

# Thiolate Complexes of Osmium(III) and Osmium(IV). Crystal Structures of $[\text{Os}(\text{SC}_6\text{F}_5)_2(\text{O}_2\text{CPh})(\text{PMe}_2\text{Ph})_2]$ and $[\text{OsCl}(\text{SC}_6\text{F}_5)_3(\text{PMe}_2\text{Ph})]$ †

Adrian Hills,<sup>a</sup> David L. Hughes,<sup>a</sup> Raymond L. Richards,<sup>\*a</sup> Maribel Arroyo,<sup>b</sup> (the late) Diana Cruz-Garriz<sup>b</sup> and Hugo Torrens<sup>b</sup>

<sup>a</sup> AFRC-IPSR Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ, UK

<sup>b</sup> Facultad de Quimica, UNAM, Ciudad Universitaria, 04510, Mexico, D.F., Mexico

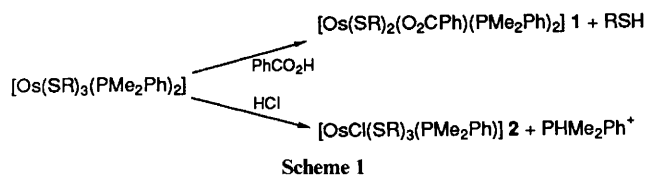
Treatment of  $[\text{Os}(\text{SR})_3(\text{PMe}_2\text{Ph})_2]$  ( $\text{R} = \text{C}_6\text{F}_5$  or  $\text{C}_6\text{HF}_4$ ) with  $\text{PhCO}_2\text{H}$  or with  $\text{HCl}$  in acetone gives, respectively, the red paramagnetic osmium(III) derivatives  $[\text{Os}(\text{SR})_2(\text{O}_2\text{CPh})(\text{PMe}_2\text{Ph})_2]$  **1** and the green, five-co-ordinate, diamagnetic osmium(IV) complexes  $[\text{OsCl}(\text{SR})_3(\text{PMe}_2\text{Ph})]$  **2**. X-Ray crystallography has shown that **1** ( $\text{R} = \text{C}_6\text{F}_5$ ) has an octahedral structure with *trans*-thiolates, *cis*-phosphines and a chelating benzoate ligand and that **2** ( $\text{R} = \text{C}_6\text{F}_5$ ) has a trigonal-bipyramidal structure with thiolates in the equatorial plane.

Thiolate ligands are of high current interest because of their relevance to catalytic processes involving metals with sulphur ligand environments (e.g. nitrogen fixation and hydrodesulphurisation) and their ability to stabilise unusual geometries and oxidation states by variation of their steric and electronic properties.<sup>1</sup>

We have been investigating the chemistry of ruthenium and osmium with thiolate ligands, particularly with co-ligands such as dinitrogen<sup>2</sup> and carbon monoxide,<sup>3</sup> where the metals are in relatively low oxidation states (II or III). Here we describe an extension of this work to the preparation of new thiolate complexes of osmium in oxidation states III and IV.

## Results and Discussion

**Preparation and Structures of  $[\text{Os}(\text{SC}_6\text{F}_5)_2(\text{O}_2\text{CPh})(\text{PMe}_2\text{Ph})_2]$  and  $[\text{OsCl}(\text{SC}_6\text{F}_5)_3(\text{PMe}_2\text{Ph})]$ .**—We are interested in the reaction of various acidic reagents with osmium thiolate complexes, undertaken in order to obtain thiolate complexes in higher oxidation states. In this particular example the reagents were  $\text{PhCO}_2\text{H}$  and  $\text{HCl}$ , which have afforded benzoate and chloride derivatives of the unsaturated osmium thiolate precursor  $[\text{Os}(\text{SR})_3(\text{PMe}_2\text{Ph})_2]$  ( $\text{R} = \text{C}_6\text{F}_5$  or  $\text{C}_6\text{HF}_4$ ) according to the reactions shown in Scheme 1.



The  $\text{Os}^{\text{III}}$  complexes **1** ( $\text{R} = \text{C}_6\text{F}_5$  or  $\text{C}_6\text{HF}_4$ ) were isolated as paramagnetic red crystals and have been structurally characterised for  $\text{R} = \text{C}_6\text{F}_5$ , which is an octahedral benzoate complex as shown in Fig. 1. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.

† (Benzoato-*O,O'*)bis(dimethylphenylphosphine)bis(pentafluorobenzenethiolato-*S*)osmium(III) and chloro(dimethylphenylphosphine)-tris(pentafluorobenzenethiolato-*S*)osmium(IV).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

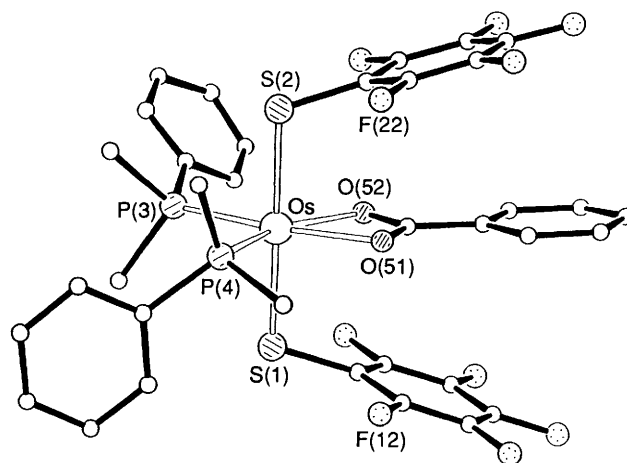


Fig. 1 View of a molecule of  $[\text{Os}(\text{SC}_6\text{F}_5)_2(\text{O}_2\text{CPh})(\text{PMe}_2\text{Ph})_2]$

The structure of **1** ( $\text{R} = \text{C}_6\text{F}_5$ ) consists of discrete essentially octahedral molecules, with one angle ( $\text{O}-\text{Os}-\text{O}$ ) rather small ( $59.7^\circ$ ) because of the constrained bite of the chelating benzoate ligand. The *trans* Os–S distances are somewhat shorter than those found<sup>3</sup> in the  $\text{Os}^{\text{II}}$  compound  $[\text{Os}(\text{SC}_6\text{F}_5)_2(\text{CO})_2(\text{PEt}_2\text{Ph})_2]$ , i.e. 2.329(1) and 2.335(1) versus 2.477(1) Å (mean). The *cis*-Os–P distances [2.293(1) and 2.300(1)] are shorter than those in the above dicarbonyl [2.407(1) (*trans*)] and in  $[\text{OsCl}(\text{SC}_6\text{F}_5)(\text{N}_2)(\text{PMe}_2\text{Ph})_3]$ <sup>2</sup> [2.375(1) and 2.381(1) (*trans*); 2.326 Å (unique)]. This shortening might be expected on passing to the higher oxidation state in **1** ( $\text{R} = \text{C}_6\text{F}_5$ ). Other dimensions are unexceptional, but it is noteworthy that the arrangement of the aryl groups of the  $\text{SC}_6\text{F}_5$  and benzoate ligands is layered, with the  $\text{C}_6\text{F}_5$  rings close to eclipsed (Fig. 2). This type of packing has been observed in other  $\text{SC}_6\text{F}_5$  complexes.<sup>4</sup>

Compounds **2** are green, diamagnetic and have the trigonal-bipyramidal structure shown in Fig. 3. Atomic coordinates for **2** ( $\text{R} = \text{C}_6\text{F}_5$ ) are listed in Table 3 and molecular dimensions in Table 4. The loss of  $\text{PMe}_2\text{Ph}$  giving five-co-ordination is presumably a consequence of steric pressure from the bulky  $\text{SC}_6\text{F}_5$  groups. Compounds **2** are rare examples of osmium(IV) thiolate complexes; the analogue  $[\text{Os}(\text{SC}_6\text{H}_2\text{Pr}^{\text{i}})_3(2,4,6)_4(\text{CH}_3\text{CN})]$  has been reported and probably has a

**Table 1** Final atomic coordinates (fractional  $\times 10^4$ ) for **1** ( $R = C_6F_5$ ) with estimated standard deviations (e.s.d.s) in parentheses

| Atom  | x         | y         | z         | Atom  | x        | y         | z        |
|-------|-----------|-----------|-----------|-------|----------|-----------|----------|
| Os    | 3053.7(1) | 2298.5(1) | 2187.6(1) | C(31) | 5717(5)  | 3187(4)   | 2631(6)  |
| S(1)  | 1947(1)   | 3723.6(7) | 1863(1)   | C(32) | 6886(10) | 3039(10)  | 3149(18) |
| C(11) | 782(4)    | 3857(3)   | 221(4)    | C(33) | 7507(14) | 3260(12)  | 2443(24) |
| C(12) | -366(4)   | 3566(3)   | -153(5)   | C(34) | 6949(17) | 3569(9)   | 1244(19) |
| F(12) | -625(3)   | 3177(2)   | 735(3)    | C(35) | 5812(14) | 3775(13)  | 778(11)  |
| C(13) | -1300(5)  | 3677(4)   | -1434(6)  | C(36) | 5178(9)  | 3572(11)  | 1456(8)  |
| F(13) | -2396(3)  | 3391(3)   | -1743(5)  | C(37) | 4754(5)  | 4059(4)   | 4100(6)  |
| C(14) | -1079(5)  | 4071(4)   | -2345(5)  | C(38) | 5962(5)  | 2232(5)   | 4928(6)  |
| F(14) | -1957(4)  | 4194(3)   | -3593(3)  | P(4)  | 2771(1)  | 1854.9(8) | 3929(1)  |
| C(15) | 46(6)     | 4380(3)   | -2029(5)  | C(41) | 3002(5)  | 2635(3)   | 5182(4)  |
| F(15) | 253(4)    | 4792(3)   | -2953(3)  | C(42) | 3962(7)  | 2451(6)   | 6443(5)  |
| C(16) | 958(4)    | 4274(3)   | -748(5)   | C(43) | 4097(9)  | 3079(7)   | 7369(7)  |
| F(16) | 2036(3)   | 4580(2)   | -475(3)   | C(44) | 3341(10) | 3855(7)   | 7043(8)  |
| S(2)  | 4269(1)   | 940.1(8)  | 2439(1)   | C(45) | 2390(9)  | 4045(5)   | 5862(8)  |
| C(21) | 3582(4)   | 427(3)    | 948(4)    | C(46) | 2226(7)  | 3424(4)   | 4901(6)  |
| C(22) | 2770(5)   | -250(3)   | 728(5)    | C(47) | 1170(5)  | 1619(4)   | 3272(5)  |
| F(22) | 2509(4)   | -514(3)   | 1667(4)   | C(48) | 3532(6)  | 746(4)    | 4819(5)  |
| C(23) | 2217(6)   | -657(4)   | -416(7)   | O(51) | 1451(2)  | 1737(2)   | 685(3)   |
| F(23) | 1430(5)   | -1281(3)  | -560(5)   | O(52) | 2637(3)  | 2479(2)   | 141(3)   |
| C(24) | 2457(7)   | -404(5)   | -1384(6)  | C(50) | 1689(3)  | 2036(3)   | -200(3)  |
| F(24) | 1895(5)   | -770(4)   | -2528(4)  | C(51) | 910(4)   | 1858(3)   | -1570(4) |
| C(25) | 3252(7)   | 254(5)    | -1221(6)  | C(52) | -77(4)   | 1331(3)   | -1888(5) |
| F(25) | 3486(5)   | 515(4)    | -2191(4)  | C(53) | -802(6)  | 1152(5)   | -3192(5) |
| C(26) | 3823(5)   | 663(3)    | -69(4)    | C(54) | -529(7)  | 1486(5)   | -4124(6) |
| F(26) | 4612(3)   | 1308(2)   | 82(4)     | C(55) | 419(6)   | 2026(5)   | -3805(5) |
| P(3)  | 4851(1)   | 2939.9(9) | 3463(1)   | C(56) | 1157(5)  | 2220(4)   | -2527(5) |

**Table 2** Selected bond dimensions for **1** ( $R = C_6F_5$ ) (distances in Å, angles in °) with e.s.d.s in parentheses. (\*) Indicates angles with e.s.d.s less than  $0.05^\circ$ 

## (a) Co-ordination sphere of the osmium atom

|                |          |               |          |
|----------------|----------|---------------|----------|
| Os-S(1)        | 2.329(1) | Os-S(2)       | 2.335(1) |
| Os-P(3)        | 2.293(1) | Os-P(4)       | 2.300(1) |
| Os-O(51)       | 2.167(2) | Os-O(52)      | 2.201(3) |
| S(1)-Os-S(2)   | 174.7(1) | P(3)-Os-P(4)  | 93.2(*)  |
| S(1)-Os-P(3)   | 90.8(*)  | S(2)-Os-P(3)  | 86.3(*)  |
| S(1)-Os-P(4)   | 91.1(*)  | S(2)-Os-P(4)  | 93.4(*)  |
| S(1)-Os-O(51)  | 90.8(1)  | S(2)-Os-O(51) | 91.3(1)  |
| P(3)-Os-O(51)  | 168.8(1) | P(4)-Os-O(51) | 97.8(1)  |
| S(1)-Os-O(52)  | 88.0(1)  | S(2)-Os-O(52) | 88.8(1)  |
| P(3)-Os-O(52)  | 109.3(1) | P(4)-Os-O(52) | 157.5(1) |
| O(51)-Os-O(52) | 59.7(1)  |               |          |

## (b) Pentafluorothiophenolate ligands

|               |          |               |          |
|---------------|----------|---------------|----------|
| S(1)-C(11)    | 1.769(4) | S(2)-C(21)    | 1.761(4) |
| Os-S(1)-C(11) | 107.6(1) | Os-S(2)-C(21) | 107.0(1) |

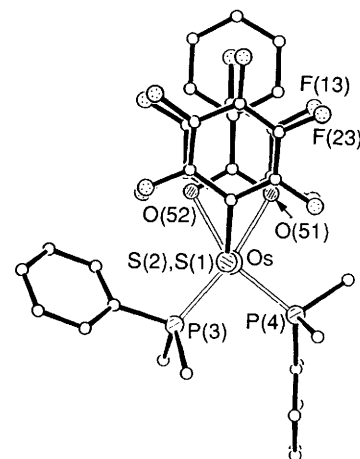
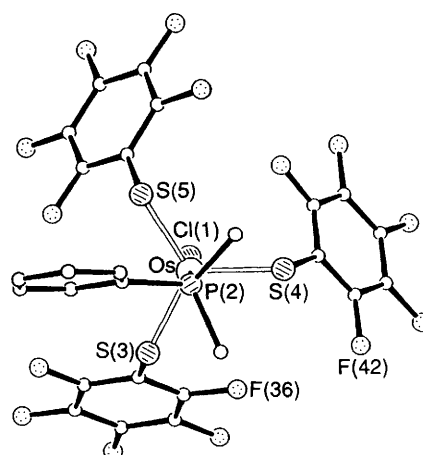
## (c) Dimethylphenylphosphine ligands

|                  |          |                  |          |
|------------------|----------|------------------|----------|
| P(3)-C(31)       | 1.803(8) | P(4)-C(41)       | 1.818(5) |
| P(3)-C(37)       | 1.834(6) | P(4)-C(47)       | 1.822(6) |
| P(3)-C(38)       | 1.827(5) | P(4)-C(48)       | 1.815(5) |
| Os-P(3)-C(31)    | 113.2(2) | Os-P(4)-C(41)    | 121.6(2) |
| Os-P(3)-C(37)    | 117.6(2) | Os-P(4)-C(47)    | 106.9(2) |
| C(31)-P(3)-C(37) | 102.3(3) | C(41)-P(4)-C(47) | 103.4(3) |
| Os-P(3)-C(38)    | 116.4(2) | Os-P(4)-C(48)    | 116.8(3) |
| C(31)-P(3)-C(38) | 103.0(3) | C(41)-P(4)-C(48) | 104.5(2) |
| C(37)-P(3)-C(38) | 102.3(3) | C(47)-P(4)-C(48) | 101.0(3) |

## (d) Benzoate ligand

|                   |          |                   |          |
|-------------------|----------|-------------------|----------|
| O(51)-C(50)       | 1.271(6) | O(52)-C(50)       | 1.270(5) |
| C(50)-C(51)       | 1.473(5) |                   |          |
| Os-O(51)-C(50)    | 92.1(2)  | Os-O(52)-C(50)    | 90.5(3)  |
| O(51)-C(50)-O(52) | 117.7(3) | O(51)-C(50)-C(51) | 121.3(4) |
| O(52)-C(50)-C(51) | 121.0(4) |                   |          |

trigonal-bipyramidal structure like its structurally characterised ruthenium analogue.<sup>5</sup> In the structures of **2** ( $R = C_6F_5$ ) and  $[Ru(SC_6H_2Pr^{1,3-2,4,6})_4(CH_3CN)]$ ,<sup>5</sup> the thiolate ligands occupy

**Fig. 2** A molecule of  $[Os(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2]$  viewed down the S(2)-S(1) vector, showing the alignment of the stacked  $SC_6F_5$  and benzoate ligands**Fig. 3** View of a molecule of  $[OsCl(SC_6F_5)_3(PMe_2Ph)]$

**Table 3** Final atomic coordinates (fractional  $\times 10^4$ ) for **2** ( $R = C_6F_5$ ) with e.s.d.s in parentheses

| Atom  | x         | y          | z         | Atom  | x         | y          | z         |
|-------|-----------|------------|-----------|-------|-----------|------------|-----------|
| Os    | 2017.0(1) | -1236.9(1) | 2561.0(1) | C(41) | 665(3)    | -2492(2)   | 3650(2)   |
| Cl(1) | -347.2(7) | -1369.1(4) | 2375.2(4) | C(42) | 160(4)    | -2483(2)   | 4460(2)   |
| P(2)  | 4314.5(7) | -1110.8(4) | 2733.5(5) | F(42) | 758(3)    | -2105(1)   | 5102(1)   |
| C(21) | 5146(3)   | -531(2)    | 2022(2)   | C(43) | -976(4)   | -2865(2)   | 4634(2)   |
| C(22) | 4464(3)   | -26(2)     | 1599(2)   | F(43) | -1429(3)  | -2852(1)   | 5439(1)   |
| C(23) | 5113(4)   | 424(2)     | 1087(3)   | C(44) | -1610(4)  | -3244(2)   | 3994(3)   |
| C(24) | 6463(4)   | 364(2)     | 982(3)    | F(44) | -2722(3)  | -3594(1)   | 4163(2)   |
| C(25) | 7148(4)   | -131(2)    | 1389(3)   | C(45) | -1143(4)  | -3255(2)   | 3184(3)   |
| C(26) | 6507(3)   | -574(2)    | 1907(2)   | F(45) | -1778(3)  | -3625(1)   | 2553(2)   |
| C(27) | 4836(3)   | -800(2)    | 3810(2)   | C(46) | -1(3)     | -2891(2)   | 3018(2)   |
| C(28) | 5145(4)   | -1919(2)   | 2604(3)   | F(46) | 444(2)    | -2941(1)   | 2227(1)   |
| S(3)  | 1885.2(7) | -182.8(4)  | 3088.2(5) | S(5)  | 2384.7(7) | -1461.1(4) | 1193.0(5) |
| C(31) | 246(3)    | 88(2)      | 3253(2)   | C(51) | 922(3)    | -1680(2)   | 579(2)    |
| C(32) | -256(3)   | 625(2)     | 2799(2)   | C(52) | 653(3)    | -2356(2)   | 321(2)    |
| F(32) | 415(2)    | 881(1)     | 2156(2)   | F(52) | 1435(2)   | -2855(1)   | 587(1)    |
| C(33) | -1458(4)  | 903(2)     | 2987(3)   | C(53) | -423(4)   | -2533(2)   | -205(2)   |
| F(33) | -1905(3)  | 1417(1)    | 2531(2)   | F(53) | -698(3)   | -3190(1)   | -432(1)   |
| C(34) | -2168(3)  | 645(2)     | 3645(3)   | C(54) | -1230(3)  | -2030(2)   | -492(2)   |
| F(34) | -3334(2)  | 913(1)     | 3835(2)   | F(54) | -2279(2)  | -2198(2)   | -1015(1)  |
| C(35) | -1701(3)  | 113(2)     | 4092(2)   | C(55) | -992(3)   | -1365(2)   | -247(2)   |
| F(35) | -2397(2)  | -133(1)    | 4738(1)   | F(55) | -1799(2)  | -874(1)    | -514(2)   |
| C(36) | -507(3)   | -163(2)    | 3900(2)   | C(56) | 88(3)     | -1194(2)   | 286(2)    |
| F(36) | -76(2)    | -672(1)    | 4370(1)   | F(56) | 315(2)    | -534(1)    | 528(1)    |
| S(4)  | 2187.7(8) | -2067.2(4) | 3470.0(6) |       |           |            |           |

**Table 4** Selected bond dimensions in **2** ( $R = C_6F_5$ ) (distances in Å, angles in °) with e.s.d.s in parentheses

## (a) Co-ordination sphere of the osmium atom\*

|               |          |              |          |
|---------------|----------|--------------|----------|
| Os-Cl(1)      | 2.408(1) | Os-S(3)      | 2.196(1) |
| Os-P(2)       | 2.339(1) | Os-S(4)      | 2.195(1) |
| Os-S(5)       | 2.201(1) |              |          |
| Cl(1)-Os-P(2) | 179.7    | P(2)-Os-S(4) | 85.9     |
| Cl(1)-Os-S(3) | 92.6     | P(2)-Os-S(5) | 85.7     |
| Cl(1)-Os-S(4) | 94.2     | S(3)-Os-S(4) | 118.1    |
| Cl(1)-Os-S(5) | 94.0     | S(3)-Os-S(5) | 122.0    |
| P(2)-Os-S(3)  | 87.6     | S(4)-Os-S(5) | 118.7    |

## (b) Dimethylphenylphosphine ligand

|               |          |                  |          |
|---------------|----------|------------------|----------|
| P(2)-C(21)    | 1.822(3) | P(2)-C(28)       | 1.814(4) |
| P(2)-C(27)    | 1.818(4) |                  |          |
| Os-P(2)-C(21) | 117.1(1) | C(21)-P(2)-C(27) | 104.3(2) |
| Os-P(2)-C(27) | 112.7(1) | C(21)-P(2)-C(28) | 105.3(2) |
| Os-P(2)-C(28) | 112.5(1) | C(27)-P(2)-C(28) | 103.7(2) |

## (c) Pentafluorothiophenolate ligands

|               |          |               |          |
|---------------|----------|---------------|----------|
| S(3)-C(31)    | 1.776(3) | S(5)-C(51)    | 1.772(3) |
| S(4)-C(41)    | 1.768(3) |               |          |
| Os-S(3)-C(31) | 114.4(1) | Os-S(5)-C(51) | 112.9(1) |
| Os-S(4)-C(41) | 113.4(1) |               |          |

\* Angles about the Os atom have e.s.d.s  $< 0.05^\circ$ .

the equatorial positions of the trigonal bipyramid. In **2** ( $R = C_6F_5$ ), the thiolate aryl substituents are all 'down' towards and around the smaller chloride ligand, whereas the above ruthenium complex analogue has the more usual 'two up-one down' arrangement. The Os-S distances [2.201(1), 2.196(1) and 2.195(1) Å] are shorter than those of **1** ( $R = C_6F_5$ ), as might be expected from a further increase of the oxidation state to Os<sup>IV</sup> and from the reduction in co-ordination number. The axial Os-P distance is, however, longer at 2.339(1) Å than the Os-P distances in **1** ( $R = C_6F_5$ ) and longer than, or close to, the Os-P distances in the osmium(II) complexes discussed above. In view of the different environment of the phosphine ligands in the series of compounds under discussion, for instance  $PMe_2Ph$  can be *trans* to O, Cl, S or P in five- and six-co-ordinate complexes, it would be unwise to draw too many inferences from these data, but clearly the oxidation state of the central metal is not

paramount in determining osmium-phosphorus bond distances.

As would be expected from their formally d<sup>4</sup> electronic arrangement and their geometry, compounds **2** are diamagnetic as is  $[Os(SC_6H_2Pr^{i_3-2,4,6})_4(MeCN)]$ .<sup>5</sup> Their <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P NMR spectra (Experimental section) are as expected if their solid-state structure is maintained in solution.

**Conclusion**

Use of the bulky  $SC_6F_5$  ligand allows stabilisation of new six-co-ordinate complexes of Os<sup>III</sup> and five-co-ordinate complexes of Os<sup>IV</sup>. The latter compounds are of potential use in further syntheses because of their unsaturation and are a likely source of reactive metal centres by reduction. Work in these areas will be reported at a later date.

**Experimental**

NMR spectra were obtained using a JEOL FX 270 instrument, with chemical shifts quoted relative to  $SiMe_4$  (<sup>1</sup>H),  $CFCl_3$  (<sup>19</sup>F) or  $P(OMe)_3$  (<sup>31</sup>P-<sup>1</sup>H}). IR spectra were obtained using a Perkin-Elmer SP3-200 instrument and magnetic data using a recording Faraday magnetic balance. 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 and this may have aided these oxidation reactions.

**Preparations.**— $[Os(SR)_2(O_2CPh)(PMe_2Ph)_2]$  **1** ( $R = C_6F_5$  or  $C_6HF_4$ ). The complex  $[Os(SR)_3(PMe_2Ph)_2]$  ( $R = C_6F_5$  or  $C_6HF_4$ ) (0.1 mmol) was dissolved in acetone (15 cm<sup>3</sup>) and  $PhCO_2H$  (0.012 g, 0.1 mmol) in acetone (15 cm<sup>3</sup>) was added and the mixture was shaken at room temperature for ca. 12 h. The resulting red solution was evaporated to dryness under vacuum to give a solid which was washed with cold ethanol and recrystallised from ethanol as red *rhombs*.

**1** ( $R = C_6F_5$ ). Yield 87%; m.p. 198 °C (decomp.);  $\mu_{eff}$  2.05 (Found: C, 41.9; H, 2.6.  $C_{35}H_{27}F_{10}O_2OsP_2S_2$  requires C, 42.6; H, 2.7%).

**1** ( $R = C_6HF_4$ ). Yield 84%; m.p. 170 °C (decomp.) (Found: C, 44.7; H, 3.4.  $C_{35}H_{29}F_8O_2OsP_2S_2$  requires C, 44.3; H, 3.1%).

$[OsCl(SR)_3(PMe_2Ph)_2]$  **2** ( $R = C_6F_5$  or  $C_6HF_4$ ). The compound  $[Os(SR)_3(PMe_2Ph)_2]$  ( $R = C_6F_5$  or  $C_6HF_4$ ) (0.1

mmol) was dissolved in acetone (15 cm<sup>3</sup>), HCl (0.1 mol dm<sup>-3</sup>, 2 cm<sup>3</sup>) was added and the mixture was shaken at room temperature for *ca.* 24 h. The resulting yellow-green solution was evaporated to dryness under vacuum. The solid product was washed with cold ethanol and recrystallised from ethanol as very dark green needles.

**2** (R = C<sub>6</sub>F<sub>5</sub>). Yield 82%; m.p. 179 °C (decomp.) (Found: C, 32.0; H, 1.1. C<sub>26</sub>H<sub>11</sub>ClF<sub>15</sub>OsPS<sub>3</sub> requires C, 32.5; H, 1.2%). NMR (CDCl<sub>3</sub>): <sup>1</sup>H, δ 2.5, 2.55, [d, <sup>2</sup>J(PH) 10.08 Hz, PCH<sub>3</sub>], 7.58–8.01 (m, C<sub>6</sub>H<sub>5</sub>); <sup>19</sup>F, δ -131.4 (2-F), -150.91, -150.99, -151.08 (4-F), -162.75 (3-F) (m, SC<sub>6</sub>F<sub>5</sub>); <sup>31</sup>P-{<sup>1</sup>H}, δ -170.33 (s, PMe<sub>2</sub>Ph).

**2** (R = C<sub>6</sub>HF<sub>4</sub>). Yield 79%; m.p. 231 °C (decomp.) (Found: C, 34.4; H, 1.6. C<sub>26</sub>H<sub>14</sub>ClF<sub>12</sub>OsPS<sub>3</sub> requires C, 34.4; H, 1.5%). NMR (CDCl<sub>3</sub>): <sup>1</sup>H, δ 2.40, 2.50 [d, <sup>2</sup>J(PH) 10.08 Hz, PCH<sub>3</sub>], 7.04 (m, C<sub>6</sub>HF<sub>4</sub>), 7.75–8.05 (m, C<sub>6</sub>H<sub>5</sub>); <sup>19</sup>F, δ -151.4, -159.6 (m, C<sub>6</sub>HF<sub>4</sub>); <sup>31</sup>P-{<sup>1</sup>H}, δ -170.55 (s, PMe<sub>2</sub>Ph).

*Crystal Structure Analysis of 1* (R = C<sub>6</sub>F<sub>5</sub>).—*Crystal data.* C<sub>35</sub>H<sub>27</sub>F<sub>10</sub>O<sub>2</sub>OsP<sub>2</sub>S<sub>2</sub>, *M* = 985.8, triclinic, space group *P*1̄ (no. 2), *a* = 12.468(2), *b* = 14.430(3), *c* = 11.736(2) Å, α = 87.20(1), β = 118.47(1), γ = 87.21(1)°, *U* = 1847.7 Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.772 g cm<sup>-3</sup>, *F*(000) = 962, μ(Mo-Kα) = 37.3 cm<sup>-1</sup>, λ(Mo-Kα) = 0.710 69 Å.

Crystals are large, deep red parallelepipeds. A typical sample, *ca.* 0.4 × 0.5 × 1.3 mm, was mounted on a glass fibre and coated with silicone grease. After photographic examination, the crystal was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters, from the settings of 25 reflections (θ *ca.* 14.5°) each centred in four orientations, and for measurement of diffraction intensities (to θ<sub>max</sub> = 25°). During processing, the intensities were corrected for Lorentz-polarisation effects, for absorption (by semi-empirical ψ-scan methods) and to eliminate negative intensities (by Bayesian statistical methods). There was no significant deterioration of the crystal.

Of the 6482 unique reflections entered into the SHELX system,<sup>6</sup> there were very few 'unobserved' reflections and, indeed, all the data were used in the structure analysis. The structure was determined by the heavy-atom method. In the refinement, by large-block-matrix least-squares methods, all the non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were included in idealised positions (in staggered orientations in the methyl groups), but their isotropic thermal parameters were refined freely. At convergence, *R* = 0.036 and *R'* = 0.034<sup>6</sup> for the 6482 reflections weighted *w* = σ<sup>-2</sup>.

In a final difference map, the six strongest peaks (1–2 e Å<sup>-3</sup>) were close to the Os atom; the next strongest, *ca.* 0.6 e Å<sup>-3</sup>, were close to the phosphine ligand atoms.

Scattering factor curves for neutral atoms were taken from ref. 7. Computer programs used in this analysis have been listed above and in Table 4 of ref. 8, and were run on the MicroVAX II machine in this laboratory.

*Crystal Structure Analysis of 2* (R = C<sub>6</sub>F<sub>5</sub>).—*Crystal data.* C<sub>26</sub>H<sub>11</sub>ClF<sub>15</sub>OsPS<sub>3</sub>, *M* = 961.2, triclinic, space group *C*1̄ (equivalent to no. 2), *a* = 10.123(1), *b* = 19.523(1), *c* = 15.550(1) Å, α = 92.079(5), β = 91.796(6), γ = 91.369(5)°, *U* = 3068.7 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 2.080 g cm<sup>-3</sup>, *F*(000) = 1832, μ(Mo-Kα) = 46.0 cm<sup>-1</sup>.

This complex crystallises as opaque, very dark green needles. One needle, *ca.* 0.15 × 0.20 × 0.40 mm, was mounted on a glass fibre for photographic and diffractometric measurements. Following a procedure very similar to that described above for **1** (R = C<sub>6</sub>F<sub>5</sub>), cell parameters were calculated from the settings of 25 reflections having θ *ca.* 10.5°, and intensity data were recorded to θ<sub>max</sub> = 25°. After processing as above, 5365 unique reflections were entered into the SHELX system.<sup>6</sup> The structure determination and refinement followed a similar course to that for **1** (R = C<sub>6</sub>F<sub>5</sub>) except that the methyl groups were refined as rigid units; the *U*<sub>iso</sub> values of the hydrogen atoms were refined freely. Refinement was complete with *R* and *R'* = 0.021<sup>6</sup> for all 5365 reflections weighted *w* = σ<sup>-2</sup>. In the final difference map, there were no features > 0.25 e Å<sup>-3</sup>.

#### Acknowledgements

We are grateful to the Consejo Nacional de Ciencia y Tecnologia and the British Council for financial support.

#### References

- 1 P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121.
- 2 D. Cruz-Garriz, S. Gelover, J. Leal, R. L. Richards and H. Torrens, *J. Chem. Soc., Dalton Trans.*, 1988, 2393.
- 3 D. Cruz-Garriz, A. Hills, D. L. Hughes, R. L. Richards, P. Sosa and H. Torrens, *J. Chem. Soc., Dalton Trans.*, 1989, 419.
- 4 R. M. Catala, D. Cruz-Garriz, A. Hills, D. L. Hughes, R. L. Richards, P. Sosa, P. Torreras and H. Torrens, *J. Organomet. Chem.*, 1989, **359**, 219.
- 5 S. A. Koch and M. Millar, *J. Am. Chem. Soc.*, 1983, **105**, 3362.
- 6 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
- 7 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
- 8 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

Received 13th November 1990; Paper 0/05104G