3)	C(8)–C(7)–C(12)	120.1(1)	C(7)–C(8)–C(9)	120.0(1)
S(1)–Ir(1)–S(2)	80.0(3)	S(1)–Ir(1)–Cl(1)	91.6(3)	F(5)–C(8)–C(9)	119.0(12)	F(6)–C(9)–C(10)	122.4(16)
S(2)–Ir(1)–Cl(1)	91.7(3)	Pt–S(1)–C(1)	113.3(9)	F(6)–C(9)–C(8)	117.5(15)	C(9)–C(10)–C(11)	120.1(1)
Pt–S(1)–Ir(1)	98.0(3)	Pt–S(2)–Ir(1)	97.0(3)	C(8)–C(9)–C(10)	119.9(1)	F(7)–C(11)–C(12)	122.4(14)
Ir(1)–S(1)–C(1)	109.4(9)	Ir(1)–S(2)–C(7)	111.0(7)	F(7)–C(11)–C(10)	117.6(14)	F(8)–C(12)–C(7)	126.0(15)
Pt–S(2)–C(7)	110.9(8)	S(1)–C(1)–C(6)	112.8(9)	C(10)–C(11)–C(12)	120.0(1)	C(7)–C(12)–C(11)	119.9(1)
S(1)–C(1)–C(2)	127.4(9)	F(1)–C(2)–C(1)	119.6(18)	F(8)–C(12)–C(11)	114.0(15)	C(17)–C(13)–C(18)	128.8(23)
C(2)–C(1)–C(6)	119.8(1)	C(1)–C(2)–C(3)	120.3(1)	C(14)–C(13)–C(17)	107.9(1)	C(15)–C(14)–C(19)	122.5(21)
F(1)–C(2)–C(3)	120.0(18)	F(2)–C(3)–C(4)	121.5(19)	C(14)–C(13)–C(18)	123.2(22)	C(16)–C(15)–C(20)	124.1(20)
F(2)–C(3)–C(2)	118.5(19)	C(3)–C(4)–C(5)	119.8(1)	C(13)–C(14)–C(15)	108.2(1)	C(14)–C(15)–C(16)	107.9(1)
C(2)–C(3)–C(4)	119.9(1)	F(3)–C(5)–C(6)	125.5(20)	C(13)–C(14)–C(19)	129.3(21)	C(14)–C(15)–C(20)	127.9(20)
F(3)–C(5)–C(4)	114.2(20)	F(4)–C(6)–C(1)	125.1(16)	C(15)–C(16)–C(21)	124.9(20)	C(15)–C(16)–C(17)	108.0(1)
C(4)–C(5)–C(6)	120.3(1)	C(1)–C(6)–C(5)	119.9(1)	C(17)–C(16)–C(21)	126.8(20)	C(13)–C(17)–C(22)	127.5(31)
F(4)–C(6)–C(5)	114.3(15)	S(2)–C(7)–C(12)	123.9(7)	C(13)–C(17)–C(16)	108.1(1)	C(16)–C(17)–C(22)	123.8(32)
S(2)–C(7)–C(8)	115.9(7)	F(5)–C(8)–C(7)	121.0(12)	C(24)–C(23)–C(28)	120.2(1)		

associated with four different conformers in solution; similarly four signals in the *m*-F region are observed at δ −160.5, −161.5, −163.0 and −164.0; in the *o*-F region four broad signals are observed at δ −124.5, −126.5, −133.0 and −134.5, without any coupling to Pt, consequently we propose the lack of solid-state interaction between these atoms in solution. On warming the sample all the *o*-F signals merge at approximately 0 °C and become broad at higher temperatures; for *p*- and *m*-F the signals change in relative intensity such that the signals at δ −156.0 and −164.0 become the most intense, due to a faster restricted rotation of the SC_6F_5 groups about C–S bond, by comparison with similar spectra reported previously.[9] Temperatures higher than 40 or lower than −40 °C were avoided because of the solvent limitations. A conductivity determination (0.5 ohm^{-1} cm^2 mol^{-1}, in acetone) was consistent with a non-electrolyte, thus there is [illegible] ionic dissociation of complex **2a**.

The ^{19}F NMR spectrum o[illegible]nplex **2b**, in $CDCl_3$ in the range −40 to 40 °C, shows bro[illegible]ill defined signals. On using $(CD_3)_2CO$ as solvent in the range −90 to 20 °C it was possible to obtain more defined signals. At −90 °C at least 13 signals were associated with *o*-F, in the range from δ −110.0 to −127.0, and 13 signals associated with *m*-F, in the range from δ −129.0 to −142.0 As for **2a**, we propose the lack of a Pt ··· F interaction as found in the solid state, because none of the observed signals in the *ortho* region could be assigned to platinum satellites. The conductivity determination (0.0 ohm^{-1} cm^2 mol^{-1}, in acetone) was consistent with a non-electrolyte, thus there is no ionic dissociation of complex **2b**. Therefore we propose again the occurrence at low temperature of a restricted rotation in the SC_6F_4H-*p* groups about the C–S bond, which on warming of the sample leads to equivalencing of signals.

Experimental

All operations were carried out under dry nitrogen using standard techniques. Solvents were purified and then distilled under nitrogen prior to use. Microanalyses were performed by Galbraith Laboratories, USA. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrometer with a Data Station 1300 over the 4000–200 cm^{-1} range as CsI pellets, NMR specta (in $CDCl_3$, at 25 °C unless otherwise specified) on a Varian VXR-300S spectrometer. 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. Compounds **1a** and **1b** were prepared as previously reported.[6] The salt $K_2[PtCl_4]$ was obtained from Aldrich.

Preparations.—$[Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2]$ **2a** ($R_F = C_6F_5$). The salt $K_2[PtCl_4]$ (0.115 g, 0.277 mmol) dissolved in deionized water (8 cm^3) was added to a solution of the complex $[Ir(C_5Me_5)(SR_F)_2]$ **1a** ($R_F = C_6F_5$) (0.20 g, 0.276 mmol) dissolved in acetone (8 cm^3) and stirred (25 °C, 6 h) giving a yellow precipitate. The reaction mixture was filtered, washed with water (2 × 3 cm^3) and dried *in vacuo* for 2 h, giving a yellow residue which was chromatographed on silica gel. Elution with chloroform–acetone (5 : 1 v/v) gave a yellow solid, **2a** (0.364 g, 77%) (Found: C, 30.9; H, 1.7; Cl, 3.8. $C_{44}H_{30}Cl_2F_{20}Ir_2PtS_4$ requires C, 30.8; H, 1.7; Cl, 4.1%). Conductivity 0.5 ohm^{-1} cm^2 mol^{-1}. NMR: ^1H, δ 1.6 (s, C_5Me_5); ^{19}F (−40 °C), δ −124.5 (br, *o*-F), −126.5 (br, *o*-F), −133.0 (br, *o*-F), −134.5 (br, *o*-F), −149.5 (br, *p*-F), −150.5 (t, *p*-F), −154.0 (t, *p*-F), −155.5 (br, *p*-F), −160.5 (br, *m*-F), −161.5 (br, *m*-F), −163.0 (br, *m*-F) and −164.0 (br, *m*-F).

$[Ir_2Pt(C_5Me_5)_2(\mu\text{-}SR_F)_4Cl_2]$ **2b** ($R_F = C_6F_4H$-*p*). This complex (0.343 g, 72%) was prepared analogously from **1b** (0.20 g, 0.29 mmol) (Found: C, 31.8; H, 2.1; Cl, 4.5. $C_{44}H_{34}Cl_2F_{16}Ir_2PtS_4$ requires C, 32.1; H, 2.1; Cl, 4.3%). Conductivity 0.0 ohm^{-1} cm^2 mol^{-1}. NMR: ^1H, δ 1.59 (s, C_5Me_5); ^{19}F (−40 °C), δ −126.8 (br, *o*-F), −133.2 (br, *o*-F), −135.0 (br, *o*-F), −138.0 (br, *m*-F), −140.0 (br, *m*-F) and −142.0 (br, *m*-F).

Crystal-structure Determinations.—$[Ir_2Pt(C_5Me_5)_2(\mu\text{-}SC_6F_5)Cl_2]$. *Crystal data* $C_{44}H_{30}Cl_2F_{20}Ir_2PtS_4$, *M* = 1717.36, crystallized from acetone–heptane as purple plate-like crystals of only moderate quality, crystal dimensions 0.18 × 0.8 × 0.07 mm, monoclinic space group *C*2/*c* (C^6_{2h}, no. 15), *a* = 43.23(7), *b* = 10.79(1), *c* = 23.93(5) Å, β = 115.75(9)°, *U* = 10 053(34) $Å^3$, *Z* = 8, D_c = 2.30 g cm^{-3}, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 84.40 cm^{-1}, *F*(000) = 6430.47.

Three-dimensional, room-temperature X-ray data were collected in the range $6.5 < 2\theta < 50.0°$ on a Stoe Stadi 2 diffractometer by the ω-scan method. The 2930 independent reflections (of 9471 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarization effects, and for absorption by Gaussian integration methods (minimum and maximum transmission coefficients 0.191 and 0.562). The data were collected for monoclinic space group *I*2/*a* with *a* = 23.93(5), *b* = 10.79(2), *c* = 39.28(8) Å, β = 82.482(17)° and transformed to monoclinic *C*2/*c* by the matrix (−101, 0–10, 100). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Initial refinements led to unacceptable geometries and thermal vibrations for the six- and five-membered rings. Consequently, constraints were applied to the ring framework atoms but not to the substituents. Hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting atoms, and refined in riding mode. Anisotropic refinement was allowed for all non-carbon atoms. Refinement converged at *R* = 0.0806 (*R'* = 0.0731, 372 parameters, mean and maximum δ/σ 0.009 and 0.041) minimum and maximum final electron density −4.28 and 2.12 e $Å^{-3}$ close to the metal atoms. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.0005F^2]$ was used in the latter stages of refinement. Complex scattering factors were taken from ref. 10 and from the program package SHELXTL[11] as implemented on a Data General DG30 computer. Atomic coordinates are in Table 3.

$[Ir_2Pt(C_5Me_5)_2(\mu\text{-}SC_6F_4H\text{-}p)_4Cl_2]\cdot C_6H_5Me$ **2b**. *Crystal data.* $C_{51}H_{42}Cl_2F_{16}Ir_2PtS_4$, *M* = 1737.54, crystallizes from toluene–carbon tetrachloride as orange hexagonal plate-like crystals of only moderate quality, approximate dimensions 0.65 × 0.70 × 0.10 mm, monoclinic, space group $P2_1/n$ (a non-standard setting of $P2_1/c$, C^5_{2h} no. 14), *a* = 12.180(11), *b* = 13.645(14), *c* = 16.493(10) Å, β = 95.86(6)°, *U* = 2726(4) $Å^3$, *Z* = 2, D_c = 2.100 g cm^{-3}, Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 77.71 cm^{-1}, *F*(000) = 1627.61.

Three-dimensional X-ray data were collected in the range $3.5 < 2\theta < 45°$ on a Nicolet R3 diffractometer by the ω-scan method (*h* 0–14, *k* 0–15, *l* −18 to 18). The 1864 independent reflections (of 4167 measured) for which $F/\sigma(F) < 3.0$ were corrected as for complex **2a** (minimum and maximum transmission coefficients 0.035 and 0.466). The structure was solved and refined as for **2a**. Constrained geometries were applied to the frameworks of the six- and five-membered rings and to a toluene molecule disordered near an inversion centre. Hydrogen atoms were treated as before. Anisotropic refinement converged at *R* = 0.0890 (*R'* = 0.0861, 279 parameters, mean and maximum δ/σ 0.023 and 0.101), minimum and maximum final electron density −1.607 and 2.531 e $Å^{-3}$ close to the metal atoms. A weighting scheme $w^{-1} = [\sigma^2(F) + 0.002\,13F^2]$ was used in the latter stages of refinement. Scattering factors as for **2a**. Atomic coordinates are in Table 4.

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

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Table 3 Atom coordinates (× 10^4) for complex **2a**

Atom	*x*	*y*	*z*
Ir(1)	1 256(1)	8 396(2)	−1 108(1)
Ir(2)	1 286(1)	6 724(2)	1 774(1)
Pt	1 305(1)	7 654(2)	375(1)
Cl(1)	1 251(3)	6 342(10)	−1 396(5)
Cl(2)	1 264(3)	8 734(9)	2 146(6)
S(1)	1 690(3)	7 958(9)	−57(5)
S(2)	908(3)	7 292(11)	752(5)
S(3)	889(3)	7 955(10)	−617(5)
S(4)	1 704(3)	7 354(10)	−1 405(5)
C(1)	1 920(7)	6 578(22)	−91(12)
C(2)	2 113	6 651	−429
C(3)	2 279	5 599	−504
C(4)	2 251	4 474	−242
C(5)	2 057	4 401	95
C(6)	1 892	5 453	170
C(7)	666(7)	8 655(22)	743(12)
C(8)	763	9 825	628
C(9)	566	10 861	608
C(10)	271	10 728	703
C(11)	173	9 559	817
C(12)	371	8 522	837
C(13)	1 002(6)	5 054(29)	1 790(12)
C(14)	1 081	5 735	2 343
C(15)	1 444	5 812	2 674
C(16)	1 589	5 180	2 324
C(17)	1 316	4 711	1 778
C(18)	1 321(13)	3 896(43)	1 267(19)
C(19)	1 957(12)	4 835(43)	2 510(20)
C(20)	1 641(11)	6 432(35)	3 315(15)
C(21)	849(11)	6 328(39)	2 577(18)
C(22)	645(12)	4 797(42)	1 313(19)
C(23)	1 534(6)	9 909(28)	−1 251(13)
C(24)	1 404	9 159	−1 792
C(25)	1 040	9 163	−2 041
C(26)	945	9 915	−1 653
C(27)	1 251	10 375	−1 165
C(28)	1 903(14)	10 199(48)	−891(22)
C(29)	1 630(12)	8 518(41)	−2 060(19)
C(30)	762(12)	8 585(42)	−2 624(18)
C(31)	628(14)	10 410(49)	−1 652(23)
C(32)	1 287(14)	11 294(45)	−636(20)
C(33)	648(7)	6 614(23)	−921(11)
C(34)	773	5 427	−712
C(35)	570	4 393	−988
C(36)	243	4 545	−1 472
C(37)	119	5 732	−1 681
C(38)	321	6 767	−1 405
C(39)	1 908(7)	8 812(19)	1 779(11)
C(40)	2 101	8 757	2 421
C(41)	2 271	9 811	2 748
C(42)	2 248	10 920	2 433
C(43)	2 055	10 975	1 791
C(44)	1 885	9 921	1 464
F(1)	2 138(7)	7 685(20)	−672(11)
F(2)	2 442(7)	5 695(31)	−833(13)
F(3)	2 397(8)	3 491(23)	−357(11)
F(4)	2 038(8)	3 361(24)	334(12)
F(5)	1 725(7)	5 276(21)	522(11)
F(6)	1 031(8)	10 100(21)	548(16)
F(7)	628(10)	11 976(24)	470(16)
F(8)	78(8)	11 773(36)	738(13)
F(9)	−96(8)	9 370(44)	954(15)
F(10)	290(9)	7 425(28)	940(18)
F(11)	1 061(7)	5 189(20)	−279(12)
F(12)	686(9)	3 314(24)	−769(13)
F(13)	47(7)	3 556(26)	−1 743(14)
F(14)	−193(7)	5 885(29)	−2 154(12)
F(15)	207(7)	7 810(24)	−1 637(12)
F(16)	2 128(6)	7 721(21)	2 731(9)
F(17)	2 447(7)	9 729(26)	3 333(13)
F(18)	2 397(7)	11 898(23)	2 770(11)
F(19)	2 028(7)	12 023(20)	1 505(11)
F(20)	1 712(8)	10 037(23)	839(12)

Table 4 Atom coordinates (× 10^4) for complex **2b**

Atom	*x*	*y*	*z*
Pt	0	0	0
Ir(1)	1417(1)	1943(1)	1055(1)
S(1)	145(8)	1666(5)	−118(5)
S(2)	1354(8)	175(6)	1060(5)
Cl(1)	2911(8)	1944(7)	269(6)
F(1)	1322(31)	531(17)	−1406(17)
F(2)	2123(35)	1269(28)	−2709(19)
F(3)	957(40)	4333(19)	−2046(20)
F(4)	64(25)	3604(15)	−772(16)
F(5)	3425(18)	162(17)	2114(11)
F(6)	5313(22)	−697(23)	1890(14)
F(7)	3957(19)	−1613(21)	−729(12)
F(8)	2042(19)	−925(21)	−506(12)
C(1)	746(20)	2035(19)	−995(13)
C(2)	1250	1442	−1534
C(3)	1642	1844	−2225
C(4)	1530	2839	−2377
C(5)	1026	3431	−1838
C(6)	634	3029	−1147
C(7)	2645(16)	−340(14)	804(15)
C(8)	3527	−289	1411
C(9)	4541	−694	1278
C(10)	4673	−1149	540
C(11)	3791	−1200	−67
C(12)	2777	−795	65
C(13)	2211(21)	2938(23)	1967(17)
C(14)	1427	3465	1444
C(15)	375	3049	1505
C(16)	508	2264	2066
C(17)	1642	2196	2351
C(18)	3439(37)	3131(41)	2018(29)
C(19)	1585(38)	4264(25)	946(22)
C(20)	−716(31)	3399(33)	1118(23)
C(21)	−449(42)	1657(40)	2364(28)
C(22)	2056(60)	1589(33)	2987(22)
C(23)	−757(66)	750(74)	4659(45)
C(24)	−1343	−66	4363
C(25)	−922	−994	4538
C(26)	86	−1105	5009
C(27)	673	−287	5306
C(28)	252	641	5131
C(29)	1785	−409	5826

Atoms C(23) to C(29) belong to a half occupancy toluene molecule.

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References

1 P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121; I. G. Dance, *Polyhedron*, 1986, **5**, 1037; R. Poli, *Chem. Rev.*, 1991, **91**, 509.
2 Z. Hou, Y. Ozawa and K. Isobe, *Chem. Lett.*, 1990, 1863 and refs. therein; A. H. Janowicz and R. G. Bergman, *J. Am. Chem. Soc.*, 1982, **104**, 352; J. K. Hoyano and W. A. G. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 3723; D. S. Glueck, F. J. Hollander and R. G. Bergman, *J. Am. Chem. Soc.*, 1989, **111**, 2719.

3 M. J. H. Russell, C. White and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1978, 849; D. P. Klein, G. M. Kloster and R. G. Bergman, *J. Am. Chem. Soc.*, 1990, **112**, 2022.

4 J. W. Kang and P. M. Maitlis, *J. Organomet. Chem.*, 1971, **30**, 127; P. M. Maitlis, *J. Organomet. Chem.*, 1981, **10**, 1; *Acc. Chem. Res.*, 1978, **11**, 301.

5 D. Cruz-Garritz, J. Garcia-Alejandre, H. Torrens, C. Alvarez, R. A. Toscano, R. Poilblanc and A. Thorez. *Transition Met. Chem.*, 1991, **16**, 130; D. Cruz-Garritz, P. Sosa, H. Torrens, A. Hills, D. L. Hughes and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1989, 419; C. Claver, A. M. Masdeu, N. Ruiz, C. Foces-Foces, F. H. Cano, M. C. Aprenda, L. A. Oro, J. Garcia-Alejandre and H. Torrens, *J. Organomet. Chem.*, 1990, **398**, 177.

6 J. J. Garcia, H. Torrens, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1991, 74; J. J. Garcia, H. Torrens, H. Adams, N. A. Bailey, A. Shacklady and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1993, 1529.

7 R. M. Catala, D. Cruz-Garritz, A. Hills, D. L. Hughes, R. L. Richards, P. Sosa and H. Torrens, *J. Chem. Soc., Chem. Commun.*, 1987, 261.

8 See, for example, R. Uson and J. Fornies, *Inorg. Chim. Acta.*, 1992, **198–200**, 165; R. Uson, J. Fornies and M. Tomas, *J. Organomet. Chem.*, 1988, **358**, 525.

9 W. A. Wan Abu Bakar, J. K. Davison, W. E. Lindsell, K. J. McCullough and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1989, 991.

10 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

11 G. M. Sheldrick, SHELXTL, An integrated system for solving, refining and displaying crystal structures from diffraction data, Revision 5.1, University of Göttingen, 1985.

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