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Ru–X–C (X = F or H) interactions in complex compounds. Preparation and crystal structures of $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$ and $[Ru(SC_6F_5)_2\{PC_6H_4(H\text{-}2)(C_6H_5)_2\}_2]$

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Abstract

The diamagnetic complex $[Ru(SR)_2(PPh_3)_2]$ and the paramagnetic compounds $[Ru(SR)_3(PR'_3)_2]$ ($R = C_6F_5$, C_6F_4H, C_6FH_4, or C_6H_5; $PR'_3 = PPh_3$, PMe_2Ph or PEt_2Ph) have been prepared by treatment of $[RuCl_2(PPh_3)_3]$ or $[RuCl_3(PR'_3)_3]$, respectively, with $[Pb(SR)_2]$ in acetone or tetrahydrofuran. An X-ray diffraction study on $[Ru(SC_6F_5)_2\{PC_6H_4(H\text{-}2)(C_6H_5)_2\}_2]$ has revealed a pseudo-octahedral structure, apparently with two C–H–Ru interactions. The complexes $[Ru(SR)_3(PR'_3)_2]$ have μ_{eff} in the range 1.8–1.9 BM and EPR spectra are reported. An X-ray study of $[Ru\{SC_6F_4(F\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$ has shown that it has essentially octahedral geometry, involving a C–F–Ru interaction.

Thiolate complexes are of much current interest, not only because of their biological and catalytic implications but also because thiols and thiolate anions undergo a wide variety of reactions with metal species [1]. The chemistry of ruthenium is prominent in studies of C–H bond activation and of unsaturated complexes which have potential as catalysts. Here we describe work which has relevance in both of these areas.

In continuation of our studies of thiolate complexes of the transition metals [2], we have been developing ruthenium-thiolate chemistry, and have found that bulky thiolate ligands are particularly effective in creating potentially unsaturated centres, leading to complexes which have intramolecular ruthenium–ligand interactions.

Table 1

Thiolate complexes of ruthenium

Compound	Yield (%)	Colour	Analyses (found (calcd.) (%))		m.p. [a] (°C)	IR bands (cm^{-1}) [b]		EPR [c]
			C	H		SR	PR$_3$	
[Ru(SC$_6$F$_5$)$_2$(PPh$_3$)$_2$]	90	purple	55.4 (56.5)	2.7 (2.9)	160–167	1082, 982, 845	1431, 1084, 519	–
[Ru(SC$_6$H$_5$)$_2$(PPh$_3$)$_2$]	90	green-brown	58.4 (58.8)	4.2 (4.1)	150–155	1021, 750, 681	1432, 1088, 535	–
[Ru(SC$_6$F$_5$)$_3$(PPh$_3$)$_2$] [d]	65	green	52.4 (52.0)	3.0 (3.0)	188–202	1084, 983, 850	1434, 1089, 520	–
[Ru(SC$_6$F$_5$)$_3$(PMe$_2$Ph)$_2$] [e]	64	green	40.9 (41.9)	2.0 (2.2)	172–178	1085, 980, 855	940, 688, 510	g_{11} 2.034, g_1 2.143 (axial spectrum)
[Ru(SC$_6$F$_5$)$_3$(PEt$_2$Ph)$_2$] [f]	32	green	41.2 (40.6)	2.5 (2.7)	130–135	1080, 974, 857	1030, 700, 500	g 2.209–1.982, g_m 2.172 (complex spectrum) [f]
[Ru(SC$_6$F$_4$H)$_3$(PPh$_3$)$_2$] [h]	61	green	55.1 (55.5)	3.7 (3.8)	137–139	1120, 918, 898	1084, 725, 698, 548	g_1 2.194, g_2 2.113, g_3 2.013 (rhombic spectrum)
[Ru(SC$_6$FH$_4$)$_3$(PPh$_3$)$_2$]	34	green	64.4 (64.4)	5.2 (4.2)	> 250	1152, 1087, 821	1084, 719, 520	–

[a] Uncorrected, in sealed tubes under dinitrogen, with decomposition. [b] Nujol mull spectra. [c] in approx. 10^{-3} molar thf solution at 150 K. [d] Molecule has 2MeOH of crystallisation. [e] μ_{eff} 1.90 BM. [f] μ_{eff} 1.85 BM. [g] Possibly isomers in solution. [h] μ_{eff} 1.86 BM.

The 14-electron species $\{RuCl_2(PPh_3)_2\}$ is a key intermediate in the mechanisms proposed for processes catalysed by $[RuCl_2(PPh_3)_3]$ [3] and we sought to obtain an analogue of this species containing bulky thiolate groups. We also sought to prepare unsaturated ruthenium(III) species, by metathesis of bulky thiolate groups into the series $[RuCl_3(PR'_3)_3]$. In both cases potentially unsaturated complexes $[Ru(SR)_2(PPh_3)_2]$ and $[Ru(SR)_3(PR'_3)_2]$ were obtained, in which the unsaturation is relieved by intramolecular Ru–X–C interactions (X = H or F, respectively) as described below. Preliminary accounts have appeared [4].

Results and discussion

A. Compounds of ruthenium(II), Ru–H–C interactions

Treatment of $[RuCl_2(PPh_3)_3]$ [5] with $Pb(SR)_2$ ($R = C_6F_5$ or C_6H_5) in acetone gave the diamagnetic complexes $[Ru(SR)_2(PPh_3)_2]$, whose physical properties are shown in Table 1. They are analogues of $[\{RuX_2(L_2)\}_2]$ (X = halogen or H; $L = PPh_3$, or $AsPh_3$) [6], but unlike these dimers, the thiolate compounds are monomeric in the solid state, presumably because the bulk of the thiolate and phosphine groups prevents dimerisation; moreover, there are Ru–H–C interactions with phenyl groups of the two phosphine ligands, as revealed by X-ray crystallography.

The crystal of $[\overline{\mathrm{Ru(SC_6F_5)_2\{P(C_6H_5)_2C_6H_4(H}}\mathrm{\text{-}2)\}_2}]$ (**A**) is shown in Fig. 1, and atomic coordinate and bond dimensions are given in Tables 2 and 3. The coordination about ruthenium shows pseudo two-fold symmetry, and can be considered to be greatly distorted octahedral, consisting of two *trans*-thiolate groups and two *cis*-phosphines, with the remaining two coordination sites occupied by hydrogens from the *ortho*-carbon of a phenyl group of each of the phosphine ligands (a weak, 'agostic', interaction) [7]. The next-nearest atoms to the ruthenium are a pair of fluorine atoms, but with Ru–F at 3.73 and 3.34 Å, we do not consider these atoms to be bonded to the ruthenium but instead to be involved in the tight packing of ligands. The Ru–P–C angles in the chelating rings are, at about 103°, much smaller than the other Ru–P–C angles (116.9–122.6°), and reflect the strains involving in achieving the agostic bonding; these must be overcome by the attractive Ru–H–C interaction. Filling the vacant octahedral sites of the metal must also be energetically favourable.

The Ru–H(12a) and Ru–H(26a) distances (2.86 and 2.80 Å, respectively) are longer than the distance reported for a similar interaction in the precursor complex $[RuCl_2(PPh_3)_3]$ (2.59 Å) [5], but similar to that in $[RuHCl(PPh_3)_3]$ (2.85 Å) [8], and are close to the values expected from Van der Waals radii [9]. The structure of the precursor analogue $[RuCl_2(Ph_2PCH_2SiMe_3)_3]$ has also been reported recently [10], but there appears to be no significant (C–H) interaction with the five-coordinate ruthenium in this case.

The Ru–P distances of **A** (2.213(5) and 2.215(4) Å) are shorter than those *cis* to H in $[RuCl_2(PPh_3)_3]$ (2.37 and 2.41 Å) [5] but very similar to that *trans* to H (2.23 Å) in the same structure. The distances and angles in the PPh_3 rings are similar to those found in other triphenylphosphine derivatives [5].

The deviation from 180° of the S(3)–Ru–S(4) angle [157.8(2)°] could be due to interaction between the sulphur and fluorine atoms of the SC_6F_5 ligands and the hydrogen atoms of the phenyl groups in the PPh_3 ligands; the Ru-bound H atoms,

Table 2

Final atomic coordinates, (fractional × 10^4), for $[\overline{\mathrm{Ru(SC_6F_5)_2\{PC_6H_4(H}}\mathrm{\text{-}2)(C_6H_5)_2\}_2}]$ (**A**) (esd's are in parentheses)

Atom	*x*	*y*	*z*
Ru	1901.0(5)	1355(1)	1246.0(5)
P(1)	1654(2)	2871(3)	956(2)
C(11a)	2343(7)	3338(12)	871(6)
C(12a)	2635(7)	2701(13)	680(6)
C(13a)	3198(8)	2947(15)	633(6)
C(14a)	3409(9)	3897(15)	761(6)
C(15a)	3085(9)	4515(17)	927(7)
C(16a)	2548(8)	4270(14)	1009(6)
C(11b)	1438(7)	3781(12)	1338(5)
C(12b)	868(8)	4035(13)	1239(6)
C(13b)	688(9)	4669(14)	1541(7)
C(14b)	1069(8)	5016(14)	1940(7)
C(15b)	1647(8)	4771(13)	2055(7)
C(16b)	1834(8)	4150(13)	1756(6)
C(11c)	1106(7)	3093(13)	371(6)
C(12c)	649(7)	2496(14)	212(6)
C(13c)	224(8)	2676(15)	−224(7)
C(14c)	270(10)	3519(17)	−472(8)
C(15c)	724(10)	4135(18)	−323(8)
C(16c)	1159(8)	3954(15)	127(7)
P(2)	1217(2)	879(3)	1567(2)
C(21a)	1336(7)	−458(12)	1649(5)
C(22a)	893(8)	−1158(14)	1585(6)
C(23a)	1049(9)	−2161(16)	1655(7)
C(24a)	1606(9)	−2466(16)	1755(7)
C(25a)	2046(9)	−1800(14)	1836(6)
C(26a)	1910(7)	−790(13)	1788(5)
C(21b)	1201(7)	1303(15)	2144(6)
C(22b)	1304(7)	2260(15)	2286(7)
C(23b)	1259(8)	2643(18)	2727(8)
C(24b)	1107(10)	2042(20)	3020(10)
C(25b)	965(11)	1069(22)	2887(10)
C(26b)	1016(10)	712(22)	2433(9)
C(21c)	462(6)	1004(11)	1194(6)
C(22c)	246(7)	404(12)	808(6)
C(23c)	−320(8)	508(13)	508(6)
C(24c)	−657(8)	1233(14)	606(7)
C(25c)	−454(8)	1885(15)	965(7)
C(26c)	127(8)	1750(13)	1283(6)
S(3)	1595(2)	641(3)	482(2)
C(31)	1994(7)	−502(12)	562(6)
C(32)	1734(8)	−1401(15)	583(6)
F(32)	1184(4)	−1459(7)	574(3)
C(33)	2023(10)	−2324(20)	628(7)
F(33)	1762(6)	−3165(9)	638(5)
C(34)	2590(11)	−2262(19)	645(7)
F(34)	2908(7)	−3146(10)	642(6)
C(35)	2880(10)	−1406(19)	608(7)
F(35)	3440(5)	−1399(11)	608(6)
C(36)	2592(10)	−513(18)	576(7)
F(36)	2856(5)	326(9)	558(4)
S(4)	2532(2)	1750(3)	2001(2)

Table 2 (continued)

Atom	*x*	*y*	*z*
C(41)	3213(7)	1757(13)	1894(6)
C(42)	3458(8)	966(15)	1745(6)
F(42)	3156(4)	101(8)	1653(4)
C(43)	4007(10)	961(18)	1683(8)
F(43)	4210(5)	128(11)	1545(6)
C(44)	4312(11)	1808(19)	1781(8)
F(44)	4863(5)	1839(13)	1730(6)
C(45)	4118(11)	2655(18)	1933(8)
F(45)	4411(5)	3522(11)	2010(6)
C(46)	3528(9)	2642(16)	1970(7)
F(46)	3350(4)	3480(8)	2116(4)
H(12a)	2463	2050	567
H(26a)	2226	−299	1851

H(12a) and H(26a), are each ca. 2.8 Å from the S atoms, S(3) and S(4) respectively and ca. 2.5 Å from the *ortho*-F atoms F(36) and F(42) (Fig. 1).

The ^{1}H NMR spectra of the complexes were uninformative in that only a broad phenyl-proton absorption in the 6.5–7.5 ppm region (rel. $SiMe_4$) was observed, with no resonance assignable to the agostic protons.

B. Compounds of ruthenium(III), Ru–F–C interactions

Treatment of *mer*-$[RuCl_3(PR'_3)_3]$ ($PR'_3 = PMe_2Ph$ or PEt_2Ph), $[RuCl_3(PPh_3)_2]\cdot MeNO_2$, $[RuCl_3(PPh_3)_2]\cdot MeOH$, or $[RuCl_2(PPh_3)_3]$ with $Pb(SR)_2$ ($R = C_6F_5$, C_6F_4H, C_6FH_4 or C_6H_5) in acetone or tetrahydrofuran (thf) produced green-brown

(*Continued on p. 226*)

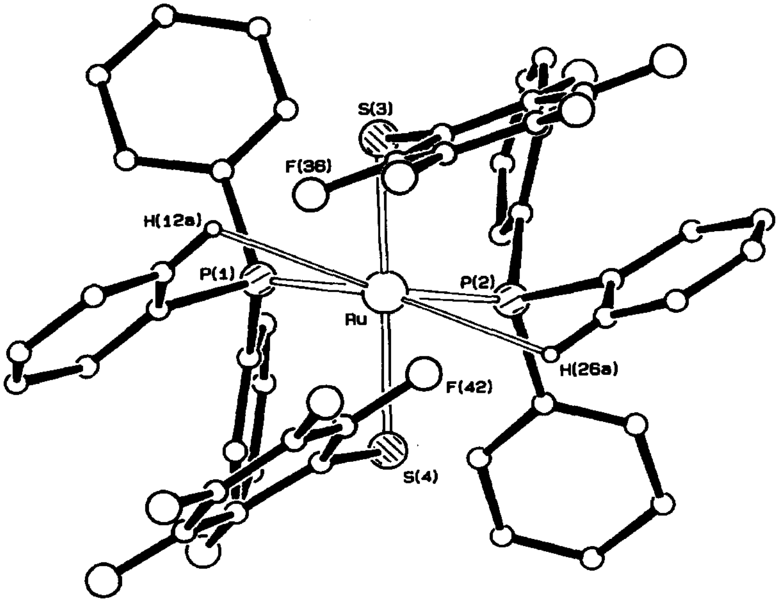

Fig. 1. A molecule of $[\overline{\mathrm{Ru(SC_6F_5)_2\{PC_6H_4(H}}\mathrm{\text{-}2)(C_6H_5)_2\}_2}]$ (A) viewed down the axis of pseudo-two-fold symmetry.

Table 3

Molecular dimensions in **A**; bond lengths (Å) and angles (°) (esd's are in parentheses)

(a) Dimensions about the Ru atom			
Ru–P(1)	2.213(5)		
Ru–P(2)	2.215(4)		
Ru–S(3)	2.334(5)		
Ru–S(4)	2.333(4)		
Ru–h(12a)	2.86		
Ru–h(26a)	2.80		
P(1)–Ru–P(2)	106.2(2)	H(12a)–Ru–P(2)	161.5
P(1)–Ru–S(3)	92.2(2)	H(12a)–Ru–S(3)	63.4
P(2)–Ru–S(3)	102.9(2)	H(12a)–Ru–S(4)	105.8
P(1)–Ru–S(4)	100.2(2)	H(26a)–Ru–P(1)	164.1
P(2)–Ru–S(4)	91.2(2)	H(26a)–Ru–P(2)	66.9
S(3)–Ru–S(4)	157.8(2)	H(26a)–Ru–S(3)	103.1
		H(26a)–Ru–S(4)	66.6
H(12a)–Ru–P(1)	64.2	H(12a)–Ru–H(26a)	126.4
(b) Bond lengths in the ligands			
P(1)–C(11a)	1.854(15)	P(2)–C(21a)	1.819(16)
P(1)–C(11b)	1.830(16)	P(2)–C(21b)	1.787(17)
P(1)–C(11c)	1.843(16)	P(2)–C(21c)	1.824(15)
C(11a)–C(12a)	1.330(19)	C(21a)–C(22a)	1.389(20)
C(11a)–C(16a)	1.358(20)	C(21a)–C(26a)	1.391(18)
C(12a)–C(13a)	1.436(20)	C(22a)–C(23a)	1.395(23)
C(13a)–C(14a)	1.380(22)	C(23a)–C(24a)	1.344(22)
C(14a)–C(15a)	1.323(23)	C(24a)–C(25a)	1.350(22)
C(15a)–C(16a)	1.420(22)	C(25a)–C(26a)	1.390(20)
C(11b)–C(12b)	1.356(19)	C(21b)–C(22b)	1.348(21)
C(11b)–C(16b)	1.394(19)	C(21b)–C(26b)	1.327(26)
C(12b)–C(13b)	1.384(21)	C(22b)–C(23b)	1.419(23)
C(13b)–C(14b)	1.331(21)	C(23b)–C(24b)	1.303(27)
C(14b)–C(15b)	1.368(20)	C(24b)–C(25b)	1.374(30)
C(15b)–C(16b)	1.373(20)	C(25b)–C(26b)	1.449(30)
C(11c)–C(12c)	1.327(19)	C(21c)–C(22c)	1.356(18)
C(11c)–C(16c)	1.381(21)	C(21c)–C(26c)	1.357(19)
C(12c)–C(13c)	1.396(21)	C(22c)–C(23c)	1.388(19)
C(13c)–C(14c)	1.363(23)	C(23c)–C(24c)	1.349(20)
C(14c)–C(15c)	1.332(25)	C(24c)–C(25c)	1.339(21)
C(15c)–C(16c)	1.435(23)	C(25c)–C(26c)	1.439(21)
S(3)–C(31)	1.785(17)	S(4)–C(41)	1.755(17)
C(31)–C(32)	1.367(20)	C(41)–C(42)	1.346(20)
C(31)–C(36)	1.426(22)	C(41)–C(46)	1.401(21)
C(32)–F(32)	1.318(17)	C(42)–F(42)	1.351(18)
C(32)–C(33)	1.405(24)	C(42)–C(43)	1.385(23)
C(33)–F(33)	1.294(23)	C(43)–F(43)	1.329(23)
C(33)–C(34)	1.351(24)	C(43)–C(44)	1.335(25)
C(34)–F(34)	1.411(24)	C(44)–F(44)	1.378(24)
C(34)–C(35)	1.365(25)	C(44)–C(45)	1.351(25)
C(35)–F(35)	1.346(23)	C(45)–F(45)	1.342(23)
C(35)–C(36)	1.370(24)	C(45)–C(46)	1.452(23)
C(36)–F(36)	1.300(21)	C(46)–F(46)	1.306(19)

Table 3 (continued)

(c) Valence angles in the ligands.

Ru–P(1)–C(11a)	102.3(5)	Ru–P(2)–C(21a)	103.4(5)
Ru–P(1)–C(11b)	118.1(5)	Ru–P(2)–C(21b)	122.2(6)
C(11a)–P(1)–C(11b)	106.5(7)	C(21a)–P(2)–C(21b)	103.7(8)
Ru–P(1)–C(11c)	122.6(6)	Ru–P(2)–C(21c)	116.9(5)
C(11a)–P(1)–C(11c)	104.0(7)	C(21a)–P(2)–C(21c)	105.0(7)
C(11b)–P(1)–C(11c)	101.7(7)	C(21b)–P(2)–C(21c)	103.7(7)
P(1)–C(11a)–C(12a)	116.4(13)	P(2)–C(21a)–C(22a)	124.3(13)
P(1)–C(11a)–C(16a)	122.0(14)	P(2)–C(21a)–C(26a)	117.1(13)
C(12a)–C(11a)–C(16a)	121.7(17)	C(22a)–C(21a)–C(26a)	118.6(16)
C(11a)–C(12a)–C(13a)	121.4(17)	C(21a)–C(22a)–C(23a)	117.9(19)
C(12a)–C(13a)–C(14a)	117.9(19)	C(22a)–C(23a)–C(24a)	122.2(21)
C(13a)–C(14a)–C(15a)	117.8(21)	C(23a)–C(24a)–C(25a)	120.9(21)
C(14a)–C(15a)–C(16a)	125.6(22)	C(24a)–C(25a)–C(26a)	118.7(20)
C(11a)–C(16a)–C(15a)	115.5(19)	C(21a)–C(26a)–C(25a)	121.5(18)
P(1)–C(11b)–C(12b)	119.3(13)	P(2)–C(21b)–C(22b)	122.7(15)
P(1)–C(11b)–C(16b)	121.7(13)	P(2)–C(21b)–C(26b)	120.9(19)
C(12b)–C(11b)–C(16b)	118.8(16)	C(22b)–C(21b)–C(26b)	115.9(21)
C(11b)–C(12b)–C(13b)	120.3(18)	C(21b)–C(22b)–C(23b)	124.5(20)
C(12b)–C(13b)–C(14b)	120.5(20)	C(22b)–C(23b)–C(24b)	118.9(25)
C(13b)–C(14b)–C(15b)	121.0(21)	C(23b)–C(24b)–C(25b)	119.8(30)
C(14b)–C(15b)–C(16b)	119.2(19)	C(24b)–C(25b)–C(26b)	119.3(31)
C(11b)–C(16b)–C(15b)	120.2(17)	C(21b)–C(26b)–C(25b)	121.4(28)
P(1)–C(11c)–C(12c)	121.0(14)	P(2)–C(21c)–C(22c)	120.6(13)
P(1)–C(11c)–C(16c)	117.5(14)	P(2)–C(21c)–C(26c)	119.7(13)
C(12c)–C(11c)–C(16c)	121.2(17)	C(22c)–C(21c)–C(26c)	119.6(16)
C(11c)–C(12c)–C(13c)	121.2(19)	C(21c)–C(22c)–C(23c)	121.7(17)
C(12c)–C(13c)–C(14c)	118.3(21)	C(22c)–C(23c)–C(24c)	118.4(19)
C(13c)–C(14c)–C(15c)	121.9(24)	C(23c)–C(24c)–C(25c)	122.4(20)
C(14c)–C(15c)–C(16c)	119.8(24)	C(24c)–C(25c)–C(26c)	118.5(19)
C(11c)–C(16c)–C(15c)	117.3(20)	C(21c)–C(26c)–C(25c)	119.2(18)
Ru–H(12a)–C(12a)	107.4	Ru–H(26a)–C(26a)	111.1
Ru–S(3)–C(31)	102.9(5)	Ru–S(4)–C(41)	102.2(6)
S(3)–C(31)–C(32)	121.8(14)	S(4)–C(41)–C(42)	125.0(15)
S(3)–C(31)–C(36)	120.7(15)	S(4)–C(41)–C(46)	117.8(15)
C(32)–C(31)–C(36)	117.4(18)	C(42)–C(41)–C(46)	117.2(17)
C(31)–C(32)–F(32)	121.4(18)	C(41)–C(42)–F(42)	118.6(17)
C(31)–C(32)–C(33)	124.1(19)	C(41)–C(42)–C(43)	124.9(21)
F(32)–C(32)–C(33)	114.5(19)	F(42)–C(42)–C(43)	116.5(19)
C(32)–C(33)–F(33)	122.7(22)	C(42)–C(43)–F(43)	119.6(22)
C(32)–C(33)–C(34)	114.4(25)	C(42)–C(43)–C(44)	116.8(25)
F(33)–C(33)–C(34)	122.9(26)	F(43)–C(43)–C(44)	123.5(24)
C(33)–C(34)–F(34)	119.4(25)	C(43)–C(44)–F(44)	119.1(24)
C(33)–C(34)–C(35)	125.6(27)	C(43)–C(44)–C(45)	124.3(27)
F(34)–C(34)–C(35)	114.5(23)	F(44)–C(44)–C(45)	116.6(23)
C(34)–C(35)–F(35)	122.7(24)	C(44)–C(45)–F(45)	124.5(23)
C(34)–C(35)–C(36)	118.7(24)	C(44)–C(45)–C(46)	117.5(25)
F(35)–C(35)–C(36)	118.6(23)	F(45)–C(45)–C(46)	117.7(21)
C(31)–C(36)–C(35)	119.7(22)	C(41)–C(46)–C(45)	119.0(21)
C(31)–C(36)–F(36)	119.3(20)	C(41)–C(46)–F(46)	124.4(18)
C(35)–C(36)–F(36)	121.0(22)	C(45)–C(46)–F(46)	116.3(19)

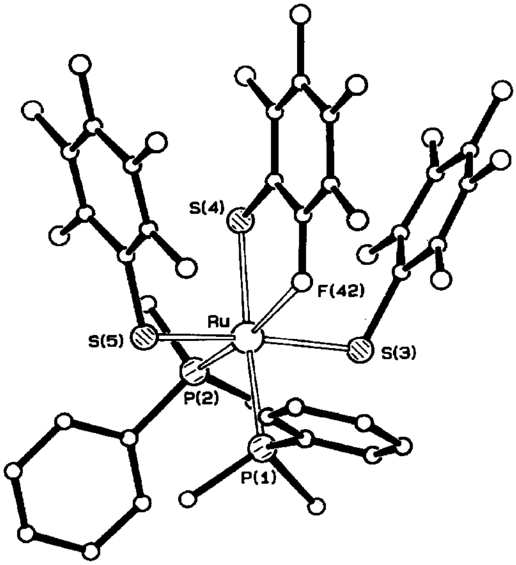

Fig. 2. A molecule of $[\overline{\mathrm{Ru}\{\mathrm{SC_6F_4(F}}\text{-}2)\}(\mathrm{SC_6F_5})_2(\mathrm{PMe_2Ph})_2]$ (**B**).

solutions. After filtering off of the precipitated $PbCl_2$, work-up and recrystallisation from methanol gave green crystals of $[\mathrm{Ru(SR)_3(PR'_3)_2}]$, whose physical properties are shown in Table 1. It is not clear how the ruthenium(II) precursor $[\mathrm{RuCl_2(PPh_3)_3}]$ was oxidised to $[\mathrm{Ru(SR)_3(PPh_3)_2}]$.

These complexes are paramagnetic, with magnetic moments in the range 1.8–1.9 BM and EPR resonances as detailed in Table 1. Again the ruthenium in these complexes is potentially unsaturated, but the crystal structure of $[\overline{\mathrm{Ru}\{\mathrm{SC_6F_4(F}}\text{-}2)\}(\mathrm{SC_6F_5})_2(\mathrm{PMe_2Ph})_2]$ (**B**) reveals that this unsaturation is relieved, at least in this particular complex and most probably in its analogues, by an Ru–C–F interaction. The structure of **B** is shown in Fig. 2, and details of atomic coordinates and bond parameters are given in Tables 4 and 5.

The coordination about ruthenium is approximately octahedral, this being achieved by the interaction of a 2-fluorine of one SC_6F_5 ligand with the metal to create an S–F chelate ligand. The Ru–F distance of 2.489(6) Å (cf. calc. 2.7 Å, for F (Van der Waals' radius) + Ru (atomic radius) [4] implies a moderate bond strength for this interaction, there, is however, no fluorine (or phosphorus) hyperfine structure in the EPR spectrum in frozen solution. The EPR spectrum of **B** is as expected for an $S = \frac{1}{2}$ spin system with axial symmetry. Its analogues have rather more complicated spectra; g values are given in Table 1.

A further feature of the structure of **B** is that the C_6F_5 groups attached to S(3) and S(5) are eclipsed about the S--S vector; they are thus aligned with the central chelating ligand to form, as close as possible, a stacked pattern. This type of packing is known for other SC_6F_5 complexes [2,13].

As might be expected, Ru–S(4) [2.419(3)Å], trans to phosphorus, is longer than the *trans*-Ru–S distances, which are both close to 2.32 Å. The Ru–P(2) distance (2.800(3) Å), *trans* to F, is significantly shorter than Ru–P(1) (2.364(3) Å), *trans* to S(4), no doubt as a consequence of the very weak *trans* influence of the C–F group.

Interactions between halocarbons and metal ions in complexes are rare; infrared evidence for halocarbon bonding has been reported and Crabtree has shown that

(*Continued on p. 229*)

Table 4. Final atomic coordinates (fractional × 10^4) for $[\overline{\text{Ru}\{\text{SC}_6\text{F}_4(\text{F}}\text{-2)}\}(\text{SC}_6\text{F}_5)_2(\text{PMe}_2\text{Ph})_2]$ (**B**) (esd's are in parentheses)

Atom	*x*	*y*	*z*
Ru	2550.5(5)	3978.5(5)	2267.9(3)
P(1)	1268(2)	3985(2)	2459(1)
C(11)	825(6)	4174(7)	1758(5)
C(12)	794(6)	3630(7)	1350(6)
C(13)	487(8)	3722(9)	810(6)
C(14)	168(8)	4396(11)	684(7)
C(15)	175(10)	4947(9)	1082(7)
C(16)	499(7)	4831(7)	1629(6)
C(17)	896(6)	4672(6)	2956(4)
C(18)	808(5)	3155(5)	2702(5)
P(2)	2871(2)	3725(2)	3211(1)
C(21)	2329(6)	3030(7)	3606(5)
C(22)	2459(7)	2298(7)	3478(5)
C(23)	2054(9)	1756(8)	3768(7)
C(24)	1565(9)	1950(10)	4185(6)
C(25)	1426(8)	2676(9)	4310(6)
C(26)	1820(7)	3223(8)	4033(5)
C(27)	3807(6)	3385(7)	3274(5)
C(28)	2868(7)	4527(7)	3692(5)
S(3)	2460(2)	5252(1)	2383(1)
C(31)	3134(7)	5695(6)	1958(7)
C(32)	3823(9)	5865(8)	2179(7)
F(32)	3986(4)	5695(4)	2736(4)
C(33)	4345(10)	6246(10)	1853(11)
F(33)	5008(5)	6400(5)	2112(5)
C(34)	4195(15)	6433(9)	1300(11)
F(34)	4727(7)	6788(5)	984(5)
C(35)	3549(14)	6231(9)	1038(8)
F(35)	3418(7)	6403(5)	484(4)
C(36)	3020(9)	5904(8)	1375(8)
F(36)	2368(5)	5759(4)	1128(3)
S(4)	3813(1)	4010(2)	1923(1)
C(41)	3729(6)	4146(5)	1169(4)
C(42)	3049(7)	4264(6)	884(6)
F(42)	2423(3)	4244(3)	1204(2)
C(43)	2978(7)	4382(6)	293(7)
F(43)	2312(3)	4501(4)	54(3)
C(44)	3615(9)	4378(7)	−49(5)
F(44)	3549(5)	4489(5)	−626(3)
C(45)	4262(8)	4241(8)	217(6)
F(45)	4883(4)	4235(4)	−126(3)
C(46)	4333(7)	4138(6)	790(5)
F(46)	4997(3)	3991(4)	1023(3)
S(5)	2390(2)	2738(2)	2033(1)
C(51)	3045(7)	2487(6)	1504(5)
C(52)	3720(8)	2199(6)	1655(6)
F(52)	3889(4)	2108(4)	2227(3)
C(53)	4233(8)	1991(7)	1275(9)
F(53)	4906(4)	1736(4)	1433(4)
C(54)	4092(11)	2049(10)	687(9)
F(54)	4585(5)	1859(5)	277(4)
C(55)	3416(11)	2307(8)	480(6)
F(55)	3262(5)	2378(5)	−84(3)
C(56)	2918(8)	2536(7)	915(7)
F(56)	2244(4)	2783(4)	720(3)

Table 5

Molecular dimensions in **B**; bond lengths (Å) and angles (°) (esd's are in parentheses)

(a) About the Ru atom.			
Ru–P(1)	2.364(3)	Ru–S(4)	2.419(3)
Ru–P(2)	2.280(3)	Ru–F(42)	2.489(6)
Ru–S(3)	2.321(3)	Ru–S(5)	2.323(3)
P(1)–Ru–P(2)	94.4(1)	S(3)–Ru–F(42)	85.0(1)
P(1)–Ru–S(3)	84.5(1)	S(4)–Ru–F(42)	76.4(2)
P(2)–Ru–S(3)	96.3(1)	P(1)–Ru–S(5)	85.7(1)
P(1)–Ru–S(4)	171.5(1)	P(2)–Ru–S(5)	93.3(1)
P(2)–Ru–S(4)	94.1(1)	S(3)–Ru–S(5)	166.8(1)
S(3)–Ru–S(4)	94.6(1)	S(4)–Ru–S(5)	93.8(1)
P(1)–Ru–F(42)	95.1(2)	F(42)–Ru–S(5)	87.0(1)
P(2)–Ru–F(42)	170.5(2)		
(b) Bond lengths in the ligands.			
P(1)–C(11)	1.822(11)	P(2)–C(21)	1.832(12)
P(1)–C(17)	1.813(11)	P(2)–C(27)	1.808(11)
P(1)–C(18)	1.803(10)	P(2)–C(28)	1.819(12)
C(11)–C(12)	1.357(18)	C(21)–C(22)	1.375(18)
C(11)–C(16)	1.359(18)	C(21)–C(26)	1.385(17)
C(12)–C(13)	1.364(19)	C(22)–C(23)	1.390(20)
C(13)–C(14)	1.378(25)	C(23)–C(24)	1.347(22)
C(14)–C(15)	1.349(25)	C(24)–C(25)	1.366(24)
C(15)–C(16)	1.397(22)	C(25)–C(26)	1.374(20)
S(3)–C(31)	1.753(14)	S(5)–C(51)	1.753(13)
C(31)–C(32)	1.380(21)	C(51)–C(52)	1.371(18)
C(31)–C(36)	1.401(24)	C(51)–C(56)	1.368(20)
C(32)–F(32)	1.344(17)	C(52)–F(52)	1.354(16)
C(32)–C(33)	1.386(25)	C(52)–C(53)	1.326(22)
C(33)–F(33)	1.367(21)	C(53)–F(53)	1.353(17)
C(33)–C(34)	1.34(3)	C(53)–C(54)	1.372(29)
C(34)–F(34)	1.364(27)	C(54)–F(54)	1.339(21)
C(34)–C(35)	1.36(4)	C(54)–C(55)	1.393(27)
C(35)–F(35)	1.323(21)	C(55)–F(55)	1.326(17)
C(35)–C(36)	1.364(28)	C(55)–C(56)	1.405(23)
C(36)–F(36)	1.335(19)	C(56)–F(56)	1.373(16)
S(4)–C(41)	1.748(10)		
C(41)–C(42)	1.410(17)		
C(41)–C(46)	1.397(16)		
C(42)–F(42)	1.349(14)		
C(42)–C(43)	1.373(20)		
C(43)–F(43)	1.340(15)		
C(43)–C(44)	1.394(21)		
C(44)–F(44)	1.339(14)		
C(44)–C(45)	1.342(21)		
C(45)–F(45)	1.369(16)		
C(45)–C(46)	1.329(18)		
C(46)–F(46)	1.341(14)		
(c) Valence angles in the ligands.			
Ru–P(1)–C(11)	105.7(4)	Ru–P(2)–C(21)	117.8(4)
Ru–P(1)–C(17)	119.0(4)	Ru–P(2)–C(27)	112.5(4)
C(11)–P(1)–C(17)	105.1(5)	C(21)–P(2)–C(27)	103.4(5)
Ru–P(1)–C(18)	120.4(3)	Ru–P(2)–C(28)	114.3(4)

Table 5 (continued)

C(11)-P(1)-C(18)	102.9(5)	C(21)-P(2)-C(28)	104.2(5)
C(17)-P(1)-C(18)	101.8(5)	C(27)-P(2)-C(28)	103.1(5)
P(1)-C(11)-C(12)	119.2(10)	P(2)-C(21)-C(22)	117.5(9)
P(1)-C(11)-C(16)	123.1(10)	P(2)-C(21)-C(26)	122.1(9)
C(12)-C(11)-C(16)	117.7(11)	C(22)-C(21)-C(26)	120.4(11)
C(11)-C(12)-C(13)	123.4(12)	C(21)-C(22)-C(23)	119.0(12)
C(12)-C(13)-C(14)	117.9(14)	C(22)-C(23)-C(24)	120.0(14)
C(13)-C(14)-C(15)	120.4(15)	C(23)-C(24)-C(25)	121.3(15)
C(14)-C(15)-C(16)	119.9(15)	C(24)-C(25)-C(26)	119.9(13)
C(11)-C(16)-C(15)	120.5(13)	C(21)-C(26)-C(25)	119.2(13)
Ru-S(3)-C(31)	109.9(4)	Ru-S(5)-C(51)	108.9(4)
S(3)-C(31)-C(32)	121.9(12)	S(5)-C(51)-C(52)	121.9(10)
S(3)-C(31)-C(36)	123.2(11)	S(5)-C(51)-C(56)	123.2(10)
C(32)-C(31)-C(36)	114.9(13)	C(52)-C(51)-C(56)	114.9(12)
C(31)-C(32)-F(32)	119.7(13)	C(51)-C(52)-F(52)	119.4(12)
C(31)-C(32)-C(33)	122.1(15)	C(51)-C(52)-C(53)	124.6(14)
F(32)-C(32)-C(33)	118.2(15)	F(52)-C(52)-C(53)	116.0(13)
C(32)-C(33)-F(33)	117.9(18)	C(52)-C(53)-F(53)	123.6(17)
C(32)-C(33)-C(34)	119.6(18)	C(52)-C(53)-C(54)	119.3(15)
F(33)-C(33)-C(34)	122.5(18)	F(53)-C(53)-C(54)	117.1(15)
C(33)-C(34)-F(34)	118.3(21)	C(53)-C(54)-F(54)	122.8(16)
C(33)-C(34)-C(35)	121.5(21)	C(53)-C(54)-C(55)	121.4(17)
F(34)-C(34)-C(35)	120.0(20)	F(54)-C(54)-C(55)	115.8(16)
C(34)-C(35)-F(35)	120.7(20)	C(54)-C(55)-F(55)	123.2(16)
C(34)-C(35)-C(36)	118.0(19)	C(54)-C(55)-C(56)	115.1(15)
F(35)-C(35)-C(36)	121.1(20)	F(55)-C(55)-C(56)	121.6(16)
C(31)-C(36)-C(35)	123.4(16)	C(51)-C(56)-C(55)	124.6(14)
C(31)-C(36)-F(36)	118.6(14)	C(51)-C(56)-F(56)	119.4(12)
C(35)-C(36)-F(36)	117.9(16)	C(55)-C(56)-F(56)	115.9(14)
Ru-S(4)-C(41)	104.0(4)		
S(4)-C(41)-C(42)	123.7(9)		
S(4)-C(41)-C(46)	122.8(9)		
C(42)-C(41)-C(46)	113.5(10)		
C(41)-C(42)-F(42)	118.5(10)		
C(41)-C(42)-C(43)	124.1(11)		
F(42)-C(42)-C(43)	117.4(11)		
Ru-F(42)-C(42)	117.3(6)		
C(42)-C(43)-F(43)	120.6(12)		
C(42)-C(43)-C(44)	118.2(12)		
F(43)-C(43)-C(44)	121.2(12)		
C(43)-C(44)-F(44)	118.4(13)		
C(43)-C(44)-C(45)	118.1(12)		
F(44)-C(44)-C(45)	123.5(14)		
C(44)-C(45)-F(45)	117.3(12)		
C(44)-C(45)-C(46)	123.7(13)		
F(45)-C(45)-C(46)	118.9(12)		
C(41)-C(46)-C(45)	122.3(12)		
C(41)-C(46)-F(46)	117.3(10)		
C(45)-C(46)-Fe(46)	120.4(11)		

cationic iridium(I) and iridium(III) complexes can bind lone pairs of iodo-, bromo- and chloro-carbons [14]. Only two fluorocarbon interactions are known [15,16], in particular the complex $[IrH_2(PPh_3)_2(8\text{-fluoroquinoline})]SbF_6$ has an N,F-chelated quinoline ligand [15]. The Ir–F distance (2.514(8) Å) of this complex resembles the Ru–F distance (2.489(6) Å) in complex **B**.

Metal–fluorocarbon interactions, although weak, may prove to be more widespread than might have been supposed. Presumably the analogues of **B** (Table 1), also have Ru–X–C (X = F or H as appropriate) interactions, but unfortunately there appears to be no diagnostic test one can apply to these paramagnetic species, other than X-ray crystallography, to establish this.

It is perhaps significant that the Ru–F–C interaction occurs in a complex of ruthenium(III), but only Ru–H–C interactions occur in the complex of ruthenium(II); it appears that the more electrophilic ruthenium(III) metal centre is required to promote the fluorocarbon interaction.

Conclusions

The unsaturated ruthenium centres, created by use of bulky thiolate and phosphine groups to prevent dimerisation, are able to achieve coordination saturation by weak (agostic), interaction with C*H* or C*F* atoms. Thus obtained are monomeric metal centres with easily displaceable groups; for example, CO is able to cleave the C–H or C–F bonds in these compounds to give carbonyl complexes [2], which will be described in detail elsewhere. It is therefore to be expected that these potentially unsaturated complexes will have catalytic activity in solution, and this possibility is being explored.

Experimental

All manipulations were carried out under dry dinitrogen using standard vacuum and Schlenk-tube techniques.

Spectroscopic data were determined with the following instruments: NMR, Jeol FX90Q; IR, Unicam SP300; EPR, Bruker ESR200D SRC operating at 9.45 GHz. Magnetic moments were measured with a recording Faraday balance and microanalysis were determined by Mr. C. Macdonald of the AFRC-IPSR Nitrogen Fixation Laboratory.

The following starting materials were prepared by published methods; $[RuCl_2(PPh_3)_3]$ [17], $[RuCl_3(PPh_3)_2] \cdot MeNO_2$ [18], $[RuCl_3(PPh_3)_2] \cdot MeOH$ [18] and $[RuCl_3(PR'_3)_3]$ [19]. All other materials were used as commercially supplied.

Preparation of complexes

Because the methods used were general, detailed descriptions will be given only for examples of each type of complex.

Bis(pentafluorothiophenolato)bis(triphenylphosphine)ruthenium(II)

Lead pentafluorothiophenolate (0.252 g; 0.4170 mmol) was added to a solution of dichlorotris(triphenylphosphine)ruthenium(II) (0.400 g; 0.4170 mmol) in acetone (25 cm^3) and the mixture was shaken at room temperature for 30 min. The brown solution changed rapidly to blue, and lead chloride separated. The $PbCl_2$ was filtered off, the blue solution evaporated to dryness, and the purple solid residue recrystallised from thf/MeOH (1/10) purple-coloured plates.

Bis(dimethylphenylphosphine)tris(pentafluorothiophenolato)ruthenium(III)

Lead pentafluorothiophenolate (0.450 g; 0.7433 mmol) was added to a solution of *mer*-tris(dimethylphenylphosphine)trichlororuthenium(III) (0.300 g; 0.4968 mmol) in acetone (25 cm^3) and the mixture shaken at room temperature for 2 h and then $PbCl_2$ was filtered off. The remaining green solution was evaporated to lower volume at reduced pressure and ethanol (10 cm^3) was added to yield green crystals.

X-ray crystallography

All computations were carried out on the VAX11/750 computer at GCRI, Littlehampton, with the programmes described in reference 20.

1. $[\overline{Ru(SC_6F_5)_2\{PC_6H_4(H}\text{-}2)(C_6H_5)_2\}_2]$ *(A).* Crystal data. $C_{48}H_{30}F_{10}P_2RuS_2$, $M = 1023.9$. Monoclinic, $C2/c$ (no. 15), a 24.030(7), b 13.402(5), c 29.184(10) Å, β 107.34(?)°, V 8971.4 Å^3, $F(000) = 4112$, $Z = 8$, μ(Mo-K_α) 5.8 cm^{-1}, D_c 1.516 g cm^{-3}. λ(Mo-$K_{\bar{\alpha}}$) 0.71069 Å.

The crystals are purple plates, the one used for the diffractometry measurements was ca. 0.12 × 0.24 × 0.48 mm, mounted on a glass fibre and coated in epoxy resin. Photographic examination showed sharp diffraction spots, but a limited range of θ for measurable intensities. Indeed, on our Enraf–Nonius CAD4 diffractometer (with monochromated Mo-radiation), intensity measurements could usefully be made only to θ_{max} 17°. Accurate cell dimensions were refined fromthe goniometer settings of 25 reflections having $10 < \theta < 11°$. During processing of the data, corrections were made for Lorentz-polarisation effects and to ensure no negative net intensities. 2605 unique reflections were then read into the SHELX program system [21] for structure determination and refinement.

The coordinates of the Ru atom were calculated from a Patterson map, and the remaining non-hydrogen atoms were localised in electron-density and difference Fourier maps. Hydrogen atoms were introduced in idealised positions. With the limited data-set, only the Ru, P, S and F atoms were refined anisotropically; the H-atoms were set to ride on the bonded C atoms.

Refinement was concluded at $R = 0.080$, $R_w = 0.071$ for 2135 reflections (all those with $I > \sigma_I$), weighted $w = (\sigma_F^2 + 0.00102\ F^2)^{-1}$. Scattering factors for C, H, F, P, Ru and S atoms were from ref. 22.

(ii) $[\overline{Ru\{SC_6F_4(F}\text{-}2)\}(SC_6F_5)_2(PMe_2Ph)_2]$ *(B).* Crystal data: $C_{34}H_{22}F_{15}P_2RuS_3$, $M = 974.7$, orthorhombic, space group $Pbca$ (no. 61), a 18.110(4), b 18.063(3), c 22.858(8) Å, V 7477.3 Å^3, $Z = 8$, D_c 1.732 g cm^{-3}, $F(000) = 3864$, μ(Mo-K_α) 7.6 cm^{-1}.

The crystals are small, very dark green square prisms. One, ca. 0.10 × 0.12 × 0.36 mm, was mounted on a glass fibre and, suspected of being slightly air-sensitive, was coated in epoxy resin. After photographic examination, accurate cell-dimensions were refined from the goniometer settings of 25 reflections having θ ca. 10°, on the Enraf–Nonius CAD4 diffractometer (using monochromated Mo-radiation). Diffraction intensities are recorded to θ_{max} 20° beyond which there were few observable reflections.

During processing, corrections were made for Lorentz and polarisation effects, and to ensure no negative intensities; no deterioration or absorption corrections were considered necessary. 3473 unique reflections were entered into the SHELX program system [21] for structure determination (by the heavy atom method) and refinement (by large-block-matrix least-squares methods). At convergence, $R =$

0.081, $R_w = 0.054$ for 2664 reflections (with $I \geq \sigma_I$) weighted $w = \sigma_F^{-2}$. [For the 1807 reflections with $I \geq 2\sigma_I$, $R = 0.044$, $R_w = 0.036$, and $w = \sigma_F^{-2}$]. Hydrogen atoms were included in idealised positions, (the methyl group H atoms in staggered conformations) and their parameters were set to ride on those of their bonded C atoms. Scattering factors for neutral atoms were used [22].

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