Thiolate Complexes of Osmium(III) with Tertiary Phosphines and their Dicarbonyl Derivatives of Osmium(II): *X*-Ray Crystal Structure of *trans,trans,trans*-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$†

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The preparation and physical properties of complexes of the type $[Os(SC_6F_5)_3(PR_3)_2]$ and $[Os(SC_6F_5)_2(CO)_2(PR_3)_2]$ (PR_3 = PMe_2Ph, $PMePh_2$, PEt_2Ph, or $PEtPh_2$), and the *X*-ray structure of *trans,trans,trans*-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$ are described.

As part of our programme to employ thiolate ligands to obtain unsaturated centres with potential catalytic properties,[1-4] we have used the reaction between *mer*-$[OsX_3(PR_3)_3]$ (X = Cl or Br; PR_3 = PMe_2Ph, $PMePh_2$, PEt_2Ph, or $PEtPh_2$) and $Pb(SC_6F_5)_2$ to form new thiolate derivatives of Os^{III} and have examined their reactions which give carbonyl derivatives of the type $[Os(SC_6F_5)_2(CO)_2(PR_3)_2]$.

Results and Discussion

Treatment of *mer*-$[OsX_3(PR_3)_3]$ with $Pb(SC_6F_5)_2$ in acetone or tetrahydrofuran (thf) at room temperature for *ca.* 3 h gives a smooth reaction with precipitation of PbX_2. After evaporation of the solution to low volume the compounds $[Os(SC_6F_5)_3(PR_3)_2]$ (**1**) have been isolated in high yield [reaction (1)].

$$mer\text{-}[OsX_3(PR_3)_3] + 1.5Pb(SC_6F_5)_2 \longrightarrow \underset{(\mathbf{1})}{[Os(SC_6F_5)_3(PR_3)_2]} + 1.5PbX_2 + PR_3 \quad (1)$$

The complexes (**1**) are purple, paramagnetic solids and they are non-conductors in nitrobenzene, thf, or acetone. Details of elemental analyses and of i.r. and n.m.r. spectra described in this paper are given in Tables 1 and 2 respectively.

$[Os(SC_6F_5)_3(PR_3)_2]$ *Complexes.*—These osmium(III) complexes are probably monomeric in the solid state like their ruthenium analogues[2] (see below). In solution, however, they are probably dimers; for $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ (**1a**) the molecular weight, measured by osmometry, corresponds to a binuclear composition (see Table 1), and presumably the PEt_2Ph, $PMePh_2$, and $PEtPh_2$ analogues are the same. The i.r. spectra reveal, in all cases, the presence of the SC_6F_5 ligands through the appearance of several new bands (at around 1 084, 972, and 845 cm^{-1}, typical of SC_6F_5),[1-4] replacing the Os–Cl stretching vibrations in the starting material. These complexes are paramagnetic (μ_{eff} = 2.2—2.5 B.M.) in the solid state and they have ^1H, ^{31}P, and ^{19}F n.m.r. spectra with broad, complicated signals indicative of the presence of paramagnetism in the molecules.

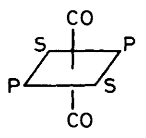
In general, for paramagnetic d^5 complexes, the ^1H n.m.r. spectra have much broader spectral absorptions than their diamagnetic analogues and these are also shifted by contact and pseudo-contact mechanisms,[5] but in the cases of $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ and $[Os(SC_6F_5)_3(PEt_2Ph)_2]$, the ^1H, ^{31}P, and ^{19}F spectra have sufficient detail to suggest an asymmetrical configuration for the SC_6F_5 and PMe_2Ph ligands, but their singlet ^{31}P spectrum suggests that the PEt_2Ph groups are equivalent. We have no proof of the configuration of the $[Os(SC_6F_5)_3(PR_3)_2]$ compounds but it is probable that they have the same octahedral structure in the solid state as the analogue $[Ru(SC_6F_5)_3(PMe_2Ph)_2]$, which has an unusual Ru–F–C bond, through the interaction of a 2-fluorine of one SC_6F_5 ligand with the metal, creating a S–F chelate ligand.[2] Unfortunately no crystals suitable for the *X*-ray structure determination of compounds (**1**) have yet been obtained.

Dicarbonyl Derivatives.—When carbon monoxide and amalgamated zinc are added to the purple solutions obtained from reaction (1) (see above) they become yellow and the dicarbonyl complexes (**2**) are isolated by the reaction sequence (2).

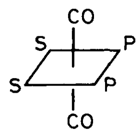
$$mer\text{-}[OsX_3(PR_3)_3] + 1.5\ Pb(SC_6F_5)_2 \longrightarrow \text{purple solution} + PbX_2 \quad (2)$$

$$\text{purple solution} + CO/Zn \longrightarrow \underset{(\mathbf{2})}{[Os(SC_6F_5)_2(CO)_2(PR_3)_2]}$$

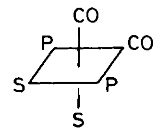
It is possible to obtain different isomers of (**2**) (see below) as can be shown by the data in Table 2. With all phosphines (PR_3 = PMe_2Ph, $PMePh_2$, PEt_2Ph, or $PEtPh_2$) isomer (**I**) was isolated as yellow crystals in higher yield than the other isomers. Configuration (**I**) is assigned to $[Os(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$ (**2a$_I$**) and $[Os(SC_6F_5)_2(CO)_2(PMePh_2)_2]$ (**2c**) since they show



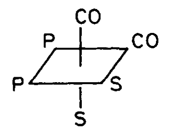
(**I**)



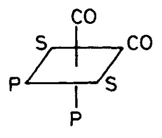
(**II**)



(**III**)



(**IV**)



(**V**)

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† *trans,trans,trans*-Dicarbonylbis(diethylphenylphosphine)bis(pentafluorothiophenolato)osmium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: B.M. = 9.27 × 10^{-24} J T^{-1}.

Table 1. Physical properties of the osmium complexes

Complex	Yield (%)	Colour	Analysis[a] (%)		M.p.[b] (°C)	μ_{eff} (B.M.)
			C	H		
(**1a**) $[Os(SC_6F_5)_3(PMe_2Ph)_2]$[c]	83	Purple	39.0 (38.4)	2.6 (2.0)	189—193	2.56
(**1b**) $[Os(SC_6F_5)_3(PEt_2Ph)_2]$	77	Purple	40.7 (40.7)	2.8 (2.7)	137—144	2.31
(**1c**) $[Os(SC_6F_5)_3(PMePh_2)_2]$	78	Purple	43.8 (44.5)	2.1 (2.2)	195—200	2.23
(**1d**) $[Os(SC_6F_5)_3(PEtPh_2)_2]$	79	Purple	46.1 (45.4)	2.3 (2.4)	209—211	2.47
(**2a**) $[Os(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$	75	Yellow	39.4 (39.1)	2.1 (2.4)	152—156	diamagnetic
(**2b**) $[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$	90	Yellow	41.2 (41.8)	3.0 (3.1)	138—142	diamagnetic
(**2c**) $[Os(SC_6F_5)_2(CO)_2(PMePh_2)_2]$	70	Yellow	45.1 (45.9)	2.4 (2.4)	144—148	diamagnetic
(**2d**) $[Os(SC_6F_5)_2(CO)_2(PEtPh_2)_2]$	73	Yellow	46.8 (47.0)	2.5 (2.8)	130—135	diamagnetic

[a] Calculated values in parentheses; all isomers gave similar analyses. [b] With decomposition. [c] Molecular weight 2 085 (2 184).

Table 2. I.r., ^1H, ^{31}P, and ^{19}F n.m.r. data for the osmium complexes[a]

Compound[a]	$\nu(CO)$[b]/cm^{-1}	^1H n.m.r.[c]	^{31}P n.m.r.[d]	^{19}F n.m.r.[e]
(**1a**)		1.72(m) (P–Me) 7.3(m) (phenyl)	–178.8(m)	–130.2(m) *para* –162.5(m) *meta* –165.1(m) *ortho*
(**1b**)		*f*	–188(s)	*f*
($\mathbf{2a_1}$) [(**I**)]	1 980	1.75(t) (*trans* P–Me, $^2J + {}^4J = 8.0$) 7.5(m) (phenyl)	–167(s)	
($\mathbf{2a_2}$) [(**II**)]	1 950	1.25(d) (*cis* P–Me, $^2J_{PH} = 8.1$) 7.6(m) (phenyl)	–166(s)	
($\mathbf{2b_1}$) [(**I**)]	1 979	1.04(q) (P–CH_3, $^3J + {}^5J = 7.9$) 2.45(nonet) (P–CH_2, $^3J + {}^4J = 3.64$) 7.3(m) (phenyl)	–163(s)	–131.86(dd) *para* –162.3(t) *ortho* –165.5(m) *meta* $^3J_{FF} = 20.75$
($\mathbf{2b_5}$) [(**V**)]	2 010, 1 945	0.86(m) (P–CH_3) 1.89(m) (P–CH_2) 7.1(m) (phenyl) ($^3J + {}^5J = 6.8$)	–164.9(s)	–136.59(dd) *para* –167.59(t) *ortho* –169.74(m) *meta* $^3J_{FF} = 24.42$
(**2c**) [(**I**)]	1 988 2 045,[g] 1 955[g]	2.4(t) (*trans* P–Me, $^2J + {}^4J = 9$) 7.6(m) (phenyl)	–168.9(s)	–132.61(dd) *para* –161.74(t) *ortho* –166.19(m) *meta* $^3J_{FF} = 20.75$
($\mathbf{2d_1}$) [(**I**)]	1 990	0.8(q) (P–CH_3) 2.7(nonet) (P–CH_2, $^3J + {}^5J = 7.8$) 7.5(m) (phenyl)	–157.2(s)	–133.15(dd) *para* –165.18(t) *ortho* –168.36(m) *meta* $^3J_{FF} = 19.53$
($\mathbf{2d_3}$) [(**III**)]	2 046, 1 972	0.8(q) (P–CH_3) 2.7(nonet) (P–CH_2) 7.5(m)	–158(s)	–135.2(dd) *para* –164.8(t) *ortho* –169.2(m) *meta* $^3J_{FF} = 19.53$
($\mathbf{2d_5}$) [(**V**)]	2 028, 1 966	0.9(m) (P–CH_3) 2.6(m) (P–CH_2) 7.3(m) (phenyl)		
($\mathbf{2d_2}$) [(**II**)]	1 979	0.9(m) (P–CH_3) 2.4(m) (P–CH_2) 7.5(m) (phenyl)		

[a] Configurations in parentheses. [b] Nujol mull spectra. [c] Relative to $SiMe_4$ in $CDCl_3$ solution, see ref. 8 for assignments of configuration, couplings, *etc.* [d] Relative to $P(OMe)_3$ in $CDCl_3$. [e] Relative to $CFCl_3$ in $CDCl_3$. [f] Very broad resonances. [g] Isomer (**V**) obtained in only 12% yield (see text). ^2J, ^3J, ^4J, and ^5J refer to couplings (in Hz) as in ref. 8.

one sharp stretching CO band in their i.r. spectra and their ^1H n.m.r. spectra show a triplet indicating substantial ^{31}P–^{31}P coupling and a mutual *trans* configuration[6–8] for the phosphine ligands. Furthermore, their ^{31}P and ^{19}F n.m.r. spectra are consistent with *trans*-PR_3 and *trans*-SC_6F_5 ligands (Table 2). The complexes $[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$ ($\mathbf{2b_1}$) and $[Os(SC_6F_5)_2(CO)_2(PEtPh_2)_2]$ ($\mathbf{2d_1}$) also have configuration (**I**) in accord with their spectroscopic properties. It is possible to observe, in the ^1H n.m.r. spectra of both compounds, a typical splitting pattern of *trans*-P–Et groups, described in analogous complexes.[8] These assignments are confirmed by the *X*-ray structure of *trans,trans,trans*-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$ ($\mathbf{2b_1}$) (see later).

For $[Os(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$ and $[Os(SC_6F_5)_2(CO)_2(PEtPh_2)_2]$, complexes of configuration (**II**) ($\mathbf{2a_2}$) and ($\mathbf{2d_2}$), are also obtained (see Experimental section). Their i.r. spectra show one sharp CO stretching absorption at a different frequency from those of isomers with configuration (**I**) (see Table 2), and their ^1H n.m.r. spectra show, for the PMe_2Ph derivative, ($\mathbf{2a_2}$), two groups of unresolved signals.

$[Os(SC_6F_5)_2(CO)_2(PEtPh_2)_2]$ ($\mathbf{2d_3}$) [configuration (**III**)] is obtained from reaction (2) using thf as solvent and recrystal-

Table 3. Final fractional atomic co-ordinates (× 10^4) for $[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Os	0	0	0
S(1)	−505(1)	803.3(8)	−2 106(1)
C(11)	490(5)	538(3)	−2 817(5)
C(12)	684(5)	−334(4)	3 164(5)
F(12)	41(3)	−1 032(2)	−3 019(3)
C(13)	1 503(6)	−523(4)	−3 676(6)
F(13)	1 661(4)	−1 393(3)	−3 958(4)
C(14)	2 141(6)	160(5)	−3 916(6)
F(14)	2 953(5)	−20(3)	−4 399(5)
C(15)	1 928(5)	1 034(5)	−3 672(6)
F(15)	2 507(4)	1 730(3)	−3 946(4)
C(16)	1 126(5)	1 220(4)	−3 126(5)
F(16)	956(3)	2 092(2)	−2 892(3)
P(2)	2 098(1)	587.7(7)	1 072(1)
C(211)	2 631(5)	901(4)	2 792(5)
C(212)	3 988(6)	1 256(4)	3 535(6)
C(221)	2 485(4)	1 584(3)	364(5)
C(222)	1 833(5)	2 455(3)	469(6)
C(231)	3 210(4)	−265(3)	1 081(5)
C(232)	3 713(5)	−890(4)	2 089(6)
C(233)	4 460(6)	−1 593(4)	2 018(8)
C(234)	4 691(6)	−1 666(4)	943(9)
C(235)	4 194(6)	−1 060(4)	−66(7)
C(236)	3 449(5)	−351(4)	0(6)
C(3)	−637(4)	1 121(3)	363(5)
O(3)	−1 042(3)	1 796(2)	484(4)

Table 4. Molecular dimensions in $[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$; bond lengths (Å) and angles (°) with e.s.d.s in parentheses

(*a*) Os environment			
Os–S(1)	2.477(1)	S(1)–Os–P(2)	93.5(1)
Os–P(2)	2.407(1)	S(1)–Os–C(3)	81.3(1)
Os–C(3)	1.938(5)	P(2)–Os–C(3)	90.5(1)
(*b*) Ligand dimensions			
S(1)–C(11)	1.755(5)	Os–S(1)–C(11)	114.3(2)
C(11)–C(12)	1.392(8)	S(1)–C(11)–C(12)	124.7(4)
C(11)–C(16)	1.396(7)	S(1)–C(11)–C(16)	120.9(4)
C(12)–F(12)	1.337(6)	C(12)–C(11)–C(16)	114.4(5)
C(12)–C(13)	1.373(8)	C(11)–C(12)–F(12)	119.6(5)
C(13)–F(13)	1.354(7)	C(11)–C(12)–C(13)	123.2(5)
C(13)–C(14)	1.362(9)	F(12)–C(12)–C(13)	117.2(5)
C(14)–F(14)	1.339(7)	C(12)–C(13)–F(13)	119.5(6)
C(14)–C(15)	1.363(9)	C(12)–C(13)–C(14)	120.5(6)
C(15)–F(15)	1.349(6)	F(13)–C(13)–C(14)	120.0(6)
C(15)–C(16)	1.384(8)	C(13)–C(14)–F(14)	120.8(6)
C(16)–F(16)	1.345(6)	C(13)–C(14)–C(15)	118.8(6)
		F(14)–C(14)–C(15)	120.4(6)
		C(14)–C(15)–F(15)	120.5(6)
		C(14)–C(15)–C(16)	120.5(5)
		F(15)–C(15)–C(16)	119.0(6)
		C(11)–C(16)–C(15)	122.5(5)
		C(11)–C(16)–F(16)	119.3(5)
		C(15)–C(16)–F(16)	118.2(5)
P(2)–C(211)	1.812(5)	Os–P(2)–C(211)	114.6(2)
P(2)–C(221)	1.827(4)	Os–P(2)–C(221)	118.8(2)
P(2)–C(231)	1.827(5)	C(211)–P(2)–C(221)	103.3(2)
C(211)–C(212)	1.547(7)	Os–P(2)–C(231)	110.5(2)
C(221)–C(222)	1.534(7)	C(211)–P(2)–C(231)	105.4(2)
C(231)–C(232)	1.375(7)	C(221)–P(2)–C(231)	103.0(2)
C(231)–C(236)	1.381(7)	P(2)–C(211)–C(212)	116.5(4)
C(232)–C(233)	1.393(8)	P(2)–C(221)–C(222)	113.4(3)
C(233)–C(234)	1.367(10)	P(2)–C(231)–C(232)	120.7(4)
C(234)–C(235)	1.356(9)	P(2)–C(231)–C(236)	120.0(4)
C(235)–C(236)	1.397(7)	C(232)–C(231)–C(236)	119.0(5)
		C(231)–C(232)–C(233)	120.1(6)
		C(232)–C(233)–C(234)	120.1(6)
		C(233)–C(234)–C(235)	120.6(6)
		C(234)–C(235)–C(236)	119.7(6)
		C(231)–C(236)–C(235)	120.5(6)
C(3)–O(3)	1.140(5)	Os–C(3)–O(3)	175.1(4)

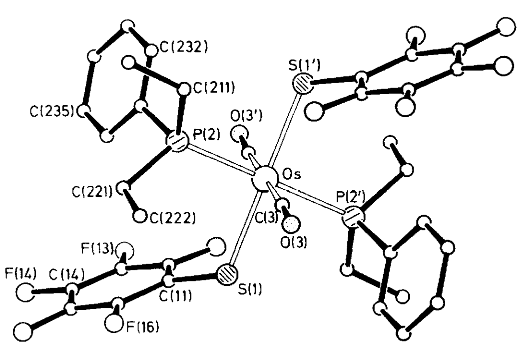

Figure. Crystal structure of *trans,trans,trans*-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$ (**$2b_I$**)

lisation from MeOH. It has two CO bands (*cis* CO) in its i.r. spectrum, a quintet and a nonet for methyl and methylene ^{31}P coupling in its ^1H n.m.r. spectrum, and one signal corresponding to a *trans*-phosphine configuration in its ^{31}P n.m.r. spectrum.

It is possible to isolate $[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$ (**$2b_5$**) [configuration (**V**)] through the interaction between *mer*-$[OsBr_2(N_2)(PEt_2Ph)_3]$ and $Pb(SC_6F_5)_2$ in thf under CO (see Experimental section). Its i.r. spectrum shows *cis*-CO groups and the ^1H n.m.r. spectrum shows *cis*-PEt_2Ph groups whose singlet ^{31}P n.m.r. spectrum indicates that they are equivalent. The ^{19}F n.m.r. pattern shows equivalent SC_6F_5 groups. No examples of configuration (**IV**) were observed.

Description of the Structure of trans,trans,trans-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$ (**$2b_I$**).—The crystal structure is shown in the Figure. In crystals of this monomeric complex, the Os atom lies on a centre of symmetry with a pseudo-octahedral co-ordination pattern confirming the spectroscopic assignment of configuration (**I**). Atomic co-ordinates are listed in Table 3 and molecular dimensions in Table 4.

The Os–S(thiolate) distance, 2.477(1) Å, is slightly shorter than that in *mer*-$[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$, 2.507(1) Å, where the thiolate is *trans* to a phosphine ligand[1] (see later); these distances are rather longer than the only others reported, 2.298(2) and 2.343(2) Å in the Os^{IV} complex *trans*-$[Os(salen)(SPh)_2]$[salen = *NN'*-ethylenebis(salicylideneiminate)].[9] There is a wide range of Os^{II}–P distances in the literature, *e.g.* in similar complexes to (**2b**), from 2.285(5) Å in *cis*-$[OsH(C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2]$[10] to 2.429(11) Å in *trans*-$[Os(CHO)(CO)(Ph_2PCH_2CH_2PPh_2)_2]^+$.[11] Steric factors are important here and our value of 2.407(1) Å reflects the bulkiness of the ligands in (**$2b_I$**). We suggest that steric effects are principally responsible for the dimensions about the Os atom in *mer*-$[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$,[1] where the Os–P (*trans* to P) distances are *ca.* 2.38 Å and the Os–P (*trans* to S) distance is rather less, at 2.326(1) Å. Corresponding to this last, short distance, the *trans*-Os–S distance is lengthened to 2.507(1) Å, despite this involving the anionic thiolate donor.

The Os–CO group in complex (**$2b_I$**) is almost linear and its dimensions are within the normal ranges.

There are several short interligand contacts, indicating tight packing of the bulky ligands, but between-molecule contacts are at normal van der Waals' distances.

Experimental

All manipulations involving air-sensitive materials, such as tertiary phosphines, were carried out using Schlenk or standard high-vacuum techniques. Solvents were degassed before use. Spectra were determined using Pye-Unicam SP3-200S (i.r.) and JEOL FX90Q (n.m.r.) instruments. Osmometry was carried out using a Hitachi-Perkin-Elmer 116 osmometer, conductivities were determined with a Portland Electronics Bridge, and magnetic moments with a recording Faraday balance. Microanalyses were by Mr. C. Macdonald of the Nitrogen Fixation Laboratory. Preparative methods were general and typical examples are given. Analytical data *etc.* for the compounds are given in Table 1. The starting complexes $[OsCl_3(PR_3)_3]$ and $[OsBr_2(N_2)(PMe_2Ph)_3]$ were prepared by published methods.[1,8]

Preparations.—Bis(dimethylphenylphosphine)tris(pentafluorothiophenolato)osmium(III), $[Os(SC_6F_5)_3(PMe_2Ph)_2]$ (**1a**). *mer*-$[OsCl_3(PMe_2Ph)_3]$ (0.2 g, 0.28 mmol) was dissolved in thf (50 cm^3) and $Pb(SC_6F_5)_2$ (0.2 g, 0.45 mmol) was added. The mixture was shaken at room temperature for *ca.* 3 h. The purple solution was filtered and then evaporated to low volume whereupon *purple crystals* deposited on standing.

Dicarbonylbis(dimethylphenylphosphine)bis(pentafluorothiophenolato)osmium(II), $[Os(SC_6F_5)_2(CO)_2(PMe_2Ph)_2]$, (**2a**). (a) *Configuration* (**I**). *mer*-$[OsCl_3(PMe_2Ph)_3]$ (0.15 g, 0.211 mmol) in acetone (50 cm^3) was shaken at room temperature with $Pb(SC_6F_5)_2$ (0.38 g, 0.63 mmol) for *ca.* 3 h. The purple solution obtained was filtered, amalgamated zinc (2 g) was added, and the mixture was shaken under CO for *ca.* 3 h. The resulting yellow solution was filtered, evaporated to low volume, and MeOH (10 cm^3) added to yield *yellow crystals*.

(b) *Configuration* (**II**). *mer*-$[OsCl_3(PMe_2Ph)_3]$ (0.2 g, 0.28 mmol) was dissolved in acetone (50 cm^3) and $Pb(SC_6F_5)_2$ (0.27 g, 0.45 mmol) was added. The mixture was shaken for *ca.* 12 h at room temperature and the $PbCl_2$ formed was filtered off. Amalgamated zinc (2 g) was added to the resulting brown solution and the mixture shaken under CO for *ca.* 3 h. The solution changed to yellow and was evaporated to low volume (10 cm^3). Methanol (20 cm^3) was added to yield *yellow crystals*.

Dicarbonylbis(diethylphenylphosphine)bis(pentafluorothiophenolato)osmium(II), $[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$, (**2b**). (a) *Configuration* (**I**). *mer*-$[OsCl_3(PEt_2Ph)_3]$ (0.04 g, 0.06 mmol) and $Pb(SC_6F_5)_2$ (0.05 g, 0.09 mmol) were shaken at room temperature in acetone (35 cm^3) for *ca.* 3 h. The orange solution changed to purple and the $PbCl_2$ deposited was filtered off. Amalgamated zinc (2 g) was added and the mixture shaken at room temperature under CO for *ca.* 3 h. The purple solution changed to yellow and was then filtered and evaporated to low volume (10 cm^3) whereupon *yellow crystals* deposited.

(b) *Configuration* (**V**). *mer*-$[OsBr_2(N_2)(PMe_2Ph)_3]$ (0.17 g, 0.2 mmol) and $Pb(SC_6F_5)_2$ (0.05 g, 0.31 mmol) were shaken at room temperature in thf (50 cm^3) for *ca.* 3 h. The pale yellow solution changed to purple and the $PbBr_2$ was filtered off. Amalgamated zinc (1 g) was added and the mixture was shaken under CO for *ca.* 3 h. The yellow solution was filtered and evaporated to dryness and acetone–MeOH (1:1) was added to yield *pale yellow crystals*.

Dicarbonylbis(methyldiphenylphosphine)bis(pentafluorothiophenolato)osmium(II), $[Os(SC_6F_5)_2(CO)_2(PMePh_2)_2]$, (**2c**). (a) *Configuration* (**I**). *mer*-$[OsCl_3(PMePh_2)_3]$ (0.3 g, 0.33 mmol) was dissolved in acetone (50 cm^3). $Pb(SC_6F_5)_2$ (0.36 g, 0.60 mmol) was added and the mixture shaken for *ca.* 3 h at room temperature. The purple solution was filtered, amalgamated zinc (2 g) was added, and the solution shaken under CO for *ca.* 3 h. The yellow solution obtained was filtered and evaporated to low volume, whereupon the compound deposited as *yellow crystals*.

(b) *Configuration* (**V**). This reaction was carried in the same fashion to (a), but acetone was used instead of thf as solvent. The product was recrystallised from diethyl ether–MeOH (1:1) as *pale yellow crystals* in very low yield (12%), m.p. 219—210 °C.

Dicarbonylbis(ethyldiphenylphosphine)bis(pentafluorothiophenolato)osmium(II), $[Os(SC_6F_5)_2(CO)_2(PEtPh_2)_2]$ (**2d**). (a) *Configuration* (**I**). *mer*-$[OsCl_3(PEtPh_2)_3]$ (0.2 g, 0.21 mmol) and $Pb(SC_6F_5)_2$ (0.19 g, 0.319 mmol) were dissolved in acetone (50 cm^3) and the mixture was shaken at room temperature for *ca.* 3 h. The purple solution was filtered and amalgamated zinc (2 g) added and then the mixture was shaken under CO for *ca.* 3 h. The resulting yellow solution was filtered and evaporated to low volume and *yellow crystals* deposited.

(b) *Configuration* (**III**). This reaction was carried out as for (a) for configuration (**I**) but thf was used as solvent and the product was crystallised from MeOH.

(c) *Configuration* (**II**). This compound was obtained by the method described for configuration (**III**) but using a long reaction time (*ca.* 12 h). The product was recrystallised from thf–diethyl ether (1:1) as *yellow crystals*.

Crystal Structure Analysis for trans,trans,trans-$[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$ (**2b$_1$**).—*Crystal data.* $[Os(SC_6F_5)_2(CO)_2(PEt_2Ph)_2]$, $C_{34}H_{30}F_{10}O_2OsP_2S_2$, $M = 976.9$, monoclinic, space group $P2_1/n$ (equivalent to no. 14), $a = 11.983(2)$, $b = 14.713(3)$, $c = 11.308(7)$ Å, $\beta = 116.77(3)°$, $U = 1\,780.0$ Å^3, $Z = 2$, $D_c = 1.822$ g cm^{-3}, $F(000) = 956$, $\mu(\text{Mo-}K_\alpha) = 38.7$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å.

The sample of small prismatic yellow crystals was shown to have crystallised mostly as multiple crystals. One, of size *ca.* 0.20 × 0.20 × 0.35 mm, was mounted on a glass fibre and shown by *X*-ray photographic examination to comprise one major crystal and very small amounts of co-crystals. Accurate cell dimensions were refined from the setting of 25 reflections having θ *ca.* 12° on an Enraf-Nonius CAD4 diffractometer with monochromated Mo radiation. Intensity data for 3 127 unique reflections ($\theta \leqslant 25°$) were recorded. During processing, corrections for Lorentz and polarisation effects, absorption and negative intensities were applied. With the SHELX program,[12] the crystal structure was determined by the heavy-atom method, and refined to convergence at $R = 0.039$, $R' = 0.036$ for 3 117 reflections (10 reflections with suspect background intensity measurements were omitted), weighted $w = \sigma_F^{-2}$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The dimensions of the methyl groups were constrained towards idealised values (allowing free rotation of the group); the co-ordinates of the other H atoms were calculated in idealised positions and set to ride on their bonded C atoms. Scattering factors for neutral atoms were used, as found in ref. 13. All computations were made on the VAX 11/750 computer at the Glasshouse Crops Research Institute, Littlehampton, using programs described in ref. 14.

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

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References

1 D. Cruz-Garritz, J. Leal, R. L. Richards, and H. Torrens, *Transition Met. Chem.*, 1983, **8**, 127.

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

3 R. M. Catala, D. Cruz-Garritz, A. Hills, D. L. Hughes, R. L. Richards, P. Terreros, and H. Torrens, *J. Organomet. Chem.*, 1987, **328**, C37.

4 D. Povey, C. Shortman, and R. L. Richards, *Polyhedron*, 1986, **5**, 269.

5 G. N. LaMar, J. P. Jesson, and P. Meakin, *J. Am. Chem. Soc.*, 1971, **93**, 1286.

6 P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1970, 334.

7 J. M. Jenkins, M. S. Lupin, and B. L. Shaw, *J. Chem. Soc. A*, 1966, 1786.

8 J. Chatt, D. P. Melville, and R. L. Richards, *J. Chem. Soc. A*, 1971, 1169.

9 C-M. Che, W-K. Cheng, and T. C. W. Mak, *Inorg. Chem.*, 1986, **25**, 703.

10 U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1971, 1118.

11 G. Smith, D. J. Cole-Hamilton, M. Thornton-Pett, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 387.

12 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

13 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.

14 H. Dadkhah, J. R. Dilworth, K. Fairman, D. L. Hughes, C. T. Kan, and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1985, 1523.

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