Dinitrogen Complexes of Osmium(II) with Thiolate Co-ligands: *X*-Ray Structure of *mer*-[$OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3$]†

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Treatment of *mer*-[$OsCl_2(N_2)(PMe_2Ph)_3$] with $S_2CNMe_2^-$ salts causes loss of N_2 and the formation of *mer*/*fac*-[$OsCl(S_2CNMe_2)(PMe_2Ph)_3$] and *cis*-[$Os(S_2CNMe_2)_2(PMe_2Ph)_2$]. Dinitrogen is, however, retained in reactions of *mer*-[$OsX_2(N_2)(PMe_2Ph)_3$] (X = Cl or Br) with RS^- (R = Ph, C_6F_5, Me, or CF_3) at 20 °C in acetone to give the series *mer*-[$OsX(SR)(N_2)(PMe_2Ph)_3$]. Under more vigorous conditions the N_2 is displaced by thiolate. The compound *mer*-[$OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3$] has an octahedral structure with N_2 *trans* to chloride; *d*(N–N) = 1.112(5) Å and *d*(Os–S) = 2.507(1) Å.

As part of our interest in the chemistry of thiolates and thioethers at transition-metal sites,[1–4] the probable involvement of sulphur at the active centre of nitrogenase[5] prompted us to search for dinitrogen complexes with sulphur-containing co-ligands. Although this is an intensively studied topic only a few examples of compounds bearing M–S and M–N≡N bonds have been reported.[6–9]

In this paper, we describe in detail the preparation and properties of a series of thiolate–dinitrogen complexes of osmium(II), one of which has been described in a preliminary communication.[6]

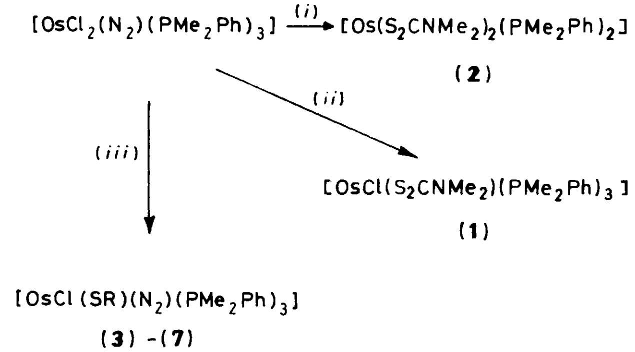
The reactions studied are summarised in the Scheme.

Results and Discussion

The reaction of *mer*-[$OsCl_2(N_2)(PMe_2Ph)_3$] with Tl[S_2CNMe_2] in acetone or 2-methoxyethanol under reflux yields a yellow crystalline compound formulated as [$OsCl(S_2CNMe_2)(PMe_2Ph)_3$] (**1**). On the other hand, if the reaction is conducted under similar conditions but using Na[S_2CNMe_2] instead of the thallium salt, the resulting yellow, crystalline product is [$Os(S_2CNMe_2)_2(PMe_2Ph)_2$] (**2**). In both cases the interactions proceed with loss of the dinitrogen ligand regardless of the time and temperature of the reaction. Compounds (**1**) and (**2**) have been reported previously by Cole-Hamilton and Stephenson[10] who obtained them, however, by a different synthetic route.

In contrast, treatment of *mer*-[$OsX_2(N_2)(PMe_2Ph)_3$] with the monodentate thiolate ligands RS^-, where R = CF_3, Me, Ph, or C_6F_5, affords dinitrogen-containing species formulated as *mer*-[$OsX(SR)(N_2)(PMe_2Ph)_3$] [X = Cl; R = Me (**3**), Ph (**4**), C_6F_5 (**5**), or CF_3 (**7**); X = Br; R = C_6F_5 (**6**)] on the basis of the spectroscopic and crystallographic studies below. Analytical and other physical data for compounds (**1**)—(**7**) are shown in Table 1. Attempts to substitute the remaining halide by SR in these compounds lead to loss of N_2 and oily products which could not be characterised.

The product [$OsCl(S_2CNMe_2)(PMe_2Ph)_3$] obtained from Tl[$S_2CNMe_2$] is a mixture (*ca.* 1:1.35) of *mer* and *fac* isomers in chloroform, as shown by integration of the corresponding ^1H and ^{31}P n.m.r. signals. The ^{31}P spectrum shows a complex multiplet (−36.2 to −40.19 p.p.m. from H_3PO_4) arising from the overlapping signals of each isomer. A similar analysis shows that *cis*-[$Os(S_2CNMe_2)_2(PMe_2Ph)_2$] has only one isomer in chloroform [simple singlet (−36.13 p.p.m. from H_3PO_4) in the ^{31}P n.m.r. spectrum].



Scheme. (*i*) Na[S_2CNMe_2]; (*ii*) Tl[S_2CNMe_2]; (*iii*) $Pb(SR)_2$ (R = C_6H_5 or C_6F_5), Na(SMe), or $AgCF_3$; 20 °C, thf

Loss of dinitrogen is not unexpected in these two reactions since, in order to form a chelate ring the alternatives are the displacement of N_2 or a phosphine. The former, with the relatively weaker bond to the metallic centre is displaced preferentially. However, it is interesting that only with Na[S_2CNMe_2] are both the N_2 and one of the PMe_2Ph ligands displaced, thus forming two chelate rings rather than leaving one dithiocarbamate as a monodentate ligand.

Complexes with Dinitrogen.—Table 2 shows the ^1H, ^{31}P-{^1H}, and ^{19}F n.m.r. data and ν(N≡N) values for compounds (**3**)—(**7**).

The n.m.r. spectra of the complexes reported here are particularly useful in assigning configuration. Both the ^1H and ^{31}P spectra show that there are two equivalent phosphine ligands which give rise to a signal of twice the intensity of that from the unique phosphine ligand. In the ^1H n.m.r. spectra the low-field signal of these complexes consists of two triplets. The more intense signal in the ^{31}P spectrum shows a doublet, thus two phosphines are *trans* and virtually coupled. The presence of only one additional triplet signal in the ^{31}P spectrum shows that the three phosphine ligands are meridional.[11] The above

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† *mer*-Chlorotris(dimethylphenylphosphine)(dinitrogen)(pentafluorothiophenolato)osmium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Physical properties of osmium(II) complexes

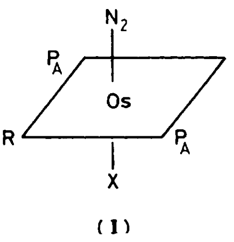
Compound	Colour	M.p. (°C)	Yield (%)	Analysis (%)[a] C	H	N
(**1**) $[OsCl(S_2CNMe_2)(PMe_2Ph)_3]$	Yellow	140—147	80	42.0	5.5	2.4
				(42.7)	(5.1)	(1.9)
(**2**) $[Os(S_2CNMe_2)_2(PMe_2Ph)_2]$	Yellow	171—173	90	37.4	5.1	3.8
				(37.4)	(4.8)	(4.0)
(**3**) $[OsCl(SMe)(N_2)(PMe_2Ph)_3]$	White	138—140[b]	50	41.7	4.7	3.5
				(41.9)	(5.0)	(3.9)
(**4**) $[OsCl(SPh)(N_2)(PMe_2Ph)_3]$	White	150—152[b]	65	46.6	4.7	3.5
				(45.4)	(4.9)	(3.6)
(**5**) $[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$	White	153[b]	60	41.0	3.7	3.1
				(41.5)	(3.8)	(3.2)
(**6**) $[OsBr(SC_6F_5)(N_2)(PMe_2Ph)_3]$	White	165[b]	55	40.0	3.5	3.0
				(39.5)	(3.6)	(3.0)
(**7**) $[OsCl(SCF_3)(N_2)(PMe_2Ph)_3]$	White	145—150[b]	90	39.4	4.7	3.0
				(39.0)	(4.3)	(3.6)

[a] Calculated values in parentheses. [b] With decomposition.

Table 2. Spectroscopic properties of dinitrogen complexes of osmium(II)

Compound	$\delta(^1H)$[a]	Multiplicity (rel. int.)[b]	$^2J(PCH)$[c]	$\delta(^{31}P)$[d]	Multiplicity (rel. int.)[b]	$^2J(PP)$[c]	$\delta(^{19}F)$[e]	Multiplicity (rel. int.)[b]	J[c,f]	$\nu(N{\equiv}N)$[g]
$[OsCl(SMe)(N_2)(PMe_2Ph)_3]$	1.84	ot(2)	9.3	−34.86	d(2)					2 077
	1.33	d(1)		−35.85	t(1)	15.24				
	1.55	s(1)								
$[OsCl(SPh)(N_2)(PMe_2Ph)_3]$	1.79	dt(2)	9.11	−38.58	d(2)					2 084
	1.28	d(1)		−42.15	t(1)	15.25				
$[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$	1.89	ot(2)	9.5	−39.90	d(2)		−162.5	t(1)	$J(p–m)$ 20.75	2 090
	1.19	d(1)		−42.90	t(1)	15.25	−165.12	m(2)	$J(o–m)$ 20.75	
							130.29	dd(2)	$J(o–p)$ 6.10	
$[OsCl_2(N_2)(PMe_2Ph)_3]$[h]	1.81	ot(2)	9.0	−35.0	m(3)					2 078
	1.32	d(1)								
$[OsHCl(N_2)(PMe_2Ph)_3]$[h]				−32.9	d(2)					2 049
				−41.1	t(1)					
$[OsCl(SCF_3)(N_2)(PMe_2Ph)_3]$	1.82	ot(2)	9.10	−48.59	d(2)	15.24	−161.88			2 078
	1.29	d(1)		−44.12	(1)[i]			*d*	$^4J(PF)$ 7.32	
$[OsBr(SC_6F_5)(N_2)(PMe_2Ph)_3]$	1.88	dt(2)	9.10	−43.2	d(2)	15.24	−163.60	t(1)	$J(p–m)$ 19.53	2 094
	1.35	d(1)		−47.20	t(1)		−166.35	m(2)	$J(o–m)$ 19.53	
							−131.22	dd(2)	$J(o–p)$ 7.2	
$[OsBr_2(N_2)(PMe_2Ph)_3]$[h]	1.99	ot(2)	9.4	−43.5	d(2)					2 100
	1.41	d(1)		−39.7	t(1)					
$[OsHBr(N_2)(PMe_2Ph)_3]$[h]				−36.4	d(2)					2 095
				−46.3	t(1)					

[a] In p.p.m., relative to $SiMe_4$ in $CDCl_3$. [b] d = Doublet, s = singlet, t = triplet, ot = overlapping triplets, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, rel. int. = relative intensity. [c] In Hz. [d] In p.p.m., relative to H_3PO_4 in $CDCl_3$. [e] In p.p.m., relative to $CFCl_3$ in $CHCl_3$. [f] *p–m* = *para–meta*; *o–m* = *ortho–meta*; *o–p* = *ortho–para*. [g] In cm⁻¹, Nujol mull spectra. [h] Taken from ref. 11 and refs. therein. [i] 12 line spectrum from *trans*-CF_3, *cis*-PMe_2Ph coupling.



(**I**)

arguments are consistent with the configuration shown in structure (**I**), confirmed crystallographically as described below.

In the series $[OsXY(N_2)(PMe_2Ph)_3]$[11] (X = Cl or Br; Y = Cl, Br, H, or SR) (Table 2) the ^{31}P resonance pattern is diagnostic of substitution of X and/or Y, where Y is *trans* to the unique PMe_2Ph ligand. For X = Cl, the triplet arising from the unique P_BMe_2Ph moves upfield as Y varies in the sequence Cl < SMe < H < SPh < SC_6F_5 and for X = Br, the variation with Y is Br < SCF_3 < H < SC_6F_5. The *trans*-P_AMe_2Ph doublet also varies with change of X and Y, essentially in the above sequence, except when Y = H, where the doublet resonates at very low field.[11]

I.r. Spectra.—All compounds show a very intense band in the range 2 049—2 100 cm⁻¹, assigned to the N–N stretching vibration. Apparently there is no simple correlation between the $\nu(N{\equiv}N)$ values and the R substituent of the *cis*-RS^- ligands. Bromo complexes have slightly higher frequencies than chloro complexes, consistent with a greater *trans* influence of bromide in these compounds. Osmium–nitrogen, osmium–phosphorus, and osmium–sulphur stretching frequencies are not assignable because the 500—400 cm⁻¹ region of the spectrum, in which these bands probably occur, is obscured by the bands of the phosphine and thiolate ligands.

X-Ray Structure of mer-[OsCl(SC_6F_5)(N_2)(PMe_2Ph)$_3$].—Bond distances and angles are shown in Tables 3 and 4, respectively and atomic co-ordinates in Table 5 . As can be seen from the Figure, in the solid state *mer*-[OsCl(SC_6F_5)(N_2)(PMe_2Ph)$_3$] has a pseudo-octahedral geometry around the metal centre. The N_2 moiety is *trans* to the chloride ion with a Cl–Os–N angle of *ca.* 177°; the N–N–Os skeleton is also close to linear [176.1(5)°]. The shortest Os–P distance [2.326(1) Å] corresponds to the phosphine ligand *trans* to SC_6F_5. The other Os–P bond lengths are longer [2.375(1) and 2.381(1) Å respectively]. This situation is reflected in the ^{31}P n.m.r. signal for the unique phosphine which is shifted up-field (see above). The angle Os–S–C is 123.9(2)°, unusually large when compared with other known examples.[1–3] This value shows a considerable deviation from the tetrahedral environment expected around the sulphur atom and is presumably a steric effect of the bulky C_6F_5 group.

The N≡N distance [1.112(5) Å] is typical of terminal dinitrogen complexes and close to the only other distance measured in an osmium dinitrogen complex,[12] 1.12(2) Å for $[Os(N_2)(NH_3)_5]^{2+}$. The phenyl rings of the P(1)Me_2Ph and the SC_6F_5 ligands are packed close to parallel.

Table 3. Bond lengths (Å) for *mer*-[OsCl(SC_6F_5)(N_2)(PMe_2Ph)$_3$]

Os–P(1)	2.375(1)	Os–P(2)	2.326(1)
Os–P(3)	2.381(1)	Os–S	2.507(1)
Os–Cl	2.421(1)	Os–N(1)	1.909(3)
P(1)–C(1a)	1.804(6)	P(1)–C(1b)	1.818(6)
P(1)–C(11)	1.829(6)	P(2)–C(2a)	1.814(6)
P(2)–C(2b)	1.816(6)	P(2)–C(21)	1.816(4)
P(3)–C(3a)	1.821(6)	P(3)–C(3b)	1.801(8)
P(3)–C(31)	1.826(5)	S–C(41)	1.757(6)
N(1)–N(2)	1.112(5)	C(11)–C(12)	1.387(9)
C(11)–C(16)	1.397(7)	C(12)–C(13)	1.395(12)
C(13)–C(14)	1.349(11)	C(14)–C(15)	1.367(12)
C(15)–C(16)	1.395(9)	C(21)–C(22)	1.389(7)
C(21)–C(26)	1.390(7)	C(22)–C(23)	1.390(7)
C(23)–C(24)	1.366(11)	C(24)–C(25)	1.347(9)
C(25)–C(26)	1.377(7)	C(31)–C(32)	1.399(7)
C(31)–C(36)	1.386(8)	C(32)–C(33)	1.399(11)
C(33)–C(34)	1.372(11)	C(34)–C(35)	1.349(9)
C(35)–C(36)	1.393(9)	C(41)–C(42)	1.394(8)
C(41)–C(46)	1.377(6)	C(42)–C(43)	1.384(10)
C(42)–F(42)	1.360(6)	C(43)–C(44)	1.357(8)
C(43)–F(43)	1.357(9)	C(44)–C(45)	1.375(10)
C(44)–F(44)	1.340(8)	C(45)–C(46)	1.381(9)
C(45)–F(45)	1.320(6)	C(46)–F(46)	1.352(7)

Conclusions

Thiolate ligands may replace halide in the *cis* position to dinitrogen in osmium complexes with little apparent structural or electronic change. However, further substitution of thiolate for halide leads to dinitrogen loss, evidently thiolate has a labilising effect on a *trans*-dinitrogen ligand in these compounds.

Experimental

All manipulations were carried out under purified dinitrogen using Schlenk-tube techniques. The i.r. spectra were measured on a Unicam SP2000 spectrometer and the n.m.r. spectra were measured using a JEOL FX90Q instrument. All solvents were degassed and dried before use. The compounds *mer*-[OsX_2(N_2)(PMe_2Ph)$_3$] were prepared by published methods.[11]

Preparation of [OsCl(S_2CNMe_2)(PMe_2Ph)$_3$].—To *mer*-[$OsCl_2$(N_2)(PMe_2Ph)$_3$] (0.2 g, 0.284 mmol) dissolved in 2-methoxyethanol (50 cm^3) was added Tl[S_2CNMe_2] (0.2 g, 0.612 mmol) and the mixture was heated under reflux for 2 h. The precipitate of TlCl was separated by filtration and the resulting yellow solution concentrated under reduced pressure to a small volume, which upon addition of diethyl ether–CH_2Cl_2 (2:1) gave yellow crystals (yield 80%), identified by analysis and spectroscopy.[10]

Preparation of [Os(S_2CNMe_2)$_2$(PMe_2Ph)$_2$].—To *mer*-[$OsCl_2$(N_2)(PMe_2Ph)$_3$] (0.2 g, 0.284 mmol) dissolved in acetone (30 cm^3) was added Na[S_2CNMe_2]·3H_2O (0.2 g, 1.04 mmol) and the mixture was heated under reflux for 18 h. The resulting yellow solution was filtered, taken to dryness, and the

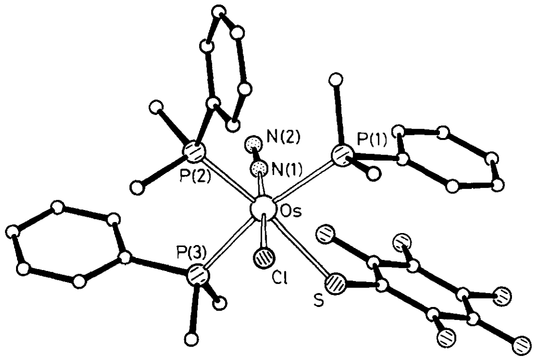


Figure. Structure of *mer*-[OsCl(SC_6F_5)(N_2)(PMe_2Ph)$_3$]

Table 4. Bond angles (°) for *mer*-[OsCl(SC_6F_5)(N_2)(PMe_2Ph)$_3$]

P(1)–Os–P(2)	97.4(1)	C(11)–C(16)–C(15)	121.3(6)	P(1)–Os–P(3)	168.1(1)	P(2)–C(21)–C(22)	118.8(4)
P(2)–Os–P(3)	94.5(1)	P(2)–C(21)–C(26)	122.1(3)	P(1)–Os–S	83.7(1)	C(22)–C(21)–C(26)	119.1(4)
P(2)–Os–S	164.2(1)	C(21)–C(22)–C(23)	119.8(6)	P(3)–Os–S	84.7(1)	C(22)–C(23)–C(24)	119.9(6)
P(1)–Os–Cl	90.7(1)	C(23)–C(24)–C(25)	120.4(6)	P(2)–Os–Cl	86.9(1)	C(24)–C(25)–C(26)	121.4(6)
P(3)–Os–Cl	89.4(1)	C(21)–C(26)–C(25)	119.4(5)	S–Os–Cl	77.3(1)	P(3)–C(31)–C(32)	120.5(4)
P(1)–Os–N(1)	90.9(1)	P(3)–C(31)–C(36)	122.1(3)	P(2)–Os–N(1)	90.7(1)	C(32)–C(31)–C(36)	117.4(5)
P(3)–Os–N(1)	89.5(1)	C(31)–C(32)–C(33)	120.5(6)	S–Os–N(1)	105.1(1)	C(32)–C(33)–C(34)	120.1(6)
Cl–Os–N(1)	177.3(1)	C(33)–C(34)–C(35)	120.3(7)	Os–P(1)–C(1a)	115.7(2)	C(34)–C(35)–C(36)	120.4(6)
Os–P(1)–C(1b)	119.1(2)	C(31)–C(36)–C(35)	121.3(5)	C(1a)–P(1)–C(1b)	102.5(3)	S–C(41)–C(42)	117.9(4)
Os–P(1)–C(11)	114.3(1)	S–C(41)–C(46)	128.6(4)	C(1a)–P(1)–C(11)	103.6(3)	C(42)–C(41)–C(46)	113.5(5)
C(1b)–P(1)–C(11)	99.2(3)	C(41)–C(42)–C(43)	123.9(5)	Os–P(2)–C(2a)	116.1(2)	C(41)–C(42)–F(42)	119.5(6)
Os–P(2)–C(2b)	115.3(2)	C(43)–C(42)–F(42)	116.6(5)	C(2a)–P(2)–C(2b)	102.2(3)	C(42)–C(43)–C(44)	119.8(6)
Os–P(2)–C(21)	119.4(2)	C(42)–C(43)–F(43)	119.0(5)	C(2a)–P(2)–C(21)	102.6(2)	C(44)–C(43)–F(43)	121.3(7)
C(2b)–P(2)–C(21)	98.4(2)	C(43)–C(44)–C(45)	119.0(6)	Os–P(3)–C(3a)	114.8(2)	C(43)–C(44)–F(44)	120.2(6)
Os–P(3)–C(3b)	112.1(2)	C(45)–C(44)–F(44)	120.7(5)	C(3a)–P(3)–C(3b)	101.5(4)	C(44)–C(45)–C(46)	119.7(5)
Os–P(3)–C(31)	122.8(1)	C(44)–C(45)–F(45)	120.0(6)	C(3a)–P(3)–C(31)	103.9(3)	C(46)–C(45)–F(45)	120.3(6)
C(3b)–P(3)–C(31)	98.7(3)	C(41)–C(46)–C(45)	124.1(5)	Os–S–C(41)	123.9(2)	C(41)–C(46)–F(46)	119.7(5)
C(11)–C(12)–C(13)	120.3(6)	C(45)–C(46)–F(46)	116.1(4)	C(12)–C(13)–C(14)	120.1(7)	N(1)–N(2)–Os	176.1(5)
C(13)–C(14)–C(15)	121.8(8)			C(14)–C(15)–C(16)	118.5(6)		

Table 5. Fractional atomic co-ordinates (× 10^4)

Atom	x	y	z
Os	2 897(1)	1 866(1)	1 968(1)
P(1)	2 403(2)	1 515(1)	3 467(1)
P(2)	1 168(1)	716(1)	1 780(1)
P(3)	3 782(2)	2 451(1)	499(1)
S	5 285(1)	2 633(1)	2 195(1)
Cl	4 885(1)	262(1)	2 143(1)
N(1)	1 282(4)	3 101(3)	1 797(2)
N(2)	299(5)	3 791(4)	1 674(3)
C(1a)	2 667(8)	381(5)	4 090(4)
C(1b)	453(7)	1 214(5)	3 960(3)
C(11)	2 603(6)	2 695(4)	3 871(3)
C(12)	3 817(7)	2 707(5)	4 349(4)
C(13)	3 853(9)	3 609(7)	4 677(4)
C(14)	2 736(10)	4 495(6)	4 506(4)
C(15)	1 534(9)	4 535(5)	4 023(4)
C(16)	1 455(7)	3 620(4)	3 717(3)
C(2a)	−679(6)	1 413(5)	1 360(4)
C(2b)	1 914(7)	−115(5)	1 046(3)
C(21)	535(5)	−398(4)	2 680(3)
C(22)	1 656(7)	−1 251(4)	3 057(3)
C(23)	1 189(10)	−2 143(5)	3 716(4)
C(24)	−368(10)	−2 178(6)	3 991(4)
C(25)	−1 455(8)	−1 346(5)	3 633(4)
C(26)	−1 039(6)	−448(5)	2 979(3)
C(3a)	5 692(6)	1 759(8)	210(4)
C(3b)	4 138(11)	3 893(6)	169(4)
C(31)	2 584(5)	2 471(4)	−349(3)
C(32)	1 173(7)	3 183(5)	−472(4)
C(33)	271(8)	3 216(6)	−1 133(5)
C(34)	768(8)	2 549(6)	−1 666(4)
C(35)	2 127(8)	1 859(5)	−1 559(4)
C(36)	3 040(6)	1 815(4)	−905(3)
C(41)	5 236(5)	3 937(4)	2 395(3)
C(42)	6 437(6)	4 087(5)	2 834(4)
C(43)	6 543(7)	5 070(6)	3 033(4)
C(44)	5 441(7)	5 960(5)	2 790(4)
C(45)	4 235(7)	5 866(4)	2 347(4)
C(46)	4 171(6)	4 875(4)	2 155(3)
F(42)	7 553(4)	3 219(3)	3 120(3)
F(43)	7 734(5)	5 112(4)	3 487(3)
F(44)	5 497(5)	6 901(3)	3 009(3)
F(45)	3 160(5)	6 726(3)	2 098(3)
F(46)	2 952(4)	4 849(3)	1 719(2)

yellow solid residue was recrystallised from toluene–methanol (2:1) (yield 90%) and identified by analysis and spectroscopy.[10]

Preparation of Dinitrogen Compounds.—Since the method is general, only a typical preparation is described. To *mer*-[$OsCl_2(N_2)(PMe_2Ph)_3$] (0.2 g, 0.284 mmol) dissolved in acetone (50 cm^3) was added a solution of $Pb(SC_6F_5)_2$ (0.17 g, 0.284 mmol) in acetone (10 cm^3). The mixture was then stirred for *ca.* 3 h. The $PbCl_2$ which precipitated was filtered off and the resulting mauve solution was concentrated under reduced pressure to a small volume (*ca.* 20 cm^3). Addition of methanol produced *white crystals* which were filtered off and recrystallised from tetrahydrofuran (thf)–methanol (1:1) (65% yield).

X-Ray Crystallographic Study of mer-[$OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3$].—A colourless crystal of dimensions 0.18 × 0.2 × 0.3 mm was grown from thf solution and mounted on a glass fibre. Data were collected on a Nicolet R3M diffractometer.

Crystal data. $C_{30}H_{33}ClF_5N_2OsP_3S$, $M = 867.2$, triclinic, $a = 8.617(6)$, $b = 12.585(12)$, $c = 16.456(19)$ Å, $\alpha = 73.44(8)$, $\beta = 83.02(8)$, $\gamma = 81.55(7)°$, $U = 1\,685.9$ Å^3, $Z = 2$, $D_c = 1.708$ g cm^{-3}, $F(000) = 852$, space group $P\bar{1}$, μ(Mo-K_α) = 41.2 cm^{-1}.

A total of 9 889 independent reflections were measured by the ω-scan technique on a Nicolet R3M diffractometer ($2\theta_{max.} = 60°$). No absorption correction was applied. The structure was solved by direct methods (SHELXTL, revision 3.0[13]) and refined by full-matrix least squares (total number of refined parameters = 388) to an R value of 0.038, with weight index R' of 0.038 from 8 500 reflections with $I > 3\sigma(I)$, weighted $w = (\sigma_F^2 + 0.001\ F^2)^{-1}$, which gave a satisfactory weighting analysis. All non-H atoms were anisotropic, H-atoms fixed at C–H = 0.96 Å with a fixed $U_{iso} = 0.06$ Å^2. A final difference map showed major peaks (to *ca.* 2 e Å^{-3}) close to the osmium atom; there was no evidence for other molecules in the structure.

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

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