Dinitrogen Complexes of Osmium(II) with Thiolate Co-ligands: X-Ray Structure of *mer*-[OsCl(SC₆F₅)(N₂)(PMe₂Ph)₃][†]

Diana Cruz-Garritz,* Silvia Gelover, and Hugo Torrens

Facultad de Quimica, UNAM, Ciudad Universitaria, 04510, Mexico, D.F., Mexico Javier Leal Centro de Investigaciones en Quimica, UANL, Monterrey, Nuevo Leon, Mexico Raymond L. Richards AFRC-IPSR, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ

Treatment of *mer*-[OsCl₂(N₂)(PMe₂Ph)₃] with S₂CNMe₂⁻ salts causes loss of N₂ and the formation of *mer/fac*-[OsCl(S₂CNMe₂)(PMe₂Ph)₃] and *cis*-[Os(S₂CNMe₂)₂(PMe₂Ph)₂]. Dinitrogen is, however, retained in reactions of *mer*-[OsX₂(N₂)(PMe₂Ph)₃] (X = Cl or Br) with RS⁻ (R = Ph, C₆F₅, Me, or CF₃) at 20 °C in acetone to give the series *mer*-[OsX(SR)(N₂)(PMe₂Ph)₃]. Under more vigorous conditions the N₂ is displaced by thiolate. The compound *mer*-[OsCl(SC₆F₅)(N₂)(PMe₂Ph)₃] has an octahedral structure with N₂ *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 nitrogenase⁵ 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-[OsCl₂(N₂)(PMe₂Ph)₃] with $Tl[S_2CNMe_2]$ in acetone or 2-methoxyethanol under reflux yields a yellow crystalline compound formulated as [OsCl(S₂- $CNMe_2$)(PMe_2Ph)₃] (1). On the other hand, if the reaction is conducted under similar conditions but using Na[S₂CNMe₂] 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 Stephenson¹⁰ who obtained them, however, by a different synthetic route.

In contrast, treatment of *mer*-[OsX₂(N₂)(PMe₂Ph)₃] with the monodentate thiolate ligands RS⁻, where R = CF₃, Me, Ph, or C₆F₅, affords dinitrogen-containing species formulated as *mer*-[OsX(SR)(N₂)(PMe₂Ph)₃] [X = Cl; R = Me (3), Ph (4), C₆F₅ (5), or CF₃ (7); X = Br; R = C₆F₅ (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 N₂ 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



$[OsCl(SR)(N_2)(PMe_2Ph)_3]$ (3) -(7)

Scheme. (i) $Na[S_2CNMe_2]$; (ii) $Tl[S_2CNMe_2]$; (iii) $Pb(SR)_2$ (R = C₆H₅ or C₆F₅), Na(SMe), or AgCF₃; 20 °C, thf

and ³¹P n.m.r. signals. The ³¹P spectrum shows a complex multiplet (-36.2 to -40.19 p.p.m. from H₃PO₄) arising from the overlapping signals of each isomer. A similar analysis shows that *cis*-[Os(S₂CNMe₂)₂(PMe₂Ph)₂] has only one isomer in chloroform [simple singlet (-36.13 p.p.m. from H₃PO₄) in the ³¹P n.m.r. spectrum].

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, ³¹P-{¹H}, and ¹⁹F n.m.r. data and $v(N\equiv N)$ 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 ³¹P 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 ³¹P spectrum shows a doublet, thus two phosphines are *trans* and virtually coupled. The presence of only one additional triplet signal in the ³¹P spectrum shows that the three phosphine ligands are meridional.¹¹ The above

[†] 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
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				ŀ	Analysis (%)"	
Compound	Colour	M.p. (°C)	Yield (%)	C	H	N
(1) $[OsCl(S_2CNMe_2)(PMe_2Ph)_3]$	Yellow	140—147	80	42.0 (42.7)	5.5 (5.1)	2.4 (1.9)
(2) $[Os(S_2CNMe_2)_2(PMe_2Ph)_2]$	Yellow	171-173	90	37.4 (37.4)	5.1 (4.8)	3.8 (4.0)
(3) $[OsCl(SMe)(N_2)(PMe_2Ph)_3]$	White	138140 ^b	50	41.7 (41.9)	4.7 (5.0)	3.5 (3.9)
(4) $[OsCl(SPh)(N_2)(PMe_2Ph)_3]$	White	150—152*	65	46.6 (45.4)	4.7 (4.9)	3.5 (3.6)
(5) $[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$	White	153 ^b	60	41.0 (41.5)	3.7 (3.8)	3.1 (3.2)
(6) $[OsBr(SC_6F_5)(N_2)(PMe_2Ph)_3]$	White	165 ^b	55	40.0 (39.5)	3.5 (3.6)	3.0 (3.0)
(7) $[OsCl(SCF_3)(N_2)(PMe_2Ph)_3]$	White	145—150 ^b	90	39.4 (39.0)	4.7 (4.3)	3.0 (3.6)

" Calculated values in parentheses. ^b With decomposition.

Table 2. Spectroscopic properties of dinitrogen complexes of osmium(11)

		Multiplicity	/		Multiplicity			Multiplicity		
Compound	$\delta({}^{1}\mathrm{H})^{a}$	(rel. int.) ^b	$^{2}J(\text{PCH})^{\circ}$	$\delta(^{31}P)^d$	(rel. int.) ^b	$^{2}J(\mathbf{PP})^{c}$	δ(¹⁹ F) ^e	(rel. int.) ^b	$J^{c,f}$	v(N≡N) ^s
$[OsCl(SMe)(N_2)(PMe_2Ph)_3]$	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	
$[OsCl_2(N_2)(PMe_2Ph)_3]^n$	1.81	ot(2)	9.0	-35.0	m(3)					2 078
	1.32	d(1)								
$[OsHCl(N_2)(PMe_2Ph)_3]^n$				- 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		4 (05) 7 22	2 0 / 8
	1.29	d(1)	0.10	-44.12	(1).		1 (2 (0	d	$^{-}J(PF)$ 7.32	2 00 4
$\left[OsBr(SC_6F_5)(N_2)(PMe_2Ph)_3\right]$	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	
	1.00		0.4	12 5	1(2)		131.22	dd(2)	J(o-p) 7.2	2 100
$[OsBr_2(N_2)(PMe_2Pn)_3]^n$	1.99	O(2)	9.4	-43.5	d(2)					2 100
	1.41	a(1)		39.7	$\mathbf{u}(1)$					2 005
$\left[OsHBr(N_2)(PMe_2Ph)_3 \right]^n$				- 36.4	a(2)					2 095
				-40.5	U (1)					

^a In p.p.m., relative to SiMe₄ in CDCl₃. ^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 H₃PO₄ in CDCl₃. ^e In p.p.m., relative to CFCl₃ in CHCl₃. ^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-CF₃, cis-PMe₂Ph coupling.



arguments are consistent with the configuration shown in

structure (I), confirmed crystallographically as described below.

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 $P_{\rm B}Me_2Ph$ moves upfield as Y varies in the sequence

In the series $[OsXY(N_2)(PMe_2Ph)_3]^{11}$ (X = Cl or Br;

 $Cl < SMe < H < SPh < SC_6F_5$ 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 $v(N\equiv N)$ 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(SC₆F₅)(N₂)(PMe₂Ph)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 $mer-[OsCl(SC_6F_5)(N_2)(P Me_2Ph_3$ has a pseudo-octahedral geometry around the metal centre. The N₂ 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 SC₆F₅. The other Os-P bond lengths are longer [2.375(1) and 2.381(1) Å respectively]. This situation is reflected in the ³¹P 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 C₆F₅ 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)Me₂Ph and the SC₆F₅ ligands are packed close to parallel.

Table 3. Bond	lengths (Å) for mer-	OsCl(SC)	6F5)(N2)	(PMe,Ph),
			(-		· · · · · · · · · · · · · · · · · · ·

$\begin{array}{l} \text{Os-P(1)} \\ \text{Os-P(3)} \\ \text{Os-Cl} \\ \text{P(1)-C(1a)} \\ \text{P(1)-C(11)} \\ \text{P(2)-C(2b)} \\ \text{P(3)-C(3a)} \\ \text{P(3)-C(3a)} \\ \text{P(3)-C(31)} \\ \text{N(1)-N(2)} \\ \text{C(11)-C(16)} \\ \text{C(13)-C(14)} \\ \text{C(15)-C(16)} \\ \text{C(23)-C(24)} \\ \text{C(25)-C(26)} \\ \text{C(23)-C(24)} \\ \text{C(25)-C(26)} \\ \text{C(33)-C(34)} \\ \text{C(35)-C(36)} \\ \text{C(41)-C(46)} \\ \text{C(42)-F(42)} \\ \text{C(42)-F(42)} \\ \end{array}$	$\begin{array}{c} 2.375(1)\\ 2.381(1)\\ 2.421(1)\\ 1.804(6)\\ 1.829(6)\\ 1.829(6)\\ 1.821(6)\\ 1.821(6)\\ 1.826(5)\\ 1.112(5)\\ 1.397(7)\\ 1.349(11)\\ 1.395(9)\\ 1.390(7)\\ 1.366(11)\\ 1.377(7)\\ 1.386(8)\\ 1.372(11)\\ 1.393(9)\\ 1.377(6)\\ 1.360($	$\begin{array}{c} \text{Os-P(2)} \\ \text{Os-S} \\ \text{Os-N(1)} \\ \text{P(1)-C(1b)} \\ \text{P(2)-C(2a)} \\ \text{P(2)-C(2a)} \\ \text{P(3)-C(3b)} \\ \text{S-C(41)} \\ \text{C(11)-C(12)} \\ \text{C(11)-C(12)} \\ \text{C(12)-C(13)} \\ \text{C(14)-C(15)} \\ \text{C(21)-C(22)} \\ \text{C(22)-C(23)} \\ \text{C(22)-C(23)} \\ \text{C(31)-C(32)} \\ \text{C(34)-C(35)} \\ \text{C(34)-C(35)} \\ \text{C(41)-C(42)} \\ \text{C(42)-C(43)} \\ \text{C(43)-C(44)} \\ \text{C(44)-C(45)} \\ \end{array}$	$\begin{array}{c} 2.326(1)\\ 2.507(1)\\ 1.909(3)\\ 1.818(6)\\ 1.814(6)\\ 1.816(4)\\ 1.801(8)\\ 1.757(6)\\ 1.387(9)\\ 1.395(12)\\ 1.367(12)\\ 1.367(12)\\ 1.390(7)\\ 1.399(7)\\ 1.399(7)\\ 1.399(7)\\ 1.399(7)\\ 1.399(11)\\ 1.39(9)\\ 1.394(8)\\ 1.384(10)\\ 1.357(8)\\ 1.375(16)\end{array}$
C(43)-F(43) C(44)-F(44) C(45)-F(45)	1.357(9) 1.340(8) 1.320(6)	C(44)–C(45) C(45)–C(46) C(46)–F(46)	1.375(10) 1.381(9) 1.352(7)

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(2) - Os - P(3)	94.5(1)	P(2)-C(21)-C(26)	122.1(3)
P(2)-Os-S	164.2(1)	C(21)-C(22)-C(23)	119.8(6)
P(1)-Os-Cl	90.7(1)	C(23)-C(24)-C(25)	120.4(6)
P(3)-Os-Cl	89.4(1)	C(21)-C(26)-C(25)	119.4(5)
P(1) - Os - N(1)	90.9(1)	P(3)-C(31)-C(36)	122.1(3)
P(3)-OsN(1)	89.5(1)	C(31)-C(32)-C(33)	120.5(6)
Cl-Os-N(1)	177.3(1)	C(33)-C(34)-C(35)	120.3(7)
Os-P(1)-C(1b)	119.1(2)	C(31)-C(36)-C(35)	121.3(5)
Os-P(1)-C(11)	114.3(1)	S-C(41)-C(46)	128.6(4)
C(1b) - P(1) - C(11)	99.2(3)	C(41)-C(42)-C(43)	123.9(5)
Os-P(2)-C(2b)	115.3(2)	C(43)-C(42)-F(42)	116.6(5)
Os-P(2)-C(21)	119.4(2)	C(42)-C(43)-F(43)	119.0(5)
C(2b) - P(2) - C(21)	98.4(2)	C(43)-C(44)-C(45)	119.0(6)
Os-P(3)-C(3b)	112.1(2)	C(45)C(44)-F(44)	120.7(5)
Os-P(3)-C(31)	122.8(1)	C(44)C(45)-F(45)	120.0(6)
C(3b)-P(3)-C(31)	98.7(3)	C(41)C(46)C(45)	124.1(5)
C(11)-C(12)-C(13)	120.3(6)	C(45)–C(46)–F(46)	116.1(4)
C(13)-C(14)-C(15)	121.8(8)		

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-[OsCl₂(N₂)(PMe₂Ph)₃] (0.2 g, 0.284 mmol) dissolved in 2-methoxyethanol (50 cm³) was added Tl[S₂CNMe₂] (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-CH₂Cl₂ (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 cm³) was added Na[S₂CNMe₂]·3H₂O (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*- $[OsCl(SC_6F_5)(N_2)(PMe_2Ph)_3]$

P(1)-Os-P(3)	168.1(1)	P(2)-C(21)-C(22)	118.8(4)
P(1)OsS	83.7(1)	C(22) - C(21) - C(26)	119.1(4)
P(3)-Os-S	84.7(1)	C(22)-C(23)-C(24)	119.9(6)
P(2)OsCl	86.9(1)	C(24)-C(25)-C(26)	121.4(6)
S-Os-Cl	77.3(1)	P(3)-C(31)-C(32)	120.5(4)
P(2)OsN(1)	90.7(1)	C(32)-C(31)-C(36)	117.4(5)
S-Os-N(1)	105.1(1)	C(32)-C(33)-C(34)	120.1(6)
Os-P(1)-C(1a)	115.7(2)	C(34)-C(35)-C(36)	120.4(6)
C(1a)-P(1)-C(1b)	102.5(3)	S-C(41)-C(42)	117.9(4)
C(1a)-P(1)-C(11)	103.6(3)	C(42)-C(41)-C(46)	113.5(5)
Os-P(2)-C(2a)	116.1(2)	C(41)-C(42)-F(42)	119.5(6)
C(2a) - P(2) - C(2b)	102.2(3)	C(42)-C(43)-C(44)	119.8(6)
C(2a)-P(2)-C(21)	102.6(2)	C(44)-C(43)-F(43)	121.3(7)
Os-P(3)-C(3a)	114.8(2)	C(43)-C(44)-F(44)	120.2(6)
C(3a)-P(3)-C(3b)	101.5(4)	C(44)-C(45)-C(46)	119.7(5)
C(3a)-P(3)-C(31)	103.9(3)	C(46)–C(45)–F(45)	120.3(6)
Os-S-C(41)	123.9(2)	C(41)-C(46)-F(46)	119.7(5)
C(12)-C(13)-C(14)	120.1(7)	N(1)–N(2)–Os	176.1(5)
C(14)-C(15)-C(16)	118.5(6)		

Table 5. Fractional atomic co-ordinates ($\times 10^4$)

Atom	x	У	Ζ
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)	-1251(4)	3 057(3)
C(23)	1 189(10)	-2 143(5)	3 716(4)
C(24)	-368(10)	-2178(6)	3 991(4)
C(25)	-1 455(8)	-1346(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)	-1133(5)
C(34)	768(8)	2 549(6)	-1 666(4)
C(35)	2 127(8)	1 859(5)	-1559(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-[OsCl₂(N₂)(PMe₂Ph)₃] (0.2 g, 0.284 mmol) dissolved in acetone (50 cm³) was added a solution of Pb(SC₆F₅)₂ (0.17 g, 0.284 mmol) in acetone (10 cm³). The mixture was then stirred for *ca*. 3 h. The PbCl₂ which precipitated was filtered off and the resulting mauve solution was concentrated under reduced pressure to a small volume (*ca*. 20 cm³). Addition of methanol produced white crystals which were filtered off and recrystallised from tetrahydrofuran (thf)–methanol (1:1) (65% yield). View Article Online

X-Ray Crystallographic Study of mer- $[OsCl(SC_6F_5)(N_2)-(PMe_2Ph)_3]$.—A colourless crystal of dimensions $0.18 \times 0.2 \times 0.3$ 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, $\alpha = 73.44(8)$, $\beta = 83.02(8)$, $\gamma = 81.55(7)^\circ$, U = 1.685.9 Å³, Z = 2, $D_c = 1.708$ g cm⁻³, F(000) = 852, space group $P\overline{I}$, $\mu(Mo-K_{\alpha}) = 41.2$ cm⁻¹.

A total of 9 889 independent reflections were measured by the ω -scan technique on a Nicolet R3M diffractometer ($2\theta_{max.} = 60^{\circ}$). 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.

Acknowledgements

We thank CONACYT (grant PCCBBNA-020927) (Mexico) and the British Council for support.

References

- 1 D. Cruz-Garritz, J. Leal, and H. Torrens, Transition Met. Chem., 1984, 9, 284.
- 2 R. M. Catala, D. Cruz-Garritz, A. Hills, D. L. Hughes, R. L. Richards, and H. Torrens, J. Chem. Soc., Chem. Commun., 1987, 261.
- 3 R. M. Catala, D. Cruz-Garritz, H. Torrens, A. Hills, D. L. Hughes, and R. L. Richards, J. Organomet. Chem., 1987, 328, C37.
- 4 D. Cruz-Garritz, G. Domenzain, and H. Torrens, *Rev. Soc. Quim. Mex.*, 1986, **30**, 11.
- W. G. Zumpft and L. E. Mortenson, *Biochim. Biophys. Acta*, 1975, 146, 1; R. R. Eady and B. E. Smith, in 'Dinitrogen Fixation,' ed. R. W. F. Hardy, Wiley, New York, 1978, vol. 2; D. M. Kurtz, R. S. McMillian, B. K. Burgess, L. E. Mortenson, and R. H. Holm, *Proc. Natl. Acad. Sci. U.S.A.*, 1979, 76, 4986.
- 6 D. Cruz-Garritz, H. Torrens, J. Leal, and R. L. Richards, *Transition Met. Chem.*, 1983, 8, 127.
- 7 M. Aresta and A. Sacco, Gazz. Chim. Ital., 1972, 102, 155.
- 8 J. Chatt, R. H. Crabtree, J. R. Dilworth, and R. L. Richards, J. Chem. Soc., Dalton Trans., 1974, 2358.
- 9 A. J. L. Pombeiro, P. B. Hitchcock, and R. L. Richards, *Inorg. Chim.* Acta, 1983, **76**, 22.
- 10 D. J. Cole-Hamilton and T. A. Stephenson, J. Chem. Soc., Dalton Trans., 1976, 2396.
- 11 J. Chatt, D. P. Melville, and R. L. Richards, J. Chem. Soc. A, 1971, 1169; J. Mason, S. Donovan-Mtunzi, and R. L. Richards, J. Chem. Soc., Dalton Trans., 1984, 469.
- 12 J. E. Fergusson, J. L. Love, and W. T. Robinson, *Inorg. Chem.*, 1972, 11, 1162.
- 13 G. M. Sheldrick, SHELXTL, Program for crystal structure determination, University of Cambridge, 1976.

Received 1st September 1987; Paper 7/1594