

Thiolate Complexes of Osmium(IV): Preparation of [Os(SR)₄(PR'₃)] (R = C₆F₅, C₆F₄H-4, C₆H₄F-4 or Ph, R' = Ph; R = C₆F₅ or C₆F₄H-4, R'₃ = Me₂Ph) and [OsCl(SC₆F₅)₂(SC₆H₄X-3)(PMe₂Ph)] (X = F or CF₃): Crystal Structures of [Os(SC₆F₄H-4)₄(PPh₃)] and [OsCl(SC₆F₅)₂(SC₆H₄CF₃-3)(PMe₂Ph)]*

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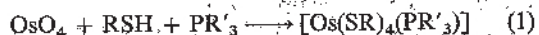
The diamagnetic osmium(IV) complexes [Os(SR)₄(PR'₃)] (R = C₆F₅, C₆F₄H-4, C₆H₄F-4, or Ph, R' = Ph; R = C₆F₅ or C₆F₄H-4, R'₃ = Me₂Ph) and [OsCl(SC₆F₅)₂(SC₆H₄X-3)(PMe₂Ph)] (X = F or CF₃) have been prepared. The complex [Os(SC₆F₄H-4)₄(PPh₃)] has an essentially trigonal-bipyramidal structure with an apical PPh₃ group [Os-P 2.391(5), Os-S_{ap} 2.414(5), mean Os-S_{eq} 2.207(7) Å]. The structure of [OsCl(SC₆F₅)₂(SC₆H₄CF₃-3)(PMe₂Ph)] is a somewhat distorted trigonal bipyramid with apical Cl⁻ and PMe₂Ph groups [Os-Cl 2.420(2), Os-P 2.340(2), mean Os-SC₆F₅ 2.206(2), Os-SC₆H₄CF₃ 2.187(2) Å]. The spectroscopic properties of these compounds are reported and the possibility of isomerism in solution is discussed.

The chemistry of iron-group metals with sulfur-donor ligands is of great interest in the study of the structure and function of iron-sulfur proteins such as the nitrogenase enzyme and ferredoxins.¹ In recent years the chemistry of thiolate ligands has received particular attention because variation of the thiolate substituents allows construction of compounds which show unusual co-ordination geometries and oxidative states and can bind small molecules, including nitrogenase substrates or inhibitors.^{2,3}

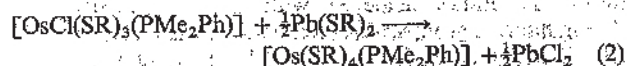
Following our interest in complexes of fluorinated thiolate ligands,⁴ we now report an extension of our work⁵ on thiolate complexes of Os^{IV} to the series [Os(SR)₄(PR'₃)] **1** (R = C₆F₅, C₆F₄H-4, C₆H₄F-4, or Ph, R' = Ph; R = C₆F₅ or C₆F₄H-4, R'₃ = Me₂Ph) and [OsCl(SC₆F₅)₂(SC₆H₄X-3)(PMe₂Ph)] **2** (X = F or CF₃). These diamagnetic, d⁴ complexes have essentially trigonal-bipyramidal geometry in the solid state, but some members of the series appear to isomerise in solution. X-Ray crystallographic and spectroscopic studies have been made.

Results and Discussion

Preparation and Crystal Structures.—Previously, [OsCl(SR)₃(PMe₂Ph)] **3** were prepared⁵ by reaction of HCl with [Os(SR)₃(PMe₂Ph)₂]. We have now prepared the related complexes **1** from OsO₄ by the general synthetic route (1).

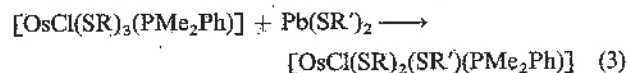


Complexes **1** with R = C₆F₅ or C₆F₄H-4 and R'₃ = Me₂Ph have also been prepared by metathesis as shown in equation (2). The complexes **1** are green (R = C₆F₅ or C₆F₄H-4) or



brown (R = C₆H₄F-4 or Ph), diamagnetic, crystalline solids which are non-conductors in acetone solution. Yields from reactions (1) and (2) are variable depending upon the substituents; representative details are given in the Experimental section and in Table 1.

Complexes **2** were obtained upon attempted metathesis of the chloride in [OsCl(SR)₃(PMe₂Ph)] **3**⁵ using Pb(SC₆H₄X-3)₂ (X = F or CF₃). The Cl⁻ ligand was not metathesised but rather one SR group was replaced, although in very low yields, as in reaction (3). It seems unlikely that this change of



reaction pathway is solely a consequence of steric shielding of the Cl⁻ by the equatorial ligands, since SC₆F₅ and SC₆F₄H-4 successfully replace the apical chloride ion as shown in reaction (2). Compounds **2** are brown, diamagnetic crystalline solids the physical properties of which, together with those of compounds **1**, are shown in Table 1.

Compounds **1** and **2** form part of a series of trigonal-bipyramidal complexes, the first members of which, [M(SR)₄L] (M = Ru or Os; R = aryl; L = CO, MeOH, MeCN, etc.), were prepared by Koch and Millar.⁶

The crystal structure of [Os(SC₆F₄H-4)₄(PPh₃)] **1b** (Fig. 1) shows it to have an essentially trigonal-bipyramidal (TBPY) co-ordination geometry with an axial PPh₃ group. Atomic coordinates are listed in Table 2 and molecular dimensions in Table 3. The structure resembles that of the analogue [OsCl(SC₆F₅)₃(PMe₂Ph)]⁵ in that the three equatorial thiolates have their R groups in the 'down' configuration, around the Cl⁻ ligand in **3** and around the thiolate in [Os(SC₆F₄H-4)₄(PPh₃)] **1b**. This arrangement differs from that in [Ru(SC₆H₂Pr^t₃-2,4,6)₄(MeCN)]⁶ and related complexes,⁶ where the thiolate ligands are in the more usual 'two up one down' arrangement.

The axial Os-S distance in complex **1b**, 2.414(5) Å, is longer

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

Table 1 Physical properties of the osmium complexes

Complex	Yield (%)	Colour	M.p./°C	Analysis (%) ^a		
				C	H	S
1a [Os(SC ₆ F ₅) ₄ (PPh ₃)]	90	Green	198–200	41.2 (40.4)	1.3 (1.2)	9.9 (10.3)
1b [Os(SC ₆ F ₄ H-4)(PPh ₃)]	62	Green	218–220	42.5 (42.9)	1.6 (1.6)	11.8 (10.9)
1c [Os(SC ₆ H ₄ F-4)(PPh ₃)]	10	Brown	170–175	49.0 (52.5)	3.3 (3.3)	13.3 (13.3)
1d [Os(SPh) ₄ (PPh ₃)]	5	Brown	165–170	54.5 (56.7)	4.1 (4.0)	13.2 (14.4)
1e [Os(SC ₆ F ₅) ₄ (PMe ₂ Ph)]	85	Green	159–163	33.9 (34.2)	1.0 (1.0)	11.7 (11.4)
1f [Os(SC ₆ F ₄ H-4)(PMe ₂ Ph)]	87	Green	185–187	36.7 (36.5)	1.4 (1.4)	12.1 (12.2)
2a [OsCl(SC ₆ F ₅) ₂ (SC ₆ H ₄ CF ₃ -3)(PMe ₂ Ph)]	8	Brown	156–158	34.1 (34.5)	1.6 (1.6)	9.9 (10.2)
2b [OsCl(SC ₆ F ₅) ₂ (SC ₆ H ₄ F-3)(PMe ₂ Ph)]	7	Brown	197–202	34.9 (35.1)	1.7 (1.7)	10.6 (10.8)

^a Calculated values in parentheses.

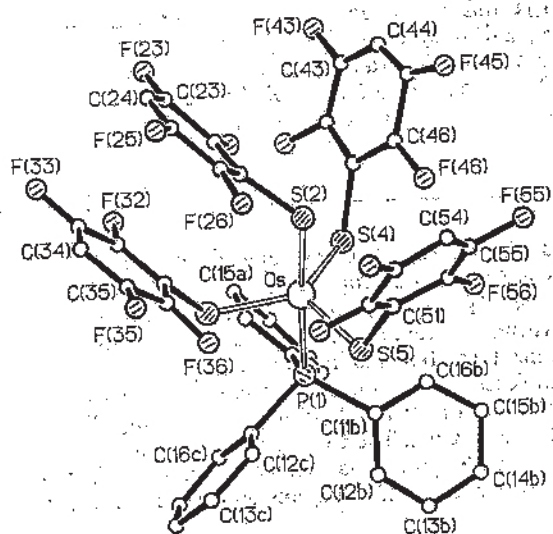


Fig. 1 Molecular structure of [Os(SC₆F₄H-4)₄(PPh₃)]

than the mean equatorial Os–S distance, 2.207(7) Å, as might be expected, since axial bonds in *TBPY* complexes are generally predicted to be longer than equatorial bonds in absence of π effects. If there is π release from the S atoms to the electron-deficient osmium(IV) centre, then this should be more pronounced in the equatorial plane, leading to further shortening of the equatorial Os–S distance relative to the axial distance.⁷ No doubt the *trans* influence of the PPh₃ ligand also affects the axial Os–S distance. The axial Os–P distance, 2.391(5) Å, is close to that found in complex 3 (R = C₆F₅), 2.339(1) Å,⁵ and 2a below, 2.340(2) Å.

The structure of [OsCl(SC₆F₅)₂(SC₆H₄CF₃-3)(PMe₂Ph)] 2a is shown in Fig. 2, with coordinates and dimensions in Tables 4 and 5. It is similar to that of 1b and of 3, being essentially trigonal-bipyramidal, with axial chloride and phosphine groups. In the equatorial plane one SC₆F₅ ligand has been replaced by an SC₆H₄CF₃-3 ligand. As in 1b and 3 (R = C₆F₅) the R groups in the equatorial SR ligands in 2a are in the 'all up' configuration and surround the Cl ligand. The Os–S_{eq} distances [mean 2.199(6) Å] in 2a are similar to those of 1b and shorter than the Os–S axial distance in 1b, as would be expected (see discussion above).

In all the analyses, that we are aware of, of complexes of Os^{IV} and Ru^{IV} containing at least three monothiolate ligands, the

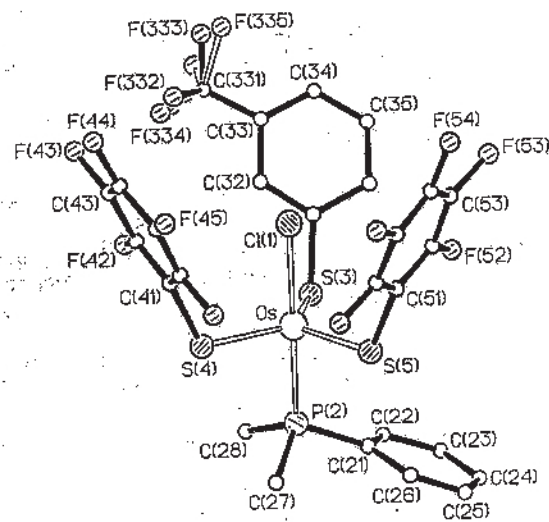


Fig. 2 Molecular structure of [OsCl(SC₆F₅)₂(SC₆H₄CF₃-3)(PMe₂Ph)]

co-ordination geometry is trigonal bipyramidal. Three thiolate ligands always occupy the equatorial sites, and the M–S_{eq} distances are remarkably constant throughout the series (Table 6). The conformation of the equatorial ligands, as we have noted, may be 'all up' or 'two up one down', and this appears to depend on (i) the nature of the substituent group in the *ortho* positions of the benzenethiolate ring (H and F groups can go 'all up', whereas Prⁱ groups are found only in the 'two up one down' arrangement; Me groups can take up either arrangement), (ii) the nature of the apical groups (carbonyl and chloride ligands can be enclosed by an 'all up' system, but MeCN ligands appear to favour the 'two up one down' arrangement), and (iii) whether the phenyl ring of an equatorial ligand can lie parallel against one of an apical ligand (as in 1b).

We note that thiolate complexes of Ru and Os in lower oxidation states normally have octahedral co-ordination patterns, sometimes achieved with agostic hydrogen or chelating fluorine groups.² When the thiolate is the very bulky SC₆H₂Prⁱ-2,4,6 ligand, the trigonal-bipyramidal form is favoured, as in [Ru(SC₆H₂Prⁱ-2,4,6)₃(NCMe)₂].

Spectroscopic Properties.—The IR spectra of complexes 1 and 2 show the expected bands for the thiolate and phosphine

Table 2 Final atomic coordinates (fractional $\times 10^4$) for $[\text{Os}(\text{SC}_6\text{F}_4\text{H-4})_2(\text{PPh}_3)]$ **1b** with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
Os	2088.8(6)	4136.1(7)	2581.7(6)	C(31)	-792(16)	3312(15)	1931(15)
P(1)	2600(4)	5790(5)	3796(4)	C(32)	-1634(16)	2570(20)	2223(19)
C(11a)	2666(17)	5612(18)	5059(15)	F(32)	-1500(12)	2294(12)	3105(10)
C(12a)	3455(24)	6180(20)	5778(19)	C(33)	-2625(18)	1948(19)	1578(17)
C(13a)	3477(25)	6001(18)	6672(17)	F(33)	-3379(11)	1200(12)	1891(14)
C(14a)	2681(22)	5332(21)	6997(17)	C(34)	-2792(25)	2206(19)	784(19)
C(15a)	1812(19)	4608(26)	6293(17)	C(35)	-1886(24)	2937(24)	373(17)
C(16a)	1798(15)	4817(18)	5339(16)	F(35)	-1965(14)	3183(14)	-512(12)
C(11b)	3937(17)	6680(22)	3704(16)	C(36)	-955(18)	3528(18)	990(19)
C(12b)	4187(20)	7781(20)	3752(23)	F(36)	-159(12)	4324(12)	739(11)
C(13b)	5225(21)	8487(20)	3874(17)	S(4)	3086(5)	3530(5)	3550(4)
C(14b)	6123(19)	8091(23)	3787(21)	C(41)	3087(15)	2157(18)	3201(20)
C(15b)	5969(19)	7041(25)	3669(18)	C(42)	2737(21)	1452(23)	3758(23)
C(16b)	4933(23)	6337(20)	3664(20)	F(42)	2083(14)	1816(15)	4565(12)
C(11c)	1631(17)	6623(19)	3783(16)	C(43)	2838(26)	458(28)	3659(28)
C(12c)	1358(19)	6821(17)	2827(19)	F(43)	2452(20)	-163(14)	4263(17)
C(13c)	700(19)	7475(21)	2795(22)	C(44)	3222(66)	90(32)	2798(63)
C(14c)	241(22)	7905(19)	3621(23)	C(45)	3726(26)	665(33)	2209(43)
C(15c)	539(28)	7722(22)	4511(18)	F(45)	4223(16)	347(17)	1449(19)
C(16c)	1229(18)	7056(19)	4548(15)	C(46)	3598(25)	1784(20)	2446(25)
S(2)	1663(5)	2547(5)	1265(4)	F(46)	4109(12)	2361(14)	1784(13)
C(21)	348(16)	1559(16)	1224(15)	S(5)	3057(5)	5111(5)	1587(4)
C(22)	-3(17)	1055(18)	1981(18)	C(51)	3288(16)	4273(17)	491(16)
F(22)	562(10)	1269(15)	2846(11)	C(52)	2614(18)	4006(16)	-424(16)
C(23)	-979(32)	143(22)	1761(31)	F(52)	1660(10)	4245(12)	-416(10)
F(23)	-1308(16)	-333(20)	2554(22)	C(53)	2838(16)	3367(21)	-1144(15)
C(24)	-1557(29)	-112(28)	875(36)	F(53)	2141(12)	3016(13)	-1986(10)
C(25)	-1225(30)	414(26)	117(26)	C(54)	3780(20)	2987(20)	-1187(20)
F(25)	-1943(18)	117(19)	-656(17)	C(55)	4475(25)	3301(24)	-358(22)
C(26)	-327(18)	1213(17)	325(30)	F(55)	5460(15)	2993(18)	-303(16)
F(26)	-9(14)	1756(16)	-433(11)	C(56)	4279(18)	3969(19)	506(16)
S(3)	343(4)	4171(5)	2812(4)	F(56)	5062(11)	4310(13)	1271(10)

Table 3 Selected molecular dimensions (bond lengths in Å, angles in °) for $[\text{Os}(\text{SC}_6\text{F}_4\text{H-4})_2(\text{PPh}_3)]$ **1b** with e.s.d.s in parentheses

(a) About the Os atom

Os-P(1)	2.391(5)	Os-S(4)	2.195(7)
Os-S(5)	2.220(6)	Os-S(2)	2.414(5)
Os-S(3)	2.203(6)		
P(1)-Os-S(2)	175.3(2)	S(3)-Os-S(4)	123.2(2)
P(1)-Os-S(3)	84.6(2)	P(1)-Os-S(5)	85.4(2)
S(2)-Os-S(3)	97.9(2)	S(2)-Os-S(5)	89.9(2)
P(1)-Os-S(4)	86.6(2)	S(3)-Os-S(5)	119.3(2)
S(2)-Os-S(4)	95.3(2)	S(4)-Os-S(5)	115.7(2)

(b) In the phosphine ligand

P(1)-C(11a)	1.812(23)	P(1)-C(11c)	1.833(27)
P(1)-C(11b)	1.770(21)		
Os-P(1)-C(11a)	114.2(8)	Os-P(1)-C(11c)	114.6(6)
Os-P(1)-C(11b)	114.9(8)	C(11a)-P(1)-C(11c)	104.0(11)
C(11a)-P(1)-C(11b)	103.9(10)	C(11b)-P(1)-C(11c)	103.9(12)

(c) In the thiolate ligands

S(2)-C(21)	1.774(18)	S(4)-C(41)	1.776(24)
S(3)-C(31)	1.796(17)	S(5)-C(51)	1.773(22)
Os-S(2)-C(21)	117.6(7)	Os-S(4)-C(41)	117.8(8)
Os-S(3)-C(31)	119.6(7)	Os-S(5)-C(51)	111.3(8)

ligands; only significant bands are reported (Table 7). The NMR spectra vary with the type of compound and substituent, as discussed below.

The ^1H , ^{19}F and ^{31}P NMR spectra of complex **1b** are as expected if the solid-state structure is maintained in solution (Table 7). Compound **1d** ($\text{R} = \text{R}' = \text{Ph}$) also shows ^1H and ^{31}P NMR spectra consistent with a trigonal-bipyramidal structure in solution. However, the analogues **1a** and **1c** ($\text{R} = \text{C}_6\text{F}_5$ or $\text{C}_6\text{H}_4\text{F-4}$, $\text{R}' = \text{Ph}$) show two ^{31}P resonances each and

magnetically different thiolate substituents. Thus these compounds are mixtures of isomers in solution. We were unable to separate isomers by chromatography.

The ^{19}F NMR spectra of complex **1a** show five signals for the 2-fluorine nuclei and also five for the 3- and 4-fluorine nuclei with the expected 2:2:1 ratio (AABBC magnetic system). The relative intensities among these signals are 6:1:1:1:1. At high temperature the set of four resonances of equal intensity coalesce with the more intense signal. The original resonance pattern is restored on cooling back to ambient temperature. Thus there appears to be a dynamic equilibrium between isomers, although it is not possible to assign the component isomers with certainty.

A range of isomers involving different orientations of the substituents at sulfur in trigonal-bipyramidal or square-pyramidal (*SPY*) structures could be in equilibrium. Also a dimeric structure such as in Scheme 1, in equilibrium with the *TBPY* structure, could account for these results, as long as the bridging thiolate substituents adopt the *syn* configuration, as has been observed in other dimeric compounds.¹⁰

For complex **1c** ($\text{R} = \text{C}_6\text{H}_4\text{F-4}$, $\text{R}' = \text{Ph}$) the ^{19}F NMR spectrum shows three magnetically different 4-F nuclei in a 6:2:3 ratio. This would be consistent with the presence of both *TBPY* (axial phosphine) and *SPY* (axial phosphine) isomers in an 8:3 ratio, but no certain assignment can be made.

The spectrum of complex **1e** ($\text{R} = \text{C}_6\text{F}_5$, $\text{R}'_3 = \text{Me}_2\text{Ph}$) is consistent with a mixture (15:1) of *TBPY* and *SPY* isomers both with phosphine in the axial position, whereas **1f** ($\text{R} = \text{C}_6\text{F}_4\text{H-4}$, $\text{R}'_3 = \text{Me}_2\text{Ph}$) appears to be a mixture of two *TBPY* isomers with axial and equatorial phosphines, in a 2:1 ratio.

Conclusion

We have established general routes to two series of osmium(IV) complexes which in the solid state appear to have *TBPY* structures containing the chemically robust trigonal arrange-

Table 4 Final atomic coordinates (fractional $\times 10^4$) for $[\text{OsCl}(\text{SC}_6\text{F}_5)_2(\text{SC}_6\text{H}_4\text{CF}_3-3)(\text{PMe}_2\text{Ph})]$ 2a with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Os	2285.3(2)	846.0(3)	3097.1(2)	F(35) ^b	3690(24)	6186(37)	3766(25)
Cl(1)	2452(1)	1982(2)	4370(1)	F(36) ^b	3576(26)	3897(45)	3011(27)
P(2)	2105(1)	-250(2)	1863(1)	S(4)	1142(1)	184(3)	3190(1)
C(21)	2921(5)	-288(8)	1418(4)	C(41)	901(4)	716(9)	4103(6)
C(22)	3020(6)	592(8)	873(6)	C(42)	490(5)	1743(10)	4110(7)
C(23)	3671(9)	602(12)	551(8)	F(42)	238(3)	2375(6)	3438(4)
C(24)	4216(8)	-306(16)	783(7)	C(43)	281(5)	2099(10)	4840(7)
C(25)	4117(7)	-1228(13)	1287(6)	F(43)	-140(3)	3132(6)	4825(4)
C(26)	3470(6)	-1175(9)	1605(6)	C(44)	533(5)	1484(10)	5573(6)
C(27)	1851(6)	-1807(8)	1945(6)	F(44)	321(3)	1846(6)	6227(4)
C(28)	1332(6)	384(9)	1066(6)	C(45)	979(5)	464(11)	5566(6)
S(3)	2389(2)	2444(2)	2357(1)	F(45)	1203(4)	-150(6)	6250(4)
C(31)	2514(7)	3796(9)	2926(5)	C(46)	1153(5)	107(9)	4845(6)
C(32)	1885(6)	4326(8)	3131(5)	F(46)	1568(4)	-891(5)	4887(4)
C(33)	1962(7)	5451(9)	3543(6)	S(5)	3318(1)	-263(2)	3566(1)
C(331)	1258(9)	5959(9)	3754(8)	C(51)	3799(5)	218(9)	4564(5)
F(331) ^a	776(9)	6378(16)	3022(10)	C(52)	4284(5)	1163(9)	4692(7)
F(332) ^a	933(10)	5236(17)	4095(11)	F(52)	4419(3)	1771(6)	4042(4)
F(333) ^a	1346(12)	6797(21)	4221(14)	C(53)	4643(6)	1506(11)	5506(9)
F(334) ^a	727(11)	5266(19)	3742(13)	F(53)	5147(4)	2445(7)	5590(5)
F(335) ^a	1636(10)	6556(17)	4585(11)	C(54)	4504(7)	903(16)	6159(8)
F(336) ^a	1107(9)	6963(16)	3364(11)	F(54)	4880(4)	1276(9)	6919(4)
C(34)	2657(9)	6014(10)	3711(7)	C(55)	4050(8)	-47(15)	6042(6)
C(35)	3267(12)	5500(14)	3494(9)	F(55)	3921(5)	-693(8)	6698(4)
C(36)	3226(8)	4383(11)	3110(8)	C(56)	3668(6)	-417(11)	5275(6)
F(32) ^b	942(16)	3874(25)	2932(18)	F(56)	3208(4)	-1330(7)	5168(4)
F(34) ^b	2546(22)	7079(40)	4095(27)				

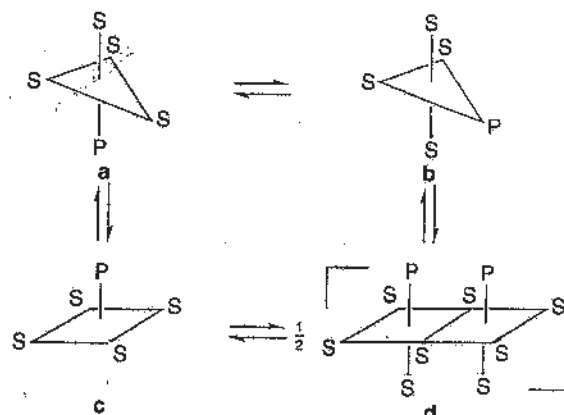
^a Site occupancy factor 0.392. ^b Site occupancy factor 0.215.

Table 5 Selected molecular dimensions (bond lengths in Å, angles in °) in $[\text{OsCl}(\text{SC}_6\text{F}_5)_2(\text{SC}_6\text{H}_4\text{CF}_3-3)(\text{PMe}_2\text{Ph})]$ 2a with e.s.d.s in parentheses

(a) About the Os atom			
Os-Cl(1)	2.420(2)	Os-S(4)	2.207(2)
Os-P(2)	2.340(2)	Os-S(5)	2.204(2)
Os-S(3)	2.187(2)		
Cl(1)-Os-P(2)	179.2(1)	S(3)-Os-S(4)	120.5(1)
Cl(1)-Os-S(3)	93.5(1)	Cl(1)-Os-S(5)	93.2(1)
P(2)-Os-S(3)	86.5(1)	P(2)-Os-S(5)	87.5(1)
Cl(1)-Os-S(4)	92.4(1)	S(3)-Os-S(5)	118.5(1)
P(2)-Os-S(4)	86.9(1)	S(4)-Os-S(5)	120.1(1)
(b) In the phosphine ligand			
P(2)-C(21)	1.780(8)	P(2)-C(28)	1.819(8)
P(2)-C(27)	1.796(9)		
Os-P(2)-C(21)	114.5(2)	Os-P(2)-C(28)	111.5(3)
Os-P(2)-C(27)	114.7(3)	C(21)-P(2)-C(28)	105.2(5)
C(21)-P(2)-C(27)	104.7(4)	C(27)-P(2)-C(28)	105.3(5)
(c) In the thiolate ligands			
S(3)-C(31)	1.757(10)	S(5)-C(51)	1.765(8)
S(4)-C(41)	1.771(8)		
Os-S(3)-C(31)	113.9(3)	Os-S(5)-C(51)	110.5(3)
Os-S(4)-C(41)	111.2(3)		

ment of thiolate groups at the metal centre. Although isomerism does occur to some extent in solution it is not at this stage clear whether it involves disruption of the trigonal set. Substituent isomerism is not unexpected in view of the fact that the analogues $[\text{M}(\text{SC}_6\text{H}_2\text{Pr}_3-2,4,6)_4(\text{MeCN})]$ and $[\text{M}(\text{SC}_6\text{Me}_4\text{H}-4)_4(\text{NCMe})]$ (M = Os or Ru) have the thiolate R groups in the 'two up one down' configuration, but other processes may occur.

Replacement of ligands in $[\text{OsCl}(\text{SR})_3(\text{PR}_3)]$ appears to be sensitive to the nature of R. Where R is more electronegative,



Scheme 1 Possible isomers in solution. The orientation of the SR groups is not given, but gives rise to additional isomers. Only isomer a is observed in the solid, see text

i.e. C_6F_5 and C_6HF_4 , chloride is replaced by incoming thiolate, but for $\text{R} = \text{C}_6\text{H}_4\text{F}$ and $\text{C}_6\text{H}_4\text{CF}_3$ thiolate is displaced.

Experimental

The NMR spectra were obtained using a JEOL FX270 instrument, with chemical shifts quoted relative to SiMe_4 (^1H), CFCl_3 (^{19}F) or $\text{P}(\text{OMe})_3$ (^{31}P - $\{^1\text{H}\}$), infrared spectra using a Perkin-Elmer SP3-200 instrument in the 4000–200 cm^{-1} region. Elemental analyses were by Mr. C. Macdonald of the Nitrogen Fixation Laboratory.

Although a dinitrogen atmosphere was used in preparations, rigorous exclusion of air was not attempted. The compounds $[\text{OsCl}(\text{SR})_3(\text{PMe}_2\text{Ph})]$,⁵ $\text{Pb}(\text{SC}_6\text{F}_5)_2$, $\text{Pb}(\text{SC}_6\text{F}_4\text{H}-4)_2$, $\text{Pb}(\text{SC}_6\text{H}_4\text{F}-3)_2$, and $\text{Pb}(\text{SC}_6\text{H}_4\text{CF}_3-3)_2$ were prepared according to published methods.¹¹

Preparations.—Compounds 1a–1d. Osmium tetroxide (2 mmol) was dissolved in ethanol (15 cm^3), then HSR (12 mmol) in ethanol was added. The mixture rapidly turned black.

Table 6 Complexes of Ru^{IV} and Os^{IV} having at least three monothiolate ligands

Complex ^a	Arrangement of thiolates ^b	Mean M-S _{eq} /Å	M-S _{ap} /Å	Opposite apical (ap) ligand	Ref.
[Os(SC ₆ F ₄ H-4) ₃ (PPh ₃)] 1b	All up	2.207(7)	2.414(5)	PPh ₃	This work
[OsCl(SC ₆ F ₃) ₂ (SC ₆ H ₄ CF ₃ -3)(PMe ₂ Ph)] 2a	All up	2.199(6)	—	—	This work
[OsCl(SC ₆ F ₃) ₃ (PMe ₂ Ph)] 3	All up	2.197(2)	—	—	5
[Ru(CO)(SC ₆ Me ₄ H-4)]	All up	2.213(5)	2.409(3)	CO	8
[Ru(SC ₆ Me ₄ H-4) ₂ (NCMe)]	2,1	2.209(7)	2.383(1)	NCMe	6(a)
[Os(SC ₆ Me ₄ H-4) ₂ (NCMe)]	2,1	—	—	—	6(a)
[Os(SC ₆ Me ₄ H-4) ₂ (NCMe)]	2,1	2.209(1)	2.372(1)	NCMe	6(a)
[Ru(SC ₆ H ₂ Pr ¹ ₃ -2,4,6) ₂ (NCMe)]	2,1	—	—	—	6(a)
[Os(SC ₆ H ₂ Pr ¹ ₃ -2,4,6) ₂ (NCMe)]	2,1	—	—	—	9
[Ru(SC ₆ H ₂ Pr ¹ ₃ -2,4,6) ₂ (NCMe)]	2,1	2.202(11)	2.328(2)	Agostic H	6(b)
[Ru(SC ₆ Me ₄ H-4) ₃ (NCMe) ₂]PF ₆ ·2thf	2,1	2.200(4)	—	—	6(b)
[Ru(SC ₆ H ₂ Pr ¹ ₃ -2,4,6) ₃ (NCMe) ₂] ^c	2,1	2.288(5)	—	—	6(b)
[Ru{SC ₆ H ₄ (F-2)}(SC ₆ F ₃) ₂ (PMe ₂ Ph) ₂] ^d	—	2.322(1) ^e	2.419(3)	PMe ₂ Ph	2

^a All trigonal bipyramidal except where noted; thf = tetrahydrofuran. ^b 2,1 = Two up one down. ^c Ruthenium(III) complex. ^d Octahedral. ^e Mutually *trans* thiolates.

Table 7 Proton, ³¹P, ¹⁹F NMR and IR data for the osmium complexes

Compound	δ(¹ H) ^a	δ(³¹ P) ^a	δ(¹⁹ F) ^a	IR ^b /cm ⁻¹
1a	7.2–7.8(m) (C ₆ H ₅)	-145.4(s) (3) -149.2(s) (1)	-127 to -133(m) (F ²) -151 to -159(m) (F ⁴) -158.5 to -165.5(m) (F ³)	1515, 1495, 980, 750, 695, 530
1b	6.3(tt) (H ⁴ , ax) 6.9(m) (H ⁴ , eq) 7.4–8(m) (C ₆ H ₅)	-147.4(s)	-130.2(m) (F ² , eq) -132.5(m) (F ² , ax) -140.2(m) (F ³ , eq) -143.5(m) (F ³ , ax)	1495, 1230, 1180, 755, 695, 530
1c	6–8(m) (C ₆ H ₅)	-150.8(s) (8) -157.2(s) (3)	-119.5(s) (F ⁴ , sp) -119.8(s) (F ⁴ , eq) -131.0(s) (F ⁴ , ax)	1590, 1490, 1230, 745, 690, 530
1d	6.1(d) 6.3(t) 6.5(t) 6.8–8(m) } (C ₆ H ₅)	-156.9(s)	—	1570, 1470, 1430, 740, 685, 525
1e	2.21(d) (1) 2.54(d) (15) 7.42–7.70(m) (PC ₆ H ₃) } (PCH ₃)	-157.6(s) (1) -160.2(s) (15)	-129.1 to -133.0(m) (F ²) -150.8(t) -151.0(t) } (F ⁴) -151.4(t) -159.0 to -165.8(m) (F ³)	1510, 1485, 1305, 1285, 980, 850, 740, 485
1f	2.20(d) (2) 2.59(d) (1) } (PCH ₃) 6.15(q), 6.25(m), 6.64(q), 6.81(q) } (HC ₆ F ₄) 7.20(m) 7.35–7.40(m) (PC ₆ H ₃)	-168.8(s) (2) -166.2(s) (1)	-137.8 -139.2 -139.5 } (F ³) -141.3 -142.8 -128.7 -129.6 -131.0 } (F ²) -131.8 -132.2	1490, 1300, 1290, 1245, 1225, 1175, 740, 480
2a	2.51(d) (PCH ₃) 7.41–7.6(m) (PC ₆ H ₃ , SC ₆ H ₄)	-170.4(s) (3,6)	-64.2(s) (CF ₃ -3) -133.7(m) (F ²) -152.7(t) (F ⁴) -164.6(m) (F ³)	1510, 1490, 1300, 1285, 1170, 1130, 1085, 980, 845, 740, 490
2b	—	—	—	1510, 1400, 1300, 1215, 980, 780, 740

^a Chemical shifts in ppm relative to SiMe₄ (¹H), P(OMe)₃ (³¹P), or CFCI₃ (¹⁹F); s = singlet, d = doublet, t = triplet, q = quintet; selected relative integrations in parentheses; eq = equatorial, ax = axial. ^b Selected bands only, KBr discs.

Triphenylphosphine (12 mmol) in ethanol (15 cm³) was added and the mixture refluxed for ca. 12 h. As the mixture cooled a green (**1a**, **1b**) or brown (**1c**, **1d**) precipitate appeared. It was filtered off, washed with cold ethanol (15 cm³) and cold hexane (15 cm³). The product was purified through a silica gel chromatographic column with hexane–chloroform as eluent and recrystallised by slow evaporation of the solvent.

Compounds 1e and 1f. The complex [OsCl(SR)₃(PMe₂Ph)] **3** (R = C₆F₃ or C₆F₄H-4) (0.2 mmol) was dissolved in acetone (25 cm³) and Pb(SC₆F₃)₂ or Pb(SC₆F₄H-4)₂ (0.12 mmol) was added. The mixture was magnetically stirred at room temperature for ca. 24 h. The resulting solution was filtered and evaporated to dryness under vacuum to give a green solid. This was washed with cold ethanol (15 cm³) and purified through a

silica gel chromatographic column with hexane-acetone as eluent, giving green crystals by slow evaporation of the solvent.

Compounds 2. The complex $[\text{OsCl}(\text{SR})_3(\text{PMe}_2\text{Ph})]_3$ ($\text{R} = \text{C}_6\text{F}_5$ or $\text{C}_6\text{F}_4\text{H-4}$) (0.2 mmol) was dissolved in acetone (25 cm^3) and $\text{Pb}(\text{SC}_6\text{H}_4\text{X-3})_2$ ($\text{X} = \text{F}$ or CF_3) (0.12 mmol) was added. The mixture was magnetically stirred at room temperature for ca. 24 h. The resulting solution was filtered and evaporated to dryness under vacuum to give a brown solid. This was washed with cold ethanol (15 cm^3) and purified through a silica gel chromatographic column with hexane-acetone as eluent, giving brown crystals by slow evaporation of the solvent.

Crystallography.— $[\text{Os}(\text{SC}_6\text{F}_4\text{H-4})_2(\text{PPh}_3)]_3$.—*Crystal data.* $\text{C}_{42}\text{H}_{19}\text{F}_{16}\text{OsPS}_4$, $M = 1177.0$, triclinic, space group $P1$ (no. 2), $a = 12.366(3)$, $b = 13.154(6)$, $c = 13.851(5)$ Å, $\alpha = 101.27(4)$, $\beta = 91.67(2)$, $\gamma = 105.86(3)^\circ$, $V = 2117.4$ Å³, $Z = 2$, $D_c = 1.846$ g cm^{-3} , $F(000) = 1140$, $\mu(\text{Mo-K}\alpha) = 33.4$ cm^{-1} , $\lambda(\text{Mo-K}\alpha) = 0.71069$ Å.

Crystals of the complex are very dark, rectangular prisms which grow in clusters. Several were cut down to shorter, approximately square prisms and mounted on glass fibres with epoxy resin. Photographic examination showed all to be twinned to some degree, and all having rather broad, diffuse diffraction spots. The best crystal, ca. $0.12 \times 0.13 \times 0.48$ mm, was transferred to our Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell dimensions (from 25 reflections with θ ca. 10.5° , each centred in four orientations) and measurement of diffraction intensities to $\theta_{\text{max}} = 22^\circ$.

During processing, intensities were corrected for Lorentz-polarisation effects, slight deterioration (ca. 4.7% overall), and absorption (analytically from the size and shape of the crystal). 5172 Unique reflections were read into the SHELX program,¹² where the structure was determined by the heavy-atom method and refined by large-block-matrix least-squares methods. All non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were included in idealised positions with isotropic thermal parameters riding on those of the parent carbon atoms. Refinement was concluded with $R = 0.086$ and $R' = 0.094$ for 4091 reflections (those having $I > 2\sigma_I$) weighted $w = (\sigma_F^2 + 0.0127F^2)^{-1}$. In the final difference map, one peak of ca. 2.5 e Å⁻³ was found between molecules about 1.9 Å from a CF group and there were several peaks below 2.3 e Å⁻³ close to the Os atom.

$[\text{OsCl}(\text{SC}_6\text{F}_5)_2(\text{SC}_6\text{H}_4\text{CF}_3-3)(\text{PMe}_2\text{Ph})]_3$.—*Crystal data.* $\text{C}_{27}\text{H}_{15}\text{ClF}_{13}\text{OsPS}_3$, $M = 939.2$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.856(3)$, $b = 11.077(1)$, $c = 16.616(3)$ Å, $\beta = 103.293(8)^\circ$, $V = 3198.3$ Å³, $Z = 4$, $D_c = 1.950$ g cm^{-3} , $F(000) = 1800$, $\mu(\text{Mo-K}\alpha) = 44.1$ cm^{-1} .

Crystals are very dark, well formed, flattened rectangular bipyramids. One, ca. $0.70 \times 0.50 \times 0.40$ mm, was mounted, in air, on a glass fibre with epoxy resin. Following a procedure similar to that for complex 1b above, the crystal was photographed, then mounted on the diffractometer. The reflections centred for refinement of the cell parameters had θ ca. 12.5° , and diffraction intensities were measured to $\theta_{\text{max}} = 25^\circ$.

During processing the absorption corrections were determined by semi-empirical Ψ -scan methods; negative net intensities were adjusted by Bayesian statistical methods. 5617 Unique reflections (in the space group $P2_1/c$) were entered into the SHELX program system, although it was noted that several of the systematically absent $h0l$ reflections had intensity measurements I rather larger than the 'unobserved' limit of $2\sigma_I$.

The structure was determined by the heavy-atom method and refined by full-matrix least-squares procedures. During the refinement process it was apparent that the $\text{SC}_6\text{H}_4\text{CF}_3$ ligand

was disordered in two ways: first, the CF_3 group had two distinct orientations, clearly resolved, and, secondly, difference maps showed peaks corresponding to F atoms bonded to all the phenyl C atoms of this ligand. In the latter case, this thiolate ligand, in ca. 21% of the molecules, is a third SC_6F_5 ligand; no evidence was found for a CF_3 group (or a $\text{SC}_6\text{H}_4\text{CF}_3$ ligand) elsewhere in the molecule. This disorder, if not quite random, in the crystal would account for the observation of measurable intensities for some of the 'systematically absent' reflections.

Except for the disordered F atoms described above, all non-hydrogen atoms were allowed anisotropic thermal parameters; the disordered F atoms were refined isotropically. Hydrogen atoms were included in idealised positions in the phosphine ligand (in staggered arrangements in the methyl groups) and the $\text{SC}_6\text{H}_4\text{CF}_3$ ligand, with isotropic thermal parameters riding on those of the parent carbon atoms. Refinement was terminated with $R = 0.051$ and $R_w = 0.056$ ¹² for 5290 reflections with $I > \sigma_I$ weighted $w = \sigma_F^2$. In a final difference map, the major peaks, at ca. 1.0 e Å⁻³ (scarcely above the noise level), were close to the Os atoms.

Scattering-factor curves for neutral atoms for both structure analyses were taken from ref. 13. Computer programs used in the analyses were listed above and in Table 4 of ref. 14 and were run on a DEC MicroVAX II machine in the Nitrogen Fixation Laboratory.

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

Acknowledgements

We are grateful to PADEP, DGAPA, (the Programa de Apoyo a Divisiones de Estudios de Posgrado and Direccion General de Apoyo al Personal Academico, Mexico) and the British Council for financial support.

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Received 22nd February 1994; Paper 4/01066C