

## Preparation of Isocyanide and Mixed Dinitrogen–Isocyanide Complexes of Rhenium(I) from Reactions of *trans*-[ReCl(N<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>4</sub>], *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>3</sub>], or *mer*-[Re(S<sub>2</sub>CNEt<sub>2</sub>)(N<sub>2</sub>)(PMe<sub>2</sub>Ph)<sub>3</sub>] with Methyl Isocyanide; Crystal Structure of *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)(CNMe)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>†</sup>

Armando J. L. Pombeiro\*

Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisbon Codex, Portugal

Peter B. Hitchcock and Raymond L. Richards

School of Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9RQ

Treatment of a tetrahydrofuran solution of *trans*-[ReCl(N<sub>2</sub>)L<sub>4</sub>] (L = PMe<sub>2</sub>Ph) or *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>] with CNMe affords the mixed dinitrogen–isocyanide complexes *mer*-[ReX(N<sub>2</sub>)(CNMe)L<sub>3</sub>] (X = Cl or S<sub>2</sub>PPh<sub>2</sub>) or [Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)(CNMe)<sub>2</sub>L<sub>2</sub>], as well as [ReX(CNMe)L<sub>3</sub>] (X = S<sub>2</sub>PPh<sub>2</sub>). Dinitrogen evolution occurs in the reaction of CNMe with *mer*-[Re(S<sub>2</sub>CNEt<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>] to give [ReX(CNMe)L<sub>3</sub>] (X = S<sub>2</sub>CNEt<sub>2</sub>) and [Re(S<sub>2</sub>CNEt<sub>2</sub>)(CNMe)<sub>2</sub>L<sub>2</sub>]. The crystal structure of *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)(CNMe)L<sub>3</sub>] has been determined.

As part of our interest in the properties of dinitrogen-bonded transition-metal centres and in the activation of small molecules by these sites, we have been investigating the reactions of Group 6 and 7 dinitrogen complexes, *e.g.* with isocyanides. In these complexes, typically of the types [M(N<sub>2</sub>)<sub>2</sub>L<sub>4</sub>] (M = Mo or W; L = PMe<sub>2</sub>Ph, PMePh<sub>2</sub>, or  $\frac{1}{2}$  dppe where dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) and *trans*-[ReCl(N<sub>2</sub>)(dppe)<sub>2</sub>], co-ordinated dinitrogen is the most substitution labile ligand, being replaced by isocyanide to give compounds of the types [M(CNR)<sub>2</sub>L<sub>4</sub>]<sup>1,2</sup> and *trans*-[ReCl(CNR)(dppe)<sub>2</sub>],<sup>3</sup> respectively. In the former system, for L = monophosphine, the lability of this ligand allows the co-ordination of further molecules of isocyanide, giving [M(CNR)<sub>3</sub>L<sub>3</sub>] and [M(CNR)<sub>4</sub>L<sub>2</sub>];<sup>2</sup> however, for *trans*-[M(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>] and *trans*-[ReCl(N<sub>2</sub>)(dppe)<sub>2</sub>], with robust chelating dppe ligands, only N<sub>2</sub> is susceptible to replacement by isocyanide.

The metal–dinitrogen bond is much stronger in the rhenium(I) complexes, with a strong  $\pi$ -electron-donor chloro ligand, than in those of Mo<sup>0</sup> or W<sup>0</sup> where the ligand *trans* to N<sub>2</sub> is also a  $\pi$ -acceptor (another N<sub>2</sub> ligand or a monophosphine). Thus the replacement of dinitrogen by isocyanide in the rhenium system requires more vigorous conditions. In order to extend the possible reaction pattern in these systems we have investigated the reactivity towards isocyanide of other rhenium(I) dinitrogen complexes which have a relatively stable Re–N<sub>2</sub> bond, but also present labile co-ligands which could then compete with N<sub>2</sub> for displacement by isocyanide. The formation of mixed dinitrogen–isocyanide complexes could then be anticipated and would allow direct comparison of the activation of N<sub>2</sub> and RNC, *e.g.* towards electrophilic attack, whilst bound to the same activating metal centre.

A few mixed complexes of this type are already known, but they have been prepared by a quite different route. For example, the organophosphite complexes *mer*-[ReCl(N<sub>2</sub>)(CNMe){P(OMe)<sub>3</sub>}]<sub>3</sub> and [ReCl(N<sub>2</sub>)(CNMe)(PPh<sub>3</sub>){P(OEt)<sub>3</sub>}]<sub>2</sub> were obtained by reaction of CNMe with the organodiazenido compounds [ReCl<sub>2</sub>(NNCOPh){P(OMe)<sub>3</sub>}]<sub>3</sub> and [ReCl<sub>2</sub>(NNCOPh)(PPh<sub>3</sub>){P(OEt)<sub>3</sub>}]<sub>2</sub>, respectively, where benzoyl chloride is another product.<sup>4</sup>

For the present study, the dinitrogen complexes *trans*-[ReCl(N<sub>2</sub>)L<sub>4</sub>], *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>], and *mer*-[Re(S<sub>2</sub>CNEt<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>] (L = PMe<sub>2</sub>Ph) were selected since they exhibit not only the above required features, but also allow inter-comparison between compounds containing bidentate sulphur-bonded ligands and that with chloride. This is important because the effect of sulphur co-ligands on the metal–dinitrogen bond has been little studied. The diphenyldithiophosphinato and the diethyldithiocarbamate complexes constitute rare examples of compounds where N<sub>2</sub> binds a sulphur-containing metal centre and their chemistry has not yet been fully explored in spite of its potential biological significance.

The X-ray structure of *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)(CNMe)L<sub>3</sub>], formed by reaction of *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>] with CNMe, has been briefly reported.<sup>5</sup> Here we present a more detailed study of this reaction and an extension to the reactions of other dinitrogen complexes with CNMe.

### Results and Discussion

*Reactions of trans*-[ReCl(N<sub>2</sub>)L<sub>4</sub>] (L = PMe<sub>2</sub>Ph) with CNMe.—Treatment of a tetrahydrofuran (thf) solution of *trans*-[ReCl(N<sub>2</sub>)L<sub>4</sub>] with CNMe (in a slight excess) affords *mer*-[ReX(N<sub>2</sub>)(CNMe)L<sub>3</sub>] (1; X = Cl) through replacement of a phosphine ligand by isocyanide. This complex was isolated as brown crystals (Table 1) with strong i.r. bands at 2 080 and 1 950 cm<sup>-1</sup> (with a shoulder at 1 930 cm<sup>-1</sup>), which are assigned to  $\nu$ (CN) and  $\nu$ (N<sub>2</sub>), respectively, by comparison with the related complex *mer*-[ReCl(N<sub>2</sub>)(CNMe){P(OMe)<sub>3</sub>}]<sub>3</sub> which exhibits<sup>4</sup> corresponding bands at 2 140 and 2 030 cm<sup>-1</sup>. The lower frequencies observed for complex (1; X = Cl) are in agreement with the stronger net electron-donor character of the phosphine relative to the phosphite ligand. Moreover,  $\nu$ (N<sub>2</sub>) of this complex occurs at a higher wavenumber than that of the parent tetrakis(phosphine) complex [ $\nu$ (N<sub>2</sub>) at 1 915 cm<sup>-1</sup>] on account of the stronger net electron-acceptor ability of the isocyanide compared to the phosphine ligand.

The meridional phosphine arrangement of complex (1; X = Cl) is confirmed by the characteristic triplet–doublet pattern (relative intensity 1:2) observed in its <sup>31</sup>P n.m.r. spectrum (Table 2). The methyl-proton resonance of the unique phosphine ligand occurs as the expected doublet in the <sup>1</sup>H n.m.r.

<sup>†</sup> *mer*-Tris(dimethylphenylphosphine)(dinitrogen-*N*)(diphenyldithiophosphinato-*S*)(methyl isocyanide)rhenium(I).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

**Table 1.** Physical data for rhenium complexes (L = PMe<sub>2</sub>Ph)

Complex	Colour	I.r. (cm <sup>-1</sup> ) <sup>a</sup>		Analysis <sup>b</sup> (%)		
		v(N <sub>2</sub> )	v(CN)	C	H	N
<i>mer</i> -[ReCl(N <sub>2</sub> )(CNMe)L <sub>3</sub> ] (1; X = Cl)	Brown	1 950s 1 930(sh)	2 080s	44.3 (44.3)	5.1 (5.1)	6.0 (6.0)
<i>mer</i> -[Re(S <sub>2</sub> PPh <sub>2</sub> )(N <sub>2</sub> )(CNMe)L <sub>3</sub> ] (1; X = S <sub>2</sub> PPh <sub>2</sub> )	Yellow	1 980s	2 100ms	49.8 (49.7)	5.0 (5.0)	4.7 (4.6)
[Re(S <sub>2</sub> PPh <sub>2</sub> )(N <sub>2</sub> )(CNMe) <sub>2</sub> L <sub>2</sub> ] (2)	Light greenish yellow	2 010s	2 120s 2 080s	46.7 (46.8)	5.0 (4.7)	6.8 (6.8)
[Re(S <sub>2</sub> PPh <sub>2</sub> )(CNMe)L <sub>3</sub> ] (3; X = S <sub>2</sub> PPh <sub>2</sub> )	Yellow		1 780s	51.3 (51.2)	5.4 (5.2)	1.7 (1.6)
[Re(S <sub>2</sub> CNEt <sub>2</sub> )(CNMe)L <sub>3</sub> ] <sup>c</sup> (3; X = S <sub>2</sub> CNEt <sub>2</sub> )	Yellow oil		1 810s			
[Re(S <sub>2</sub> CNEt <sub>2</sub> )(CNMe) <sub>2</sub> L <sub>2</sub> ] <sup>c</sup> (5)	Dark red oil		2 070s			

<sup>a</sup> In Nujol mull. <sup>b</sup> Required values in parentheses. <sup>c</sup> Not obtained in an analytically pure state.

**Table 2.** Proton and <sup>31</sup>P n.m.r. data for rhenium complexes (L = PMe<sub>2</sub>Ph)

Complex	<sup>1</sup> H N.m.r. <sup>a</sup>			<sup>31</sup> P N.m.r. <sup>b</sup>		
	δ	Integration	Assignment	δ	Integration	Assignment
<i>mer</i> -[ReCl(N <sub>2</sub> )(CNMe)L <sub>3</sub> ] (1; X = Cl)	7.6—7.1(m)	15(15)	PMe <sub>2</sub> Ph	164.7(d) <sup>c</sup>	2	2 <i>trans</i> -PMe <sub>2</sub> Ph
	3.07(s)	3(3)	CNMe	169.7(t) <sup>c</sup>	1	Unique PMe <sub>2</sub> Ph
	1.68—1.54(m)	12(12)	2 <i>trans</i> -PMe <sub>2</sub> Ph			
	1.38(d) <sup>d</sup>	6(6)	Unique PMe <sub>2</sub> Ph			
<i>mer</i> -[Re(S <sub>2</sub> PPh <sub>2</sub> )(N <sub>2</sub> )(CNMe)L <sub>3</sub> ] (1; X = S <sub>2</sub> PPh <sub>2</sub> )	8.1—7.0(m)	25(25)	PMe <sub>2</sub> Ph + S <sub>2</sub> PPh <sub>2</sub> <sup>-</sup>	77.6(d) <sup>e</sup>	1	S <sub>2</sub> PPh <sub>2</sub> <sup>-</sup>
	2.95(s)	3(3)	CNMe	169.6(d) <sup>f</sup>	2	2 <i>trans</i> -PMe <sub>2</sub> Ph
	1.6—1.3(m)	18(18)	PMe <sub>2</sub> Ph	174.8(dt) <sup>g</sup>	1	Unique PMe <sub>2</sub> Ph
	8.2—7.1(m)	20(20)	PMe <sub>2</sub> Ph + S <sub>2</sub> PPh <sub>2</sub> <sup>-</sup>	75.6(t) <sup>h</sup>	1	S <sub>2</sub> PPh <sub>2</sub> <sup>-</sup>
[Re(S <sub>2</sub> PPh <sub>2</sub> )(N <sub>2</sub> )(CNMe) <sub>2</sub> L <sub>2</sub> ] (2)	3.12(s)	6(6)	CNMe	169.4(d) <sup>i</sup>	2	2PMe <sub>2</sub> Ph
	1.8—1.4(m)	12(12)	PMe <sub>2</sub> Ph			
	7.9—7.0(m)	25(25)	PMe <sub>2</sub> Ph + S <sub>2</sub> PPh <sub>2</sub> <sup>-</sup>	39.8(s,br)	1	S <sub>2</sub> PPh <sub>2</sub> <sup>-</sup>
	3.43(s)	3(3)	CNMe	159.2(s,br)	2	2PMe <sub>2</sub> Ph
<i>mer</i> -[Re(S <sub>2</sub> CNEt <sub>2</sub> )(CNMe)L <sub>3</sub> ] (3; X = S <sub>2</sub> CNEt <sub>2</sub> )	1.60—1.15(m)	18(18)	PMe <sub>2</sub> Ph	162.4(s,br)	1	Unique PMe <sub>2</sub> Ph
	7.8—7.0(m)	15(15)	PMe <sub>2</sub> Ph	158.2(m,br)	2	<i>trans</i> -PMe <sub>2</sub> Ph <sup>c</sup>
	3.49(q) <sup>j</sup>	5(4)	S <sub>2</sub> CN(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> <sup>-</sup>	166.5(m,br)	1	Unique PMe <sub>2</sub> Ph
	3.04(s)	4(3)	CNMe			
	1.90(t) <sup>k</sup>	12(12)	2 <i>trans</i> -PMe <sub>2</sub> Ph			
	1.38—1.05(m)	13(12)	Unique PMe <sub>2</sub> Ph + S <sub>2</sub> CN(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> <sup>-</sup>			
[Re(S <sub>2</sub> CNEt <sub>2</sub> )(CNMe) <sub>2</sub> L <sub>2</sub> ] (5)	7.9—6.9(m)	10(10)	PMe <sub>2</sub> Ph	106.9(s)		PMe <sub>2</sub> Ph
	3.65(q) <sup>l</sup>	4(4)	S <sub>2</sub> CN(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> <sup>-</sup>			
	2.42(s)	5(6)	CNMe			
	1.75(d) <sup>m</sup>	12(12)	PMe <sub>2</sub> Ph			
	1.30(t) <sup>l</sup>	6(6)	S <sub>2</sub> CN(CH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub> <sup>-</sup>			
<i>mer</i> -[Re(S <sub>2</sub> PPh <sub>2</sub> )(N <sub>2</sub> )L <sub>3</sub> ] <sup>n</sup>	8.0—7.0(m)	25(25)	PMe <sub>2</sub> Ph + S <sub>2</sub> PPh <sub>2</sub> <sup>-</sup>	32.9(s)	1	S <sub>2</sub> PPh <sub>2</sub> <sup>-</sup>
	1.60—1.20(m)	18(18)	PMe <sub>2</sub> Ph	165.2(s)	2	2 <i>trans</i> -PMe <sub>2</sub> Ph
				168.9(s)	1	Unique PMe <sub>2</sub> Ph

<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub>; δ values in p.p.m. relative to internal SiMe<sub>4</sub>. <sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub>; δ values in p.p.m. upfield from external P(OMe)<sub>3</sub>. <sup>c</sup> <sup>2</sup>J(PReP) = 17.8 Hz. <sup>d</sup> <sup>2</sup>J(HP) = 6.8 Hz. <sup>e</sup> <sup>3</sup>J(PP) = 41.5 Hz (coupling to the unique PMe<sub>2</sub>Ph, see below). <sup>f</sup> <sup>2</sup>J(PReP) = 19.5 Hz. <sup>g</sup> Doublet (*J* = 41.5 Hz) of triplets (*J* = 19.5 Hz) due to coupling to S<sub>2</sub>PPh<sub>2</sub><sup>-</sup> (doublet) and to 2 *trans*-PMe<sub>2</sub>Ph (triplet). <sup>h</sup> <sup>3</sup>J(PP) = 20.8 Hz. <sup>i</sup> <sup>3</sup>J(PP) = 20 Hz. <sup>j</sup> <sup>3</sup>J(HH) = 7.0 Hz. <sup>k</sup> <sup>2</sup>J(PH) + <sup>4</sup>J(PH) = 2 × 3.2 Hz. <sup>l</sup> <sup>3</sup>J(HH) = 7.3 Hz. <sup>m</sup> <sup>2</sup>J(PH) = 13.3 Hz. <sup>n</sup> Included for comparative purposes.

spectrum, whereas for the two *trans* phosphines a complex pattern is observed.

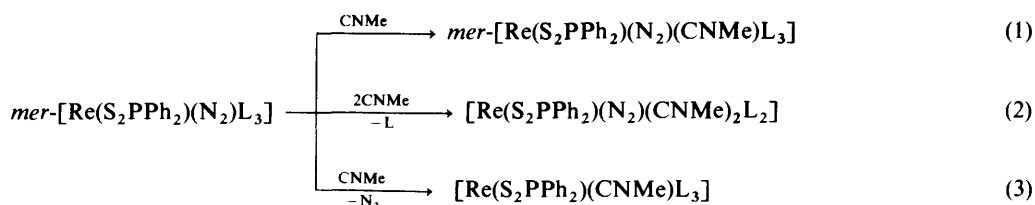
Although the available spectroscopic data do not allow assignment of the relative position, in the plane, of Cl, N<sub>2</sub>, CNMe, and the unique phosphine ligand, we believe the chloro ligand (which is the best π-electron donor) is *trans* to N<sub>2</sub>, thus stabilizing the Re—N<sub>2</sub> bond, as is observed in the related complexes *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>]<sup>5</sup> and *mer*-[ReCl(N<sub>2</sub>)(CNMe){P(OMe)<sub>3</sub>}]<sub>3</sub>.<sup>4</sup>

Besides complex (1; X = Cl), other species are formed in the reaction of *trans*-[ReCl(N<sub>2</sub>)L<sub>4</sub>] with CNMe, but they were not isolated in a pure state. A strong i.r. band at 1 780 cm<sup>-1</sup> is possibly due to *trans*-[ReCl(CNMe)L<sub>4</sub>] since the related

complexes *trans*-[ReCl(CNMe)(dppe)]<sub>3</sub> and [Re(S<sub>2</sub>PPh<sub>2</sub>)(CNMe)L<sub>3</sub>] (see below) exhibit v(CN) at ca. 1 800 and 1 780 cm<sup>-1</sup>, respectively.

**Reactions of *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>] (L = PMe<sub>2</sub>Ph) with CNMe.**—Treatment of a thf solution of *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>] with CNMe (molar ratio ≤ 2:1) affords a variety of complexes which may be separated by careful, repeated recrystallization from thf-methanol or diethyl ether.

The chelating diphenyldithiophosphinato ligand may undergo a bidentate to unidentate rearrangement with addition of the isocyanide to the metal centre, giving the mixed complex *mer*-[ReX(N<sub>2</sub>)(CNMe)L<sub>3</sub>] (1; X = S<sub>2</sub>PPh<sub>2</sub>), analogous to



(1; X = Cl) [equation (1)]. Further replacement of a phosphine ligand by a second molecule of isocyanide may occur to give the dinitrogenbis(isocyanide) complex  $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)(\text{CNMe})_2\text{L}_2]$  (2) [reaction (2)] in which the  $\text{N}_2$  ligand is retained in spite of the presence of two isocyanide co-ligands which are strong competitors for the available metal  $d$ -electron density. Evolution of  $\text{N}_2$  from  $\text{mer-[Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)\text{L}_3]$  with replacement by CNMe also occurs [reaction (3)] to give the isocyanide complex  $[\text{ReX}(\text{CNMe})\text{L}_3]$  (3; X =  $\text{S}_2\text{PPh}_2$ ), the formation of which is favoured by a stoichiometric amount of isocyanide under an argon atmosphere.

The complexes in this study have been obtained by simple replacement reactions of the parent dinitrogen compounds. However, mixed dinitrogen-isocyanide complexes related to (1; X =  $\text{S}_2\text{PPh}_2$  or Cl), the organophosphite compounds  $\text{mer-[ReCl}(\text{N}_2)(\text{CNMe})\{\text{P}(\text{OMe})_3\}_3]$  and  $[\text{ReCl}(\text{N}_2)(\text{CNMe})(\text{PPh}_3)\{\text{P}(\text{OEt})_3\}_2]$ , have been prepared<sup>4</sup> by reactions of CNMe with organodiazene species, as mentioned above. This route has also been used for the syntheses of related mixed carbonyl-dinitrogen compounds, such as  $[\text{ReCl}(\text{N}_2)(\text{CO})\{\text{P}(\text{OMe})_3\}_3]$  and  $[\text{ReCl}(\text{N}_2)(\text{CO})(\text{PPh}_3)_2\{\text{P}(\text{OMe})_3\}]$ ,<sup>6</sup> as well as  $[\text{ReCl}(\text{N}_2)(\text{CO})_2\text{L}_2]$  (L =  $\text{PPh}_3$ ,  $\text{PEtPh}_2$ , or  $\text{PP}^n\text{Ph}_2$ ),<sup>7</sup> a dicarbonyl analogue of (2).

In the i.r. spectrum (Table 1) of  $\text{mer-[Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)(\text{CNMe})\text{L}_3]$  (1; X =  $\text{S}_2\text{PPh}_2$ ),  $\nu(\text{CN})$  and  $\nu(\text{N}_2)$  occur at 2 100 and 1 980  $\text{cm}^{-1}$ , respectively. These values are comparable to those of the analogous complex (1; X = Cl). For  $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)(\text{CNMe})_2\text{L}_2]$  (2), however, the corresponding bands occur at 2 120 and 2 080 and 2 010  $\text{cm}^{-1}$ . Although a clear assignment in complex (2) is not possible and considerable coupling between the CN and the  $\text{N}_2$  stretching vibrations may occur, as for  $\nu(\text{CO})$  and  $\nu(\text{N}_2)$  of the related complex  $[\text{ReCl}(\text{N}_2)(\text{CO})_2(\text{PPh}_3)_2]$ ,<sup>7</sup> we suggest, by analogy with the other mixed dinitrogen-isocyanide complexes, that the lowest-wavenumber band (2 010  $\text{cm}^{-1}$ ) is associated with the  $\text{N}_2$  ligand. As expected on the basis of the stronger net electron-acceptor character of CNMe compared to the phosphine ligand,  $\nu(\text{N}_2)$  is higher for complex (2) than for (1).

The complex  $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{CNMe})\text{L}_3]$  (3) exhibits a strong i.r. band at 1 780  $\text{cm}^{-1}$  which is assigned to  $\nu(\text{CN})$  of ligating isocyanide. This appears to be the lowest  $\nu(\text{CN})$  value so far reported for a terminal methyl isocyanide ligand, being even lower than that observed<sup>3</sup> at ca. 1 800–1 830  $\text{cm}^{-1}$  for  $\text{trans-[ReCl}(\text{CNMe})(\text{dppe})_2]$ . The parent complex  $\text{mer-[Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)\text{L}_3]$  has  $\nu(\text{N}_2)$  at 1 935  $\text{cm}^{-1}$  which is lower than that observed for  $\text{trans-[ReCl}(\text{N}_2)(\text{dppe})_2]$  (1 975  $\text{cm}^{-1}$ ). These observations suggest a strong  $\pi$ -electron-donor character for the  $\text{S}_2\text{PPh}_2^-$  ligand.

The molecular structure of complex (1; X =  $\text{S}_2\text{PPh}_2$ ) has been authenticated by X-ray analysis<sup>5</sup> and is depicted in Figure 1. Selected bond lengths and angles are listed in Table 3. The anionic electron-donor ligand is *trans* to dinitrogen thus stabilizing its bond to the metal, as is observed<sup>4</sup> for chloride in  $\text{mer-[ReCl}(\text{N}_2)(\text{CNMe})\{\text{P}(\text{OMe})_3\}_3]$  (4).

In complex (1; X =  $\text{S}_2\text{PPh}_2$ ) the Re–N (or C) bond lengths [1.83(1) or 1.93(1) Å] are somewhat shorter than those of complex (4) [1.98(1) or 2.07(2) Å], whereas the N–N (or C–N) distances are somewhat longer in (1; X =  $\text{S}_2\text{PPh}_2$ ) [1.13(1) or 1.20(2) Å] than in (4) [1.04(2) or 1.12(2) Å].<sup>4</sup> In agreement with

Table 3. Selected intramolecular distances (Å) and angles ( $^\circ$ ) with e.s.d.s in parentheses

Re–S(1)	2.548(2)	Re–P(2)	2.450(3)
Re–P(3)	2.501(3)	Re–P(4)	2.366(3)
Re–N(2)	1.829(9)	Re–C(1)	1.926(13)
S(1)–P(1)	2.025(4)	S(2)–P(1)	1.964(4)
P(1)–C(3)	1.862(10)	P(1)–C(9)	1.828(12)
P(2)–C(15)	1.854(14)	P(2)–C(16)	1.806(14)
P(2)–C(17)	1.829(11)	P(3)–C(23)	1.859(13)
P(3)–C(24)	1.816(12)	P(3)–C(25)	1.816(11)
P(4)–C(31)	1.84(2)	P(4)–C(32)	1.811(14)
P(4)–C(33)	1.858(11)	N(1)–C(1)	1.20(2)
N(1)–C(2)	1.39(2)	N(2)–N(3)	1.126(13)
S(1)–Re–P(2)	87.9(1)	S(1)–Re–P(3)	82.2(1)
S(1)–Re–P(4)	92.5(1)	S(1)–Re–N(2)	170.2(3)
S(1)–Re–C(1)	93.3(4)	P(2)–Re–P(3)	90.7(1)
P(2)–Re–P(4)	176.1(1)	P(2)–Re–N(2)	87.6(3)
P(2)–Re–C(1)	86.5(4)	P(3)–Re–P(4)	93.2(1)
P(3)–Re–N(2)	89.1(3)	P(3)–Re–C(1)	174.7(4)
P(4)–Re–N(2)	92.6(3)	P(4)–Re–C(1)	89.7(4)
N(2)–Re–C(1)	95.2(5)	Re–S(1)–P(1)	117.6(1)
S(1)–P(1)–S(2)	119.8(2)	S(1)–P(1)–C(3)	103.4(3)
S(1)–P(1)–C(9)	108.4(3)	S(2)–P(1)–C(3)	109.4(3)
S(2)–P(1)–C(9)	110.4(4)	C(3)–P(1)–C(9)	104.1(5)
Re–P(2)–C(15)	121.7(4)	Re–P(2)–C(16)	112.8(5)
Re–P(2)–C(17)	116.7(4)	C(15)–P(2)–C(16)	100.7(6)
C(15)–P(2)–C(17)	102.0(6)	C(16)–P(2)–C(17)	99.6(5)
Re–P(3)–C(23)	119.7(4)	Re–P(3)–C(24)	113.7(4)
Re–P(3)–C(25)	119.7(3)	C(23)–P(3)–C(24)	101.0(6)
C(23)–P(3)–C(25)	96.6(5)	C(24)–P(3)–C(25)	103.1(5)
Re–P(4)–C(31)	111.6(5)	Re–P(4)–C(32)	120.1(5)
Re–P(4)–C(33)	118.6(3)	C(31)–P(4)–C(32)	98.9(7)
C(31)–P(4)–C(33)	100.5(7)	C(32)–P(4)–C(33)	103.8(6)
C(1)–N(1)–C(2)	168(1)	Re–N(2)–N(3)	174(1)
Re–C(1)–N(1)	169(1)		

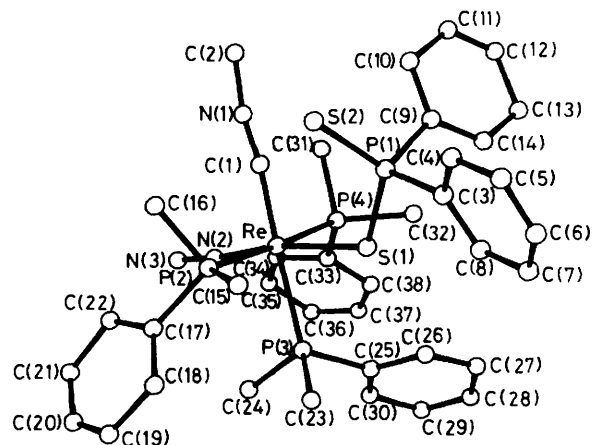


Figure 1. The molecular structure and atom numbering scheme of  $\text{mer-[Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)(\text{CNMe})(\text{PMe}_2\text{Ph})_3]$



Figure 2. Possible structures for the complex  $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)(\text{CNMe})_2\text{L}_2]$  (2;  $\text{L} = \text{PMe}_2\text{Ph}$ )

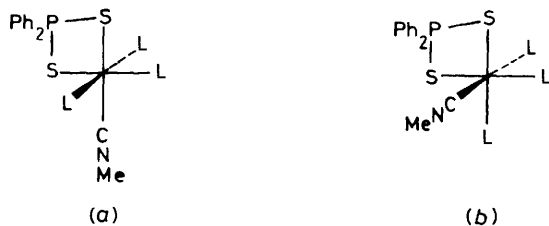


Figure 3. Possible structures for the complex  $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{CNMe})\text{L}_3]$  (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ,  $\text{L} = \text{PMe}_2\text{Ph}$ )

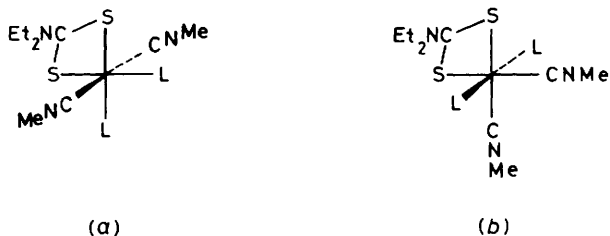


Figure 4. Possible structures for the complex  $[\text{Re}(\text{S}_2\text{CNEt}_2)(\text{CNMe})_2\text{L}_2]$  (5;  $\text{L} = \text{PMe}_2\text{Ph}$ )

these features,  $\nu(\text{N}_2)$  and  $\nu(\text{CN})$  for complex (1;  $\text{X} = \text{S}_2\text{PPh}_2$ ) (1 980 and 2 100  $\text{cm}^{-1}$ ) occur at lower values than for (4) (2 030 and 2 140  $\text{cm}^{-1}$ ). These observations clearly show the stronger net electron-donor ability of the dithiophosphinato/phosphine ligands relative to the chloride/phosphite combination, the former stabilizing to a greater extent the metal to dinitrogen and the metal to isocyanide bonds.

In the  $^{31}\text{P}$  n.m.r. spectrum (Table 2) of complex (1;  $\text{X} = \text{S}_2\text{PPh}_2$ ) the characteristic doublet-triplet pattern for a meridional arrangement of phosphine ligands is complicated by coupling to the phosphorus nucleus of the dithiophosphinato ligand. Thus, although a doublet ( $J = 19.5$  Hz) is observed at  $\delta = 169.6$  p.p.m. for the two *trans* phosphines, due to coupling to the unique phosphine ligand, the resonance of the latter occurs as a doublet ( $J = 41.5$  Hz) of triplets ( $J = 19.5$  Hz) centred at  $\delta = 174.8$  p.p.m. on account of the coupling to  $\text{S}_2\text{PPh}_2^-$  (doublet) and to two *trans*- $\text{PMe}_2\text{Ph}$  ligands (triplet). In accord, a doublet resonance ( $J = 41.5$  Hz) at  $\delta = 77.6$  p.p.m. is observed for  $\text{S}_2\text{PPh}_2^-$ . Thus, only the coupling between  $\text{S}_2\text{PPh}_2^-$  and  $\text{PMe}_2\text{Ph}$  which is *trans* to an isocyanide is detected; the coupling between  $\text{S}_2\text{PPh}_2^-$  and the phosphorus nuclei of the two *trans* phosphines is not observed.

The phosphorus resonance of the unidentate  $\text{S}_2\text{PPh}_2^-$  ligand in the complex  $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)(\text{CNMe})_2\text{L}_2]$  (2) has a  $\delta$  value (75.6 p.p.m.) which is similar to that of (1;  $\text{X} = \text{S}_2\text{PPh}_2$ ) (77.6 p.p.m.), but for  $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{CNMe})\text{L}_3]$  (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ) with a bidentate  $\text{S}_2\text{PPh}_2^-$  ligand this resonance occurs at a much lower field ( $\delta = 39.8$  p.p.m., comparable to that measured, also in this study, for *mer*- $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)\text{L}_3]$  (32.9 p.p.m.)). A similar trend was observed by another author<sup>8</sup> for other phosphorodithiolate ligands,  $\text{S}_2\text{P}(\text{OR})_2^-$ ,

bidentate co-ordination corresponding to a resonance at lower field than for unidentate.

For complex (2), the  $\text{S}_2\text{PPh}_2^-$  resonance ( $\delta = 75.6$  p.p.m.) occurs as a triplet whereas a doublet with the same coupling constant ( $J$  ca. 20 Hz) is observed for the two  $\text{PMe}_2\text{Ph}$  phosphines, which suggests (see above) that the latter two equivalent ligands are not *trans* to each other. Hence, assuming that the strong electron donor  $\text{S}_2\text{PPh}_2^-$  is *trans* to  $\text{N}_2$ , as expected, a *cis* arrangement of the two phosphine ligands (each being *trans* to an isocyanide) is favoured over the alternative *trans* geometry (Figure 2).

In complex  $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{CNMe})\text{L}_3]$  (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ) the bidentate character of the dithiophosphinato ligand is evidenced by the low-field resonance ( $\delta = 39.8$  p.p.m.) of the phosphorus nucleus, as mentioned above. Apart from this resonance, the  $^{31}\text{P}$  n.m.r. spectrum consists of two other singlets at 159.2 and 162.4 p.p.m., the former with double the intensity of the latter which has the same intensity as the singlet ascribed to the dithiophosphinato ligand. These data suggest that the resonance at 159.2 p.p.m. corresponds to two equivalent phosphines, that at 162.4 p.p.m. to the third phosphine. Two structures are possible (Figure 3), one (a) with a meridional arrangement of the phosphine ligands and the isocyanide *trans* to  $\text{S}_2\text{PPh}_2^-$ , and the other (b) with a facial arrangement of the phosphines, two of them being *trans* to  $\text{S}_2\text{PPh}_2^-$ .

Although an unambiguous selection between these two plausible structures is not possible, (a) is favoured over (b) on account of the following observations: in the i.r. spectrum,  $\nu(\text{CN})$  occurs at a very low wavenumber which suggests a strong, net electron-donor *trans* ligand (such as  $\text{S}_2\text{PPh}_2^-$ ), instead of another ligand (such as a phosphine) which would be able to  $\pi$ -accept and, hence, to compete with the isocyanide for the metal *d*-electron density; the  $^{31}\text{P}$  and the  $^1\text{H}$  n.m.r. spectra of complex (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ) are very similar to those of the related dinitrogen compound *mer*- $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)\text{L}_3]$ , suggesting the same geometry for both complexes.

In all the dithiophosphinato complexes studied, the phosphinic methyl-proton magnetic resonances are complicated as a result of overlap of multiplets and, hence, are not so valuable as the  $^{31}\text{P}$  n.m.r. spectra for assignment of the geometry of the compounds.

All the compounds are non-electrolytes in nitromethane, in agreement with their non-ionic character.

*Reactions of mer- $[\text{Re}(\text{S}_2\text{CNEt}_2)(\text{N}_2)\text{L}_3]$  ( $\text{L} = \text{PMe}_2\text{Ph}$ ) with CNMe.*—Treatment of a thf solution of *mer*- $[\text{Re}(\text{S}_2\text{CNEt}_2)(\text{N}_2)\text{L}_3]$  with an excess of methyl isocyanide (8:1), upon irradiation by a tungsten filament, leads to loss of the dinitrogen ligand with formation of species formulated as the mono- and the bis-isocyanide complexes  $[\text{ReX}(\text{CNMe})\text{L}_3]$  (3;  $\text{X} = \text{S}_2\text{CNEt}_2$ ) and  $[\text{Re}(\text{S}_2\text{CNEt}_2)(\text{CNMe})_2\text{L}_2]$  (5). These species were obtained as oils and never as analytically pure solids, even upon attempted recrystallizations from thf-methanol or -diethyl ether. They were, however, characterized by spectroscopic data.

Complex (3;  $\text{X} = \text{S}_2\text{CNEt}_2$ ) has  $\nu(\text{CN})$  at 1 810  $\text{cm}^{-1}$ , which is comparable to the value (1 780  $\text{cm}^{-1}$ ) observed for the analogous compound (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ). For the bis(isocyanide) complex (5),  $\nu(\text{CN})$  occurs as a broad band at 2 070  $\text{cm}^{-1}$ . This value is comparable to those shown by the mixed complexes (1) and (2) but higher than those observed for complexes (3) with only one isocyanide and without other strong electron-acceptor ligands.

Complex (3;  $\text{X} = \text{S}_2\text{CNEt}_2$ ) appears to contain a meridional phosphine arrangement as suggested by a triplet resonance pattern observed in the  $^1\text{H}$  n.m.r. spectrum (Table 2) at  $\delta = 1.90$  p.p.m. which integrates for 12 protons and is assigned to the methyl protons of two *trans*-phosphine ligands; the triplet

pattern arises from virtual coupling to both phosphorus nuclei with  $|^2J(\text{PH}) + ^4J(\text{PH})| = 6.4$  Hz. In the  $^{31}\text{P}$  n.m.r. spectrum, two unresolved multiplets are observed at 158.2 and 166.5 p.p.m. with a relative integration of 2:1. In the  $^{31}\text{P}$  n.m.r. spectrum of complex (5) only a singlet is observed (at 106.9 p.p.m.) which indicates that both phosphines are equivalent. Hence, two possible structures may be considered (Figure 4), one (a) corresponding to a *cis*-phosphine (and a *trans*-isocyanide) arrangement and the other (b) to a *trans*-phosphine (and a *cis*-isocyanide) geometry. Infrared data do not allow us to choose between these two possible structures since both of them correspond to a  $C_{2v}$  point-group symmetry and two  $\nu(\text{CN})$  i.r.-active bands would be expected ( $A_1 + B_1$  and  $A_1 + B_2$ , respectively); only one broad band is observed, at *ca.* 2 070  $\text{cm}^{-1}$ , probably as a result of overlap of the two expected bands. However, in the  $^1\text{H}$  n.m.r. spectrum, the phosphinic methyl-proton resonance occurs as a doublet ( $J = 13.3$  Hz), at  $\delta = 1.75$  p.p.m., which suggests both phosphines are equivalent and mutually *cis*.<sup>9,10</sup> Hence, we favour the geometry (a) for complex (5).

### Conclusions

Although dinitrogen is commonly a substitution labile ligand in its complexes and can undergo ready replacement by other two-electron donor species such as isocyanides or carbon monoxide,<sup>1,2</sup> in certain complexes replacement of co-ligands can occur with retention of the metal-dinitrogen bond. Thus, *trans*- $[\text{W}(\text{N}_2)_2(\text{PPh}_2\text{Me})_4]$  gives  $[\text{W}(\text{N}_2)_2(\text{PPh}_2\text{Me})_3(\text{py})]$  (py = various pyridines)<sup>11</sup> and phosphine may be replaced by isocyanide with retention of ligating  $\text{N}_2$  in the rhenium complexes described above. In the case of *trans*- $[\text{W}(\text{N}_2)_2(\text{PPh}_2\text{Me})_4]$ , probably phosphine is the most easily displaced ligand because its loss releases steric pressure between these bulky groups, as is observed in the formation of *mer*- $[\text{Mo}(\text{N}_2)_3(\text{PP}^n\text{Ph})_3]$  from *trans*- $[\text{Mo}(\text{N}_2)_2(\text{PP}^n\text{Ph})_4]$ .<sup>12</sup>

Preferential displacement of phosphine probably occurs in the rhenium complexes described in this work partly for steric reasons, but also because the  $\text{Re}-\text{N}_2$  bond is stabilized by  $\pi$ -electron release from the  $\text{Cl}^-$  or  $\text{S}_2\text{PPh}_2^-$  ligand in the *trans* position, which increases  $\pi$  donation from  $\text{Re}$  to  $\text{N}_2$ . This occurs to such an extent that replacement of a phosphine co-ligand by isocyanide or addition of isocyanide with concomitant bi-to-uni-dentate rearrangement of  $\text{S}_2\text{PPh}_2^-$  occurs in preference to  $\text{N}_2$  displacement. Mixed dinitrogen-isocyanide complexes are formed by this route, and it is notable that the stabilizing effect of the dithiophosphinato ligand on the *trans*  $\text{Re}-\text{N}_2$  bond allows the co-ordination of two molecules of methyl isocyanide, a strong electron acceptor and competitor for the available metal  $d$  electrons, without evolution of the dinitrogen ligand.

However, the rupture of the  $\text{Re}-\text{N}_2$  bond is promoted, *e.g.* by light, in agreement with expectations based on some simplified molecular-orbital schemes,<sup>13</sup> and isocyanide complexes may be formed by preferential replacement of the dinitrogen ligand by isocyanide as is observed, *e.g.* at the  $\text{Re}(\text{S}_2\text{CNEt}_2)_3$  centre.

Hence, the displacement of a dinitrogen ligand from a metal centre is governed by a delicate balance between the electronic and geometrical features of the binding centre and the experimental conditions employed, apart from the properties of the displacing agent itself.

### Experimental

All the reactions were carried out using standard inert-gas flow and vacuum techniques. Solvents were purified by standard techniques and the compounds *trans*- $[\text{ReCl}(\text{N}_2)\text{L}_4]$ ,<sup>14</sup> *mer*- $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)\text{L}_3]$ ,<sup>15</sup> *mer*- $[\text{Re}(\text{S}_2\text{CNEt}_2)(\text{N}_2)\text{L}_3]$ ,<sup>15</sup> and  $\text{CNMe}$ <sup>16</sup>

were prepared by published methods;  $\text{L} = \text{PMe}_2\text{Ph}$  throughout.

Infrared measurements were carried out on a Perkin-Elmer 577 or 683 spectrometer,  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectra on a JEOL FX90Q spectrometer. Conductivities were measured using a Portland Electronics P310 conductivity bridge.

*Reaction of trans*- $[\text{ReCl}(\text{N}_2)\text{L}_4]$  with  $\text{CNMe}$ .—A solution of the dinitrogen complex (0.100 g, 0.0982 mmol) in *thf* (10  $\text{cm}^3$ ) was treated with 0.75  $\text{cm}^3$  of a 0.194 mol  $\text{dm}^{-3}$  solution of  $\text{CNMe}$  (0.146 mmol) in *thf* and left stirring under dinitrogen for 3 d. The solution was then concentrated under vacuum and pentane was added until a yellow powder precipitated; it was filtered off and the solution was concentrated to a yellow oil. Pentane was added again and complex (1;  $\text{X} = \text{Cl}$ ) precipitated as big brown crystals upon prolonged cooling at *ca.*  $-20^\circ\text{C}$ ; they were filtered off and dried under vacuum (*ca.* 20 g, *ca.* 29% yield).

*Reactions of mer*- $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)\text{L}_3]$  with  $\text{CNMe}$ .—Methyl isocyanide (0.021  $\text{cm}^3$ , 0.446 mmol) was added to a *thf* solution (13  $\text{cm}^3$ ) of *mer*- $[\text{Re}(\text{S}_2\text{PPh}_2)(\text{N}_2)\text{L}_3]$  (0.230 g, 0.263 mmol) which was left stirring overnight under irradiation by a 150-W tungsten-filament bulb at a distance of *ca.* 80 cm. The solution was then concentrated under vacuum, and addition of methanol led to the precipitation of unreacted dinitrogen complex which was filtered off. Concentration of the solution gave an oil which, by addition of methanol and stirring, formed a yellow powder. This was filtered off, washed with cold methanol, and dried under vacuum; further crops could be obtained by repeating the above treatment to the filtered solution (concentration until formation of an oil followed by addition of methanol and stirring). The various crops of the yellow powder were mixtures, in variable proportions, as shown by i.r. spectroscopy, of complexes (1;  $\text{X} = \text{S}_2\text{PPh}_2$ ), (2), and (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ) which were separated by careful recrystallization from *thf*-diethyl ether-pentane, as follows.

The yellow solid was dissolved in a mixture of diethyl ether and *thf*, the solution was filtered, concentrated, and complex (2) precipitated as a crystalline yellow solid upon slow addition of pentane. The solid was filtered off, washed with pentane, and dried under vacuum (*ca.* 70 mg, *ca.* 32% yield). Big yellow crystals (one of which was used for the X-ray analysis) of complex (1;  $\text{X} = \text{S}_2\text{PPh}_2$ ) separated out of the filtered solution and were filtered off, washed with *thf*-pentane, and dried under vacuum (*ca.* 65 mg, *ca.* 27% yield). The filtered solution was concentrated under vacuum until a yellow powder was formed; the solution was filtered and, after addition of pentane, complex (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ) precipitated as a yellow crystalline solid. It was filtered off, washed with *thf*-pentane, and dried under vacuum (*ca.* 40 mg, *ca.* 17% yield).

The relative amounts of the products of these reactions are dependent on the experimental conditions and, *e.g.*, the yield of complex (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ) is considerably higher (see below) if the reaction is carried out under argon and using isocyanide in a 1:1 molar ratio, relative to the dinitrogen complex; however, a portion of unreacted  $\text{N}_2$  complex was recovered and complex (2) was also isolated, in a much lower yield, from the solution. A typical preparation was as follows.

Methyl isocyanide (0.0110  $\text{cm}^3$ , 0.234 mmol) was added to a *thf*-methanol (35:25) solution of the dinitrogen complex (0.202 g, 0.231 mmol) which was left stirring under argon for *ca.* 2 d. The solution was then concentrated under vacuum and methanol was added until yellow unreacted dinitrogen complex separated out. The solution was filtered and concentrated to an oil. Methanol was added and the system was stirred overnight until a yellow powder of complex (3;  $\text{X} = \text{S}_2\text{PPh}_2$ ) formed. This was filtered off, washed with cold methanol, and dried under

**Table 4.** Fractional atomic co-ordinates ( $\times 10^4$ ) with estimated standard deviations (e.s.d.s) in parentheses for *mer*-[Re(S<sub>2</sub>PPh<sub>2</sub>)(N<sub>2</sub>)(CNMe)(PMe<sub>2</sub>Ph)<sub>3</sub>]

Atom	x	y	z	Atom	x	y	z
Re	2 290.1(4)	482.6(2)	2 500.1(0)	C(15)	4 302(15)	956(10)	4 035(12)
S(1)	2 898(3)	-526(2)	3 398(2)	C(16)	4 587(11)	1 560(8)	2 533(16)
S(2)	5 448(4)	-492(3)	2 729(3)	C(17)	3 054(14)	2 131(8)	3 504(11)
P(1)	4 238(3)	-1 041(2)	3 108(3)	C(18)	3 055(17)	2 298(11)	4 359(13)
P(2)	3 544(3)	1 264(2)	3 170(3)	C(19)	2 553(17)	3 013(13)	4 558(15)
P(3)	988(3)	665(2)	3 579(3)	C(20)	2 246(17)	3 427(12)	4 019(14)
P(4)	1 166(3)	-285(2)	1 786(3)	C(21)	2 231(19)	3 323(14)	3 240(17)
N(1)	3 961(14)	279(8)	1 185(10)	C(22)	2 741(15)	2 631(11)	2 950(12)
N(2)	1 779(10)	1 280(7)	2 012(8)	C(23)	1 446(15)	737(10)	4 613(12)
N(3)	1 507(14)	1 751(10)	1 652(12)	C(24)	236(14)	1 484(10)	3 484(12)
C(1)	3 380(14)	311(9)	1 742(11)	C(25)	-11(12)	-7(8)	3 756(8)
C(2)	4 690(18)	105(12)	608(14)	C(26)	286(16)	-699(11)	3 998(13)
C(3)	4 598(11)	-1 518(8)	4 029(9)	C(27)	-479(18)	-1 235(11)	4 092(14)
C(4)	5 623(15)	-1 713(10)	4 149(12)	C(28)	-1 517(17)	-1 039(11)	4 033(13)
C(5)	5 909(17)	-2 088(11)	4 862(14)	C(29)	-1 868(17)	-393(10)	3 787(13)
C(6)	5 164(15)	-2 221(10)	5 379(11)	C(30)	-1 055(14)	135(9)	3 634(11)
C(7)	4 125(16)	-2 049(10)	5 288(12)	C(31)	1 640(21)	-428(12)	774(16)
C(8)	3 809(14)	-1 686(9)	4 576(11)	C(32)	1 016(17)	-1 209(11)	2 081(13)
C(9)	3 917(11)	-1 757(8)	2 418(11)	C(33)	-195(12)	15(8)	1 590(9)
C(10)	4 443(17)	-1 771(12)	1 699(14)	C(34)	-324(16)	642(10)	1 164(13)
C(11)	4 088(21)	-2 352(13)	1 186(14)	C(35)	-1 310(18)	897(11)	1 000(14)
C(12)	3 370(20)	-2 804(12)	1 362(15)	C(36)	-2 199(19)	525(12)	1 308(16)
C(13)	2 815(17)	-2 801(12)	2 115(14)	C(37)	-2 049(16)	-83(11)	1 669(13)
C(14)	3 166(13)	-2 250(8)	2 608(14)	C(38)	-1 037(15)	-372(9)	1 839(12)

vacuum. Further crops of this compound could be obtained from the mother-liquor through a similar treatment (concentration until oily, addition of methanol, and stirring for a prolonged time until formation of a yellow solid) (total amount *ca.* 0.11 g, *ca.* 35% yield). The final yellow crop which was obtained consisted mainly of complex (2) which was, however, isolated in low yield (*ca.* 15 mg, *ca.* 8% yield).

**Reactions of *mer*-[Re(S<sub>2</sub>CNEt<sub>2</sub>)(N<sub>2</sub>)L<sub>3</sub>] with CNMe.**—Methyl isocyanide (0.23 cm<sup>3</sup>, 4.89 mmol) was added to a thf solution (25 cm<sup>3</sup>) of the dinitrogen complex (0.470 g, 0.605 mmol) which was then left stirring under irradiation from two 100-W tungsten-filament bulbs for *ca.* 7 d. The solution was then concentrated and methanol was added until a small amount of a yellow solid was formed which was then filtered off. The filtered solution was concentrated again, methanol added, and the system cooled to *ca.* -20 °C to give a yellow oil of complex (3; X = S<sub>2</sub>CNEt<sub>2</sub>) from which the solution was decanted. Concentration of this solution and cooling to *ca.* -20 °C afforded an oily species; ether was then added and the solution was concentrated again and cooled to give a brown oil containing complex (5).

**Crystal Structure Determination.**—*Crystal data.* C<sub>38</sub>H<sub>46</sub>N<sub>3</sub>-P<sub>4</sub>ReS<sub>2</sub>, *M* = 919.0, orthorhombic, *a* = 12.780(5), *b* = 18.706(5), *c* = 17.014(5) Å, *U* = 4 067.4 Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.50 g cm<sup>-3</sup>, *F*(000) = 1 848, Mo-*K*<sub>α</sub> radiation, λ = 0.710 69 Å, μ = 34.4 cm<sup>-1</sup>, space group *Pna*2<sub>1</sub> from systematic absences of *0kl* for *k* + *l* odd and *h0l* for *h* odd and the successful refinement.

Data were measured on an Enraf-Nonius CAD4 diffractometer using a crystal of size *ca.* 0.70 × 0.50 × 0.35 mm sealed in a thin-walled glass capillary under argon. Since the crystal was large the Mo *X*-radiation was zirconium-filtered rather than monochromated. Preliminary cell dimensions were found using the SEARCH and INDEX routines of the CAD4 and final values were calculated from the setting angles for 25 reflections with θ *ca.* 15°. Intensities for *hkl* reflections with 2 < θ < 25° were measured by a θ-2θ scan with a scan width of Δθ = (0.8 +

0.35 tan θ)°. The scan rate for each reflection was determined by a rapid pre-scan at 10° min<sup>-1</sup> in θ at which point any reflection with *I* < σ(*I*) was coded as unobserved. The remaining reflections were rescanned at such a speed as to give a minimum value of σ(*I*)/*I* of 0.05 subject to a maximum scan time of 60 s. Two standard reflections monitored every hour showed no significant variation. Data were corrected for Lorentz polarization (Lp) effects and for absorption, and after averaging any equivalent reflections, 3 071 with |*F*<sup>2</sup>| > σ(*F*<sup>2</sup>) were used in the structure refinement. The values of σ(*F*<sup>2</sup>) were taken as [σ<sup>2</sup>(*I*) + (0.02/*I*)<sup>2</sup>]<sup>1/2</sup>/Lp.

The structure was solved by routine heavy-atom methods. Refinement was by full-matrix least squares with the Re, S, and P atoms anisotropic and other atoms isotropic. Refinement converged at *R* = 0.048, *R*' = 0.057, when the maximum shift/error was 0.03 and the weighting scheme was *w* = 1/σ<sup>2</sup>(*F*). A final difference map was everywhere featureless.

The structure solution and refinement was done on a PDP 11/34 computer using the Enraf-Nonius Structure Determination Package. Scattering factors for neutral atoms were taken from ref. 17. Final atom co-ordinates are listed in Table 4.

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