PREPARATION AND ELECTROCHEMISTRY OF THIOLATE-PHOSPHINE COMPLEXES OF OSMIUM

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Abstract—The paramagnetic, octahedral complexes [Os(SC$_6$F$_5$)$_2$(O$_2$CR)(PMe$_2$Ph)$_2$] (R = C$_6$F$_5$, **1**; C$_6$H$_4$CF$_3$-2, **2**; C$_6$H$_4$CF$_3$-3, **3**; C$_6$H$_4$CF$_3$-4, **4**; C$_6$H$_4$F-2, **5**; C$_6$H$_4$F-3, **6**; C$_6$H$_4$F-4, **7**; CH$_3$, **8**; CF$_3$, **9**) have been prepared by treatment of the penta-coordinated complex [Os(SC$_6$F$_5$)$_3$(PMe$_2$Ph)$_2$] with the corresponding fluoro-carboxylic acid. The diamagnetic, pentacoordinate, osmium(IV) complexes [OsX(SR)$_3$(PR$_3^1$)] [X = Cl, Br or SR; R = C$_6$F$_4$H-4 or C$_6$F$_5$; PR$_3^1$ = PMe$_2$Ph, PPh$_3$, P(C$_6$H$_4$Y-4)$_3$ (Y = F, OMe, CF$_3$, Me or Cl)] (**10–14, 18, 20–23**), show two successive one-electron reductions. Electrochemical data are also given for [Os(SC$_6$F$_5$)$_3$(PMe$_2$Ph)$_2$] (**19**). Crown Copyright © 1996 Elsevier Science Ltd

Thiolate ligands have recently attracted much attention due to their propensity to stabilize unusual metallic complexes which are potentially relevant to a variety of catalytic processes.[1-5] For example, thiolate complexes of molybdenum have given information helpful in understanding the role of this metal in industrial hydrodesulfurization catalysis[6] and in enzymes such as xanthine oxidase[7] and nitrogenase.[4] The latter enzyme has at its functional centre (the so-called iron–molybdenum cofactor, FeMoco) both molybdenum and iron in a sulfur environment.[8] Therefore, study of the metals of groups 6 and 8 of the Periodic Table with sulfur donor ligands is of relevance to the function of FeMoco. In this paper we describe a further extension of our studies[1-3,5] of thiolate complexes of the group 8 metals. We have previously investigated the binding of dinitrogen at osmium(II)–thiolate sites,[1] the preparation of osmium(IV) thiolates, and some chemistry of thiolate complexes of osmium (III) with benzoic acid.[5] In this paper we describe an extension of this work to the preparation of new examples of carboxylate–thiolate complexes of

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osmium(III) and of thiolate complexes of osmium(IV), and an investigation of the electrochemistry of the latter compounds.

RESULTS AND DISCUSSION

Preparation of the complexes $[Os(SC_6F_5)_2(O_2CR)(PMe_2Ph)_2]$ (R = C_6F_5, **1**; $C_6H_4CF_3$-2, **2**; $C_6H_4CF_3$-3, **3**; $C_6H_4CF_3$-4, **4**; C_6H_4F-2, **5**; C_6H_4 F-3, **6**; C_6H_4F-4, **7**; CH_3, **8**; CF_3, **9**)

The reaction of the pentacoordinated complex $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ with various carboxylic acids RCO_2H, in acetone at room temperature, yields the compounds $[Os(SC_6F_5)_2(O_2CR)(PMe_2Ph)_2]$, **1–9**, according to reaction (1).

$$[Os(SC_6F_5)_3(PMe_2Ph)_2] + RCO_2H \rightarrow$$

$$[Os(SC_6F_5)_2(O_2CR)(PMe_2Ph)_2] + C_6F_5SH \quad (1)$$
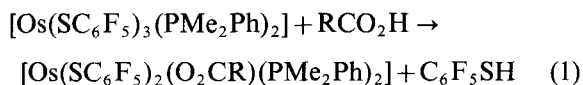
All carboxylate derivatives were obtained as stable, red, crystalline solids, with μ_{eff} values in the range expected for paramagnetic osmium(III) species (1.85–1.98 BM). Details of reaction conditions, elemental analyses and yields are given in the Experimental section. Molecular weight determinations by fast atom bombardment (FAB) mass-spectrometry show these products to be monomeric. High or considerable intensities were found for ions resulting from the loss of one thiolate ligand in all the compounds (**1–9**). Signals of ions resulting from the loss of one phosphine ligand were also observed for all these compounds. Although the molecular ion in the FAB spectrum for **9** is absent, this spectrum shows fragments where the $CF_3CO_2^-$ ion is present.

Infrared spectra of all complexes reveal the presence of both SC_6F_5 and PMe_2Ph ligands. They also show absorptions attributable to the carboxylate ligand. For complexes **2–8**, the asymmetric carboxylate stretching vibration, $v(OCO)_{asym}$, appears in the 1505–1480 cm^{-1} range, whereas the corresponding symmetric stretching vibration, $v(OCO)_{sym}$, occurs between 1410–1445 cm^{-1}. Unfortunately some of these bands appear in the region where the C—F stretching vibrations of the SC_6F_5 groups are found and their presence is inferred from the intensified or broader resulting shape of these absorptions. In any case, the value of $\Delta v(OCO)_{asym-sym}$ is in the expected[9,10] range (60–80 cm^{-1}).

The perfluorocarboxylate derivatives $[Os(SC_6F_5)_2(O_2CC_6F_5)(PMe_2Ph)_2]$ (**1**) and $[Os(SC_6F_5)_2(O_2CCF_3)(PMe_2Ph)_2]$ (**9**) have $\Delta v(OCO)_{asym-sym}$ values of 122 and 222 cm^{-1}, respectively.

For all complexes, therefore, the $\Delta v(OCO)_{asym-sym}$ values are consistent with the presence of chelating carboxylate ligands.[9,10]

The structure of $[Os(SC_6F_5)_2(O_2CC_6H_5)(PMe_2Ph)_2]$ has been shown by X-ray diffraction to be an octahedron with *trans*-thiophenolates, *cis*-phosphines and a chelating benzoate group,[5] whereas the structure of the closely related complex $[OsBr_2(O_2CMe)(PPh_3)_2]$ has been established as an octrahedral arrangement with *cis*-Br ligands, *trans*-phosphines and chelating acetate.[11]

The different coordination positions adopted by the phosphines in these complexes probably reflects steric demands by the larger ligands, rather than an electronic influence of the anions or the nature of the remote substituents on the carboxylate skeleton. There does, however, appear to be little energetic difference between the alternative geometries since $[OsBr_2(O_2CR^2)(PPh_3)_2]$ (R^2 = aryl) appear to have an octahedral structure with *trans*- instead of *cis*-Br ligands and chelated arylcarboxylates.[12]

On balance, it appears most likely that compounds **1–9** have *trans*-pentafluorothiophenolate groups, *cis*-phosphines and chelating carboxylic ligands.

Preparation of the complexes $[Os(SR)_4(PR_3^1)]$ [R = C_6F_4H-4, R^1 = C_6F_4Y-4 (Y = F, MeO, CF_3, Me or Cl); R = C_6F_5, PR_3^1 = $PMePh_2$; R = C_6F_4H-4, PR_3^1 = $PEtPh_2$ or $PMePh_2$] *and* $[OsBr(SC_6F_5)_3(PMe_2Ph)]$ (**10–18**)

The preparation of these new compounds follows published methods[5,13] and details of their characterization are given in the Experimental section.

Electrochemical properties of the complexes $[OsX(SR)_3(PR_3^1)]$ [X = Cl, R = C_6F_4H, PR_3^1 = PMe_2Ph; X = Cl, Br, R = C_6F_5, PR_3^1 = PMe_2Ph; X = SC_6F_5, PR_3^1 = PPh_3 or PMe_2Ph; X = SC_6F_4H-4, PR_3^1 = $P(C_6H_4Y$-4$)_3$ (Y = F, MeO, CF_3, Me or Cl)] and $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ were investigated by cyclic voltammetry at Pt or vitreous carbon electrodes in THF or CH_2Cl_2 containing 0.2 M $[NBu_4][BF_4]$. The data (Table 1) show that each osmium(IV) thiolate complex underwent a diffusion-controlled, reversible, one-electron reduction to the osmium(III) anion. The diffusion-controlled nature of the primary electron-transfer step was established by the linear dependence of the magnitude of the peak-current upon the square-root of the potential scan-rate. That the process involves the addition of a single electron was confirmed by the observation

Table 1. Electrochemical data for osmium complexes[a]

Compound	$E_{1/2}Os^{IV/III}$ (V)	$E_{1/2}Os^{III/II}$ (V)	Solvent etc.
[OsCl(SC$_6$F$_4$H-4)$_3$(PMe$_2$Ph)][5]	−0.8	−1.42[b], −1.56	THF/[NBu$_4$]][BF$_4$][c]
20	−0.81	−1.41[b], −1.35	CH$_2$Cl$_2$/[NBu$_4$][BF$_4$][c]
[OsCl(SC$_6$F$_5$)$_3$(PMe$_2$Ph)][5]	−0.82	−1.52[b], −1.43	CH$_2$Cl$_2$/[NBu$_4$][BF$_4$][c]
21			
[OsBr(SC$_6$F$_5$)$_3$(PMe$_2$Ph)]	−0.74	−1.38[b], −1.32	THF/[NBu$_4$][BF$_4$][c]
18	−0.78	−1.32, −1.43	CH$_2$Cl$_2$/[NBu$_4$][BF$_4$][c]
[Os(SC$_6$F$_5$)$_4$(PMe$_2$Ph)][13]	−0.5	−1.33	THF/[NBu$_4$][BF$_4$][c]
22			
[Os(SC$_6$F$_5$)$_4$(PPh$_3$)][13]	−0.67	−1.43	THF/[NBu$_4$][BF$_4$][c]
23			
[Os(SC$_6$F$_4$H-4)$_4${P(C$_6$H$_4$Me-4)$_3$}]	−0.86	−1.43	THF/[NBu$_4$][BF$_4$][c]
13			
[Os(SC$_6$F$_4$H-4)$_4${P(C$_6$H$_4$CF$_3$-4)$_3$}]	−0.63	−1.28	THF/[NBu$_4$][BF$_4$][c]
10			
[Os(SC$_6$F$_4$H-4)$_4${P(C$_6$H$_4$Cl-4)$_3$}]	−0.7	−1.35	THF/[NBu$_4$][BF$_4$][c]
11			
[Os(SC$_6$F$_4$H-4)$_4${P(C$_6$H$_4$F-4)$_3$}]	−0.73	−1.39	THF/[NBu$_4$][BF$_4$][c]
12			
[Os(SC$_6$F$_4$H-4)$_4${(PC$_6$H$_4$OMe-4)$_3$}]	−0.86	−1.54	THF/[NBu$_4$][BF$_4$][c]
14			
[Os(SC$_6$F$_5$)$_3$(PMe$_2$Ph)$_2$][5]		−0.79, +0.44[d]	THF/[NBu$_4$][BF$_4$][c]
19			

[a] Vitreous carbon electrode, referenced to ferrocene–ferricinium.

[b] This value is E_p^{red}, an irreversible, one-electron process.

[c] Under argon; see text for experiments under other gases.

[d] This value is E_p^{ox}, an irreversible, one-electron process.

that $\Delta E_p = |{}^1E_p^{red} - {}^1E_o^{ox}|$ is close to 60 mV for each of the complexes.

The ratio i_p^{ox}/i_p^{red} for each of the osmium (IV)/osmium(III) systems was close to one over the range of scan-rates 20–300 mV s^{-1}, thus showing that the osmium(III) anions have stabilities at room temperature of at least several seconds. Figure 1(b) shows a typical voltammogram for the tetrathiolate complexes and Fig. 1(a) that typical for the trithiolate halido-species.

The redox potentials for the osmium(IV)/osmium(III)-couple are dependent on the nature of the phosphine, the thiolate and the halide, as would be expected. For example, replacing the 4-OMe substituent in [Os(SC$_6$F$_4$H-4)$_4${P(C$_6$H$_4$OMe-4)}] by the CF$_3$ group shifts $^1E_{1/2}^{ox}$, the primary reduction potential, 230 mV positive; changing the thiolate in [OsCl(SC$_6$F$_4$H-4)$_3$(PMe$_2$Ph)] to SC$_6$F$_5$ has a relatively small effect upon $^1E_{1/2}^{ox}$ of ca 20 mV; replacing Cl in [OsCl(SC$_6$F$_5$)$_3$(PMe$_2$Ph)] by Br causes a shift in the reduction potential to a value ca 80 mV more positive. Whereas these observations are not particularly surprising, there appears an anomalous shift in potential when PMe$_2$Ph in

[Os(SC$_6$F$_5$)$_4$(PMe$_2$Ph)] is formally replaced by PPh$_3$: a shift in $^1E_{1/2}^{ox}$ to a value 80 mV more negative is observed.

The osmium(IV) thiolate complexes undergo a further single electron-transfer at potentials negative of the osmium(IV)/osmium(III)-couple. These reductions are partially reversible at normal scanrates. As might be expected, trends in the values of $^2E_{1/2}^{red}$ parallel those observed for the primary osmium(IV)/osmium(III)-couple. There is a considerable difference in the relative reversibility of the secondary process for the tetrathiolate and the trithiolate halido-complexes: the osmium(II)-dianions containing the tetrathiolate system are evidently more stable than the trithiolate halido-dianions as illustrated by the cyclic voltammograms of Fig. 1.

It is possible that the halido-osmium(II) dianions are less stable than the tetrathiolate species because Cl$^-$ (or Br$^-$) is more rapidly lost from the coordination sphere than is an arylthiolate ligand. However, an alternative explanation is that the sterically less demanding halide ligand allows a more facile rearrangement of the trigonal bipyramidal
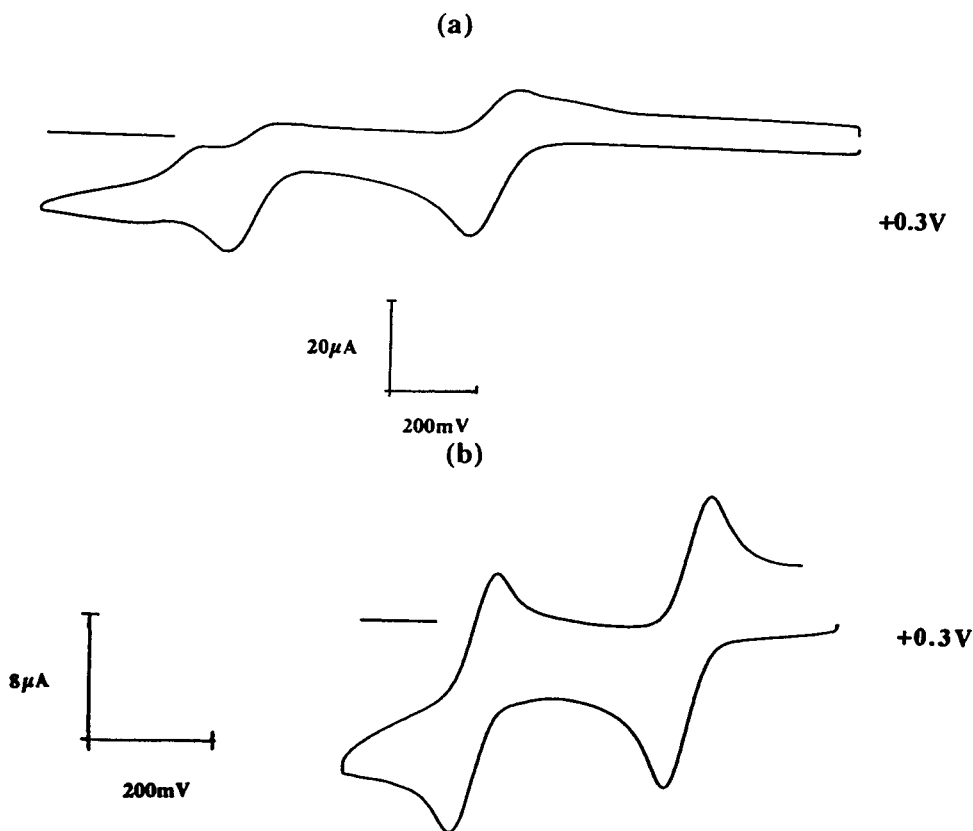
(a)

(b)

Fig. 1. Cyclic voltammograms of (a) [OsCl(SC$_6$F$_4$H)$_3$(PMe$_2$Ph)] and (b) [Os(SC$_6$F$_4$H)$_4${P(C$_6$H$_4$OMe-4)$_3$}] recorded under argon at a vitreous carbon electrode in 0.2 M [NBu$_4$]BF$_4$ and THF solvent at a scan-rate of 100 mV s^{-1}, showing primary and secondary reductions.

geometry to a square pyramidal form (see also Table 2).

EXPERIMENTAL

Infrared spectra (as KBr discs) were obtained using a Perkin–Elmer FTIR-1600 instrument. Magnetic data were determined using Gouy's method on a recording Johnson–Matthey magnetic balance. Elemental analyses were by Galbraith Laboratories Inc. FAB-mass spectrometric molecular weights (*m/z* values) were determined on a MS-Varian instrument at the UAM, Madrid, Spain. Since all complexes proved stable to air, reactions were carried out in open systems and at room temperature.

All carboxylic acids were used as supplied by Aldrich Chemical Co. The complexes [Os(SC$_6$F$_5$)$_3$ (PMe$_2$P)$_2$] and [OsX(SR)$_3$(PR$_3^1$)] were prepared as published.[5,13]

Electrochemical measurements were made using a Hi-Tek Instrument type D7-101 potentiostat and type PPR1 waveform generator. Voltammograms were recorded on a Philips PM 8043 X-Y recorder

and potentials were calibrated using the ferrocinium–ferrocene couple as internal standard. Electrolytes [tetrahydrofuran (THF) or CH$_2$Cl$_2$] were 0.2 M in [NBu$_4$][BF$_4$] and solvents were freshly distilled under argon from an appropriate drying agent.

Preparation of complexes: [Os(SC$_6$F$_5$)$_2$(O$_2$CR) (PMe$_2$Ph)$_2$]

The method used was general. The complex [Os(SC$_6$F$_5$)$_3$(PMe$_2$Ph)$_2$] (0.2 mmol) was dissolved in acetone (40 ml), RCO$_2$H (0.3 mmol) was added and the mixture was shaken at room temperature for *ca* 48 h. The resulting red solution was evaporated to dryness *in vacuo* to give a red solid which was washed with cold ethanol and recrystallized from acetone–ethanol solution as red crystals.

1 (R = C$_6$F$_5$). Yield 86%; m.p. 194–198°C (decomp.); μ_{eff}, 1.90 BM (Found: C, 39.0; H, 2.1; S, 6.0. C$_{35}$H$_{22}$F$_{15}$O$_2$OsP$_2$S$_2$ requires C, 39.1; H, 2.1; S, 6.0%); *m/z* 1077 (1077).

2 (R = C$_6$H$_4$CF$_3$-2). Yield 89%; m.p. 224–228°C

Table 2. ^{1}H, ^{31}P, ^{19}F NMR data for osmium complexes

Complex	δ (^{1}H)^a	δ (^{31}P)^a	δ (^{19}F)^a
10	6.31 q (H^4, ax) (1) 7.00 m (H^4, eq) (3) 7.88 m (C$_6$H$_4$)	-132.72 s	-129.89 m (F^2, eq) -131.74 m (F^2, ax) -139.22 m (F^3, eq) -142.51 m (F^3, ax)
11	6.29 q (H^4, ax) (1) 6.97 m (H^4, eq) (3) 7.62–7.26 m (C$_6$H$_4$)	-134.38 s	-129.94 m (F^2, eq) -131.90 m (F^2, ax) -139.38 m (F^3, eq) -142.72 m (F^3, ax)
12	6.29 q (H^4, ax) (1) 6.98 m (H^4, eq) (3) 7.75–7.29 m (C$_6$H$_4$)	-135.61 s	-130.02 m (F^2, eq) -132.04 m (F^2, ax) -139.54 m (F^3, eq) -142.90 m (F^3, ax)
13	2.45 s (Me) 6.25 q (H^4, ax) (1) 6.93 m (H^4, eq) (3) 7.63–7.35 m (C$_6$H$_4$)	-135.98 s	-130.01 m (F^2, eq) -132.30 m (F^2, ax) -140.05 m (F^3, eq) -143.34 m (F^3, ax)
14	3.88 s (OMe) 6.25 q (H^4, ax) (1) 6.93 m (H^4, eq) (3) 7.05–7.66 m (C$_6$H$_4$)	-137.83 s	-130.07 m (F^2, eq) -132.37 m (F^2, ax) -140.04 m (F^3, eq) -143.37 m (F^3, ax)
15	2.4 d (CH$_3$) 2.75 d (CH$_3$) 2.8 d (CH$_3$) 7.6–7.4 m (C$_6$H$_5$)	-154.5 s (2.3) -156.5 s (14.6) -157.9 s (1)	
16	1.5 dt (CH$_3$) 3.1 q (CH$_2$) 6.2 q (H^4, ax) (1) 6.9 m (H^4, eq) (3) 7.4–8.0 m (C$_6$H$_5$)	-142.5 s	-126.4 m (F^2, eq) -128.8 m (F^2, ax) -136.2 m (F^3, eq) -139.7 m (F^3, ax)
17	2.4 d (CH$_3$) 2.8 d (CH$_3$) 6.2 m (H^4, ax) (1) 6.65 m (H^4, ap) (1.5)^b 6.8 m (H^4, trans) (1.5)^b 6.95 m (H^4, eq) (3) 7.15 m (H^4, cis) (3)^b 7.4–8.0 m (C$_6$H$_5$)	-154.9 s (1) -156.5 s (1.5)	-129.5 m (F^2) -131.2 m (F^2) -131.6 m (F^2) -132.1 m (F^2) -138.0 m (F^3) -139.3 m (F^3) -139.6 m (F^3) -141.6 q (F^3) -142.8 q (F^3)

^{a} Chemical shifts in ppm relative to SiMe$_4$ (^{1}H), P(OMe)$_3$ (^{31}P), or CFCl$_3$ (^{19}F); s = singlet, d = doublet, t = triplet, q = quintet; selected relative integrations in parentheses; eq = equatorial, ax = axial. H^4, F^2, etc. refer to position of nucleus in aromatic ring.

^{b} These signals are assigned to another isomer in solution with a square pyramid geometry with the phosphine in a base position; proportion with respect to the trigonal bipyramidal isomer is 1 : 1.5; ap = apical, trans = trans to phosphine, cis = cis to phosphine.

(decomp.); μ_{eff}, 1.90 BM (Found: C, 40.0; H, 2.5; S, 6.2. $C_{36}H_{26}F_{13}O_2OsP_2S_2$ requires C, 41.0; H, 2.5; S, 6.1%); m/z 1055 (1055).

3 (R = $C_6H_4CF_3$-3). Yield 94%; m.p. 217–221°C (decomp.); μ_{eff}, 1.95 BM (Found: C, 41.6; H, 2.5; S, 6.6. $C_{36}H_{26}F_{13}O_2OsP_2S_2$ requires C, 41.0; H, 2.5; S, 6.1%); m/z 1055 (1055).

4 (R = $C_6H_4CF_3$-4). Yield 90%; m.p. 225–229°C (decomp.); μ_{eff}, 1.94 BM (Found: C, 40.7; H, 2.2; S, 6.2. $C_{36}H_{26}F_{13}O_2OsP_2S_2$ requires C, 41.0; H, 2.5; S, 6.1%); m/z 1055 (1055).

5 (R = C_6H_4F-2). Yield 96%; m.p. 197–201°C; μ_{eff}, 1.86 BM (Found: C, 41.7; H, 2.6; S, 6.4. $C_{35}H_{26}F_{11}O_2OsP_2S_2$ requires C, 41.9; H, 2.6; S, 6.4%); m/z 1005 (1005).

6 (R = C_6H_4F-3). Yield 98%; m.p. 219–223°C (decomp.); μ_{eff}, 1.86 BM (Found: C, 41.6; H, 2.6; S, 6.7. $C_{35}H_{26}F_{11}O_2OsP_2S_2$ requires C, 41.9; H, 2.6; S, 6.4%); m/z 1005 (1005).

7 (R = C_6H_4F-4). Yield 99%; m.p. 225–229°C (decomp.); μ_{eff}, 1.95 BM (Found: C, 41.8; H, 2.6; S, 6.5. $C_{35}H_{26}F_{11}O_2OsP_2S_2$ requires C, 41.9; H, 2.6; S, 6.4%); m/z 1005 (1005).

8 (R = CH_3). Yield 97%; m.p. 185–189°C (decomp.); μ_{eff}, 1.98 BM (Found C, 39.1; H, 2.6; S, 6.8. $C_{30}H_{25}F_{10}O_2OsP_2S_2$ requires C, 39.0; H, 2.7; S, 6.9%); m/z 925 (925).

9(R = CF_3). Yield 86%; m.p. 174–178°C (decomp.); μ_{eff} 1.85 BM (Found: C, 36.1; H, 2.4; S, 6.4. $C_{30}H_{22}F_{13}O_2OsP_2S_2$ requires C, 36.9; H, 2.3; S, 6.6%);

Preparation of the complexes: [Os(SR)$_4$(PR$_3^1$)] [R = C_6F_4H-4, R^1 = C_6F_4Y-4 (Y = F, MeO, CF$_3$, Me or Cl); R = C_6F_5, R^1 = C_6F_4Y-4 (Y = CF$_3$, or F); R = C_6F_5, PR$_3^1$ = PMePh$_2$; R = C_6F_4H-4, PR$_3^1$ = PEtPh$_2$] **(10–17)**

This followed the published procedure[13] and details of their characterization are given below in Tables 2–6. The brown complex [OsBr(SC$_6$F$_5$)$_3$ (PMe$_2$Ph)] **(18)** was prepared by the published pro-

Table 4. IR data for osmium complexes[a]

Complex	PR$_3$	SR
10	1176, 1136, 1062	1492, 918, 880
11	1084, 1014, 820	1492, 918, 882
12	1230, 831, 532	1491, 919, 882
13	1098, 1026, 538	1492, 918, 878
14	1095, 808, 711	1492, 918, 884
15	1087, 889, 692	1510, 1087, 979
16	1097, 747, 515	1429, 1176, 917
17	884, 738, 503	1430, 1176, 916

[a] Selected bands only, KBr discs, cm^{-1}.

Table 5. Analytical data for osmium complexes[a]

Complex	%C	%H	%S
10	39.5 (39.1)	1.0 (1.2)	8.9 (9.3)
11	39.6 (39.4)	1.1 (1.3)	9.4 (10.0)
12	41.0 (41.0)	1.5 (1.3)	10.2 (10.4)
13	45.2 (44.2)	2.0 (2.1)	10.2 (10.5)
14	41.6 (42.6)	2.2 (2.0)	9.1 (10.1)
15	37.5 (37.4)	1.3 (1.1)	10.8 (10.8)
16	39.7 (40.4)	1.8 (1.7)	11.2 (11.3)
17	39.8 (39.9)	1.7 (1.6)	12.4 (12.3)

[a] Calculated values in parentheses.

cedure[5] and had the following properties. Yield 86.9%; m.p. 205°C. (Found: C, 31.0; H, 1.1; S, 9.5. $C_{26}H_{11}BrF_{15}OsPS_3$ requires C, 31.0; H, 1.1; S, 9.6%). NMR (CDCl$_3$): ^{1}H, δ 2.51, 2.55 [d, ^2J(PH) 10.45 Hz, PCH_3], 7.58–8.03 (m, C_6H_5); ^{19}F, δ −131.63, −131.66, −131.69 (2-F), −151.4, −151.47, −151.55 (4-F), −162.65, −162.72,

Table 3. Physical properties of the osmium complexes

Complex		Yield (%)	Colour	M.p. (°C)
10	[Os(SC$_6$F$_4$H-4){P(C$_6$H$_4$CF$_3$-4)$_3$}]	61	Green	192–195
11	[Os(SC$_6$F$_4$H-4){P(C$_6$H$_4$Cl-4)$_3$}]	59	Green	220–223
12	[Os(SC$_6$F$_4$H-4){P(C$_6$H$_4$F-4)$_3$}]	60	Green	214–216
13	[Os(SC$_6$F$_4$H-4){P(C$_6$H$_4$Me-4)$_3$}]	58	Green	219–221
14	[Os(SC$_6$F$_4$H-4){P(C$_6$H$_4$OMe-4)$_3$}]	61	Green	225–229
15	[Os(SC$_6$F$_5$)$_4$(PMePh$_2$)]	33	Green	197–199
16	[Os(SC$_6$F$_4$H-4)$_4$(PEtPh$_2$)]	38	Green	187–189
17	[Os(SC$_6$F$_4$H-4)$_4$(PMePh$_2$)]	41	Green	186–188

Table 6. ^{13}C NMR data^a for osmium complexes

Complex	SC$_6$F$_4$H-4	P(C$_6$H$_4$-Y-4)
10	107.38 (C^1, J_{F-C} = 23.3) 146.32 (C^2, J_{F-C} = 249.9) 143.41 (C^3, J_{F-C} = 257.5) 99.63 (C^4, J_{F-C} = 23.2)	133.39 (C^1, J_{P-C} = 53.3) 134.57 (C^2, J_{P-C} = 9.3) 126.34 (C^3, J_{P-C} = 6.9) 134.43 (C^4)
11	107.12 (C^1, J_{F-C} = 22.7) 146.26 (C^2, J_{F-C} = 258.1) 143.39 (C^3, J_{F-C} = 260.9) 99.33 (C^4, J_{F-C} = 23.7)	127.86 (C^1, J_{P-C} = 55.9) 135.24 (C^2, J_{P-C} = 10.2) 129.75 (C^3, J_{P-C} = 11.2) 139.17 (C^4)
12	107.07 (C^1, J_{F-C} = 22.0) 146.28 (C^2, J_{F-C} = 251.6) 143.48 (C^3, J_{F-C} = 251.6) 99.27 (C^4, J_{F-C} = 23.2)	125.50 (C^1, J_{P-C} = 55.7) 136.32 (C^2, J_{P-C} = 9.3) 116.82 (C^3, J_{P-C} = 11.6) 165.08 (C^4)
13	106.61 (C^1, J_{F-C} = 23.2) 146.18 (C^2, J_{F-C} = 248.2) 143.68 (C^3, J_{F-C} = 249.0) 98.82 (C^3, J_{F-C} = 24.4)	126.87 (C^1, J_{P-C} = 58.0) 134.08 (C^2, J_{P-C} = 9.3) 129.82 (C^3, J_{P-C} = 11.6) 142.26 (C^4) 21.55 (C^5)
14	106.61 (C^1, J_{F-C} = 23.2) 146.24 (C^2, J_{F-C} = 243.6) 143.33 (C^3, J_{F-C} = 251.6) 98.80 (C^4, J_{F-C} = 23.2)	121.39 (C^1, J_{P-C} = 62.6) 135.71 (C^2, J_{P-C} = 9.3) 114.63 (C^3, J_{P-C} = 11.0) 162.21 (C^4) 55.41 (C^5)

^{a} Chemical shifts in ppm relative to SiMe$_4$; assignments and coupling constants (in Hz) in parentheses. C^1, C^3, etc. refer to position of nucleus in aromatic ring.

−162.78 (3-F) (SC$_6$F$_5$); ^{31}P{^{1}H}, δ −171.82 (s, PMe$_2$Ph).

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