Tris(dimethylphenylphosphine)(dinitrogen)(dithiocarbamato)rhenium Complexes and their Reactions with Hydrogen Halides

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The complexes *mer*-$[Re(S_2CNR_2)(N_2)(PMe_2Ph)_3]$ (I; R = Me or Et) have been prepared from *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ and $Na[S_2CNR_2]$. With an excess of HX (X = Cl or Br) in tetrahydrofuran (thf) solution they give the dihydrido-complexes $[ReH_2(S_2CNR_2)X(PMe_2Ph)_3]X$, (II), which on treatment with NEt_3 give $[ReH(S_2CNR_2)X(PMe_2Ph)_3]$, (III). Complexes (III) give $[ReH(S_2CNR_2)_2(PMe_2Ph)_2]$, (IV), on reaction with $Na[S_2CNR_2]$. The spectroscopic properties of these complexes are described, particularly the ^1H n.m.r. spectra which are solvent dependent. The complexes *mer*-$[Re(L)(N_2)(PMe_2Ph)_3]$ (L = S_2COEt or S_2PPh_2) have also been prepared.

REACTIONS of dinitrogen complexes with halogen acids fall into three classes: (*a*) loss of dinitrogen with concomitant loss of dihydrogen or formation of a hydrido-complex;[1] (*b*) protonation of the metal atom with retention of dinitrogen;[1,2] and (*c*) protonation and reduction of a dinitrogen ligand.[2] Reactions of types (*a*) and (*b*) have been observed for dinitrogen complexes of rhenium which contain tertiary phosphine ligands.[3] In view of the variation of basic strength of dinitrogen co-ordinated to rhenium when the co-ligands are varied,[4] and the oft-repeated conjecture that dinitrogen is protonated and reduced on molybdenum in nitrogenase in a sulphur-ligand environment, we have prepared a number of dinitrogen complexes of rhenium which contain ligating sulphur. We hoped thereby to induce protonation of the dinitrogen [reaction type (*c*) above] through the expected greater electron-donor power of the dialkyldithiocarbamate anion which approaches the zwitterion canonical form $R_2\overset{+}{N}{=}CS_2^{2-}$ in complex compounds.[5] The dithiocarbamate complexes which we obtained were of the type $[Re(S_2CNR_2)(N_2)(PMe_2Ph)_3]$. They were much more reactive towards hydrogen halides than were the parent complexes *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ but underwent reaction (*a*) to give a new series of hydrido-complexes of rhenium which we describe below.

RESULTS AND DISCUSSION

Dinitrogen Complexes.—The complexes *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ or *mer*-$[ReCl(N_2)(py)(PMe_2Ph)_3]$ (py =

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[1] J. Chatt and R. L. Richards in 'The Chemistry and Biochemistry of Nitrogen Fixation,' ed. J. R. Postgate, Plenum Press, London, 1971, p. 57.

[2] J. Chatt, G. A. Heath, and R. L. Richards, *J.C.S. Chem. Comm.*, 1972, 1010.

[3] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J.C.S. Dalton*, 1973, 612.

[4] J. Chatt, R. H. Crabtree, E. A. Jeffrey, and R. L. Richards, *J.C.S. Dalton*, 1973, 1167 and refs. therein.

[5] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kem.*, 1956, **B29**, 75.

TABLE 1

Dinitrogen and hydrido-complexes

Complex	Appearance	Yield/%	Analyses [a]/%			$\bar{\nu}(N_2)$ [b]/cm^{-1}	$\bar{\nu}$(ReH) [b]/cm^{-1}	$\nu(S_2CNR_2)$ [b]/cm^{-1}	Λ [c]/S cm^2 mol^{-1}	M [d]
			C	H	N					
mer-[Re(S_2CNMe_2)(N_2)(PMe_2Ph)$_3$]	Red prisms	80	43·2 (43·3)	5·3 (5·2)	5·4 (5·6)	1 945s		1 495		
mer-[Re(S_2CNEt_2)(N_2)(PMe_2Ph)$_3$]	Red prisms	80	45·0 (44·8)	5·8 (5·6)	5·3 (5·4)	1 945s		1 493		
mer-[Re(S_2COEt)(N_2)(PMe_2Ph)$_3$]	Red prisms	5	43·0 (42·4)	5·0 (5·1)	3·6 (3·7)	1 964s				
mer-[Re(S_2PPh_2)(N_2)(PMe_2Ph)$_3$]	Yellow prisms	10	49·3 (49·4)	4·9 (4·9)	3·2 (3·2)	1 940s				
[ReCl(H)$_2$(S_2CNMe_2)(PMe_2Ph)$_3$]Cl	Light yellow prisms	80	40·9 (40·9)	5·2 (5·2)	2·0 (1·9) [e]		2 080vw	1 512	110	
[ReBr(H)$_2$(S_2CNMe_2)(PMe_2Ph)$_3$]Br	Yellow solid	80	36·0 (36·8)	4·5 (4·6)	1·4 (1·6)		2 075vw	1 498		
[ReCl(H)$_2$(S_2CNEt_2)(PMe_2Ph)$_3$]Cl	Yellow solid	75	42·6 (42·4)	5·8 (5·5)	1·7 (1·7) [f]		2 060vw	1 511	116	
[ReBr(H)$_2$(S_2CNEt_2)(PMe_2Ph)$_3$]Br	Yellow prisms	70	36·4 (36·2)	5·0 (4·9)	1·5 (1·5)		2 060vw	1 504		
[ReCl(H)$_2$(S_2CNMe_2)(PMe_2Ph)$_3$][PF_6]	Yellow solid	65			3·5 (3·4) [g]					
[ReCl(H)$_2$(S_2CNEt_2)(PMe_2Ph)$_3$][PF_6]	Yellow solid	70			3·5 (3·4) [g]					
[ReCl(H)(S_2CNMe_2)(PMe_2Ph)$_3$]	Yellow crystals	60	45·1 (45·0)	5·9 (5·5)	1·9 (1·9)		2 067w	1 510	5·3	
[ReBr(H)(S_2CNMe_2)(PMe_2Ph)$_3$]	Yellow crystals	65	41·0 (40·9)	4·8 (5·0)	1·6 (1·7)		2 065w	1 499		
[ReCl(H)(S_2CNEt_2)(PMe_2Ph)$_3$]	Yellow crystals	55	46·4 (46·5)	5·8 (5·8)	1·8 (1·9)		2 048w	1 504		720 (744) [a]
[ReBr(H)(S_2CNEt_2)(PMe_2Ph)$_3$]	Yellow crystals	60	42·2 (42·3)	5·0 (5·3)	1·7 (1·7)		2 050w	1 498		
[ReH(S_2CNMe_2)$_2$(PMe_2Ph)$_2$]	Dark red prisms	60	38·0 (37·6)	4·9 (5·0)	4·2 (4·0)		n.o.			
[ReH(S_2CNEt_2)$_2$(PMe_2Ph)$_2$]	Dark red prisms	70	41·1 (41·1)	5·3 (5·5)	3·6 (3·7)		n.o.			650 (690) [a]

[a] Calculated values are given in parentheses. [b] Nujol mull; s = strong, w = weak, v = very, n.o. = not observed. [c] In *ca.* 10^{-3}M-nitromethane solution for cationic complexes. [d] In *ca.* 10^{-3}M-$C_2H_4Cl_2$ solution. [e] Cl, 8·4 (8·9)%. [f] Cl, 8·9 (9·6)%. [g] Cl Analyses.

pyridine) react with Na[S_2CNR_2] (R = Me or Et) when heated under reflux in acetone to give the orange dithiocarbamato-complexes (I) [equation (1)] (the methyl analogue has already been described [4]). These dinitrogen

$$\textit{trans}\text{-}[\mathrm{ReCl(N_2)(PMe_2Ph)_4}] + \mathrm{Na[S_2CNR_2]} \longrightarrow \textit{mer}\text{-}[\mathrm{Re(S_2CNR_2)(N_2)(PMe_2Ph)_3}]\ \mathrm{(I)} + \mathrm{NaCl} + \mathrm{PMe_2Ph} \quad (1)$$

complexes are very soluble in organic solvents and crystallise as red prisms from light petroleum. The dithio-salts Na[S_2PPh_2] and K[S_2COEt] readily gave the complexes *mer*-[Re(L)(N_2)(PMe_2Ph)$_3$] (L = S_2PPh_2 or S_2COEt) from *mer*-[Re(L)(N_2)(py)(PMe_2Ph)$_3$]. Unlike their dithiocarbamato-analogues, these dinitrogen complexes decompose in chloroform solution even under an atmosphere of dinitrogen. There is no correlation between $\nu(N_2)$ and the stability of these dinitrogen complexes (see Table 1), in accord with similar observations on other series.[1]

The reaction of excess of hydrogen halide HX (X = Cl or Br) with complexes (I) in tetrahydrofuran (thf) solution at 20 °C gave the salts (II), with quantitative evolution of dinitrogen [equation (2)]. The yellow eight-

$$\textit{mer}\text{-}[\mathrm{Re(S_2CNR_2)(N_2)(PMe_2Ph)_3}] + 2\mathrm{HX} \longrightarrow [\mathrm{ReH_2(S_2CNR_2)X(PMe_2Ph)_3}]\mathrm{X}\ \mathrm{(II)} + \mathrm{N_2} \quad (2)$$

co-ordinate salts (II), crystallised from the reaction mixture, are sparingly soluble in water but are soluble in common organic solvents. They are 1 : 1 electrolytes in nitromethane solution and the halide anion may be replaced by PF_6^- [equation (3)]. The Re–H absorption in

$$[\mathrm{ReH_2(S_2CNR_2)X(PMe_2Ph)_3}]\mathrm{X} + \mathrm{Na[PF_6]} \xrightarrow{\mathrm{H_2O}} [\mathrm{ReH_2(S_2CNR_2)X(PMe_2Ph)_3}][\mathrm{PF_6}] + \mathrm{NaX} \quad (3)$$

the i.r. spectra of the complexes (Table 1) was very weak, as is often found for cationic hydrido-salts.[6] With HCl, the *O*-ethyl dithiocarbonato- and diphenyldithiophosphato-complexes also lost dinitrogen at 20 °C but the only isolated complex was, in each case, *mer*-[$ReCl_3$(PMe_2Ph)$_3$]. Presumably these two dithio-ligands are not sufficiently strongly electron donating to stabilise the hydrido-complex. Unlike dithiocarbamate the dithiocarbonate anion tends to the canonical form $ROCS_2^-$ in its complex compounds.[5] The complex *trans*-[ReCl(N_2)(py)(PMe_2Ph)$_3$] also gave *mer*-[$ReCl_3$(PMe_2Ph)$_3$] on treatment with HCl but only when heated under reflux in thf.[7]

Dehydrohalogenation of the Cationic Hydrido-complexes.—This occurs when (II) were treated with triethylamine or pyridine in benzene solution [equation (4)] to give the uncharged mono-hydrido-complexes (III) in high yield.

$$\mathrm{(II)} + \mathrm{NEt_3} \longrightarrow [\mathrm{ReH(S_2CNR_2)X(PMe_2Ph)_3}]\ \mathrm{(III)} + [\mathrm{Et_3HN}]\mathrm{X} \quad (4)$$

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[6] R. H. Crabtree, A. R. Dias, M. L. H. Green, and P. J. Knowles, *J. Chem. Soc.* (*A*), 1971, 1350.

[7] N. E. Hooper, D. Phil. Thesis, Sussex, 1973.

On treatment with an excess of HX in thf solution, complexes (III) reverted to the parents (II). Complexes (III) are soluble in common organic solvents but not in water and they are non-conducting in nitromethane solution. A weak band in their i.r. spectra at 2 050—2 020 cm^{-1} is assigned to ν(Re–H) (Table 1). With Na[S_2CNR_2] in acetone solution the chloro-analogues reacted smoothly at 20 °C to give the bis(dithiocarbamato) complexes (IV) [equation (5)]. Analytical data,

$$[ReCl(H)(S_2CNR_2)(PMe_2Ph)_3] + Na[S_2CNR_2] \longrightarrow [ReH(S_2CNR_2)_2(PMe_2Ph)_2]\ (IV) + PMe_2Ph + NaCl \quad (5)$$

etc., for these dinitrogen and hydrido-complexes are given in Table 1.

^{1}H *N.m.r. Spectra* (*Table* 2).—(i) Complexes (II) had spectra which were solvent independent. The P*Me*$_2$Ph resonance pattern indicated that two of these ligands are equivalent but their methyl groups are magnetically inequivalent. The unique phosphorus ligand has equivalent methyl groups and therefore apparently lies in a symmetry plane. When CD_2Cl_2 solutions of (II) were cooled to −100 °C, the P*Me*$_2$Ph signals broadened considerably, suggesting that these molecules are fluxional in solution at higher temperatures.

TABLE 2

^{1}H N.m.r. spectra of the dithiocarbamato-complexes [a]

Complex	Solvent	τ(CH_2N) or τ(CH_3N)	τ(P–CH_3)	τ(CH_3CH_2N)	τ(ReH)
[$Re(S_2CNMe_2)(N_2)(PMe_2Ph)_3$]	*b*	6·60 (s)	8·04 (t), 8·16 (t), 8·50 (d)		
	c	6·62 (s)	7·95 (s), 8·05 (s), 8·40 (d)		
[$Re(S_2CNEt_2)(N_2)(PMe_2Ph)_3$]	*b*	6·38 (p) ^{d}	8·35 (t), 8·38 (t), 8·72 (d)	8·90 (t) ^{e}	
	f	6·70 (q) ^{d}	8·12 (t), 8·20 (t), 8·56 (d)	8·98 (t) ^{e}	
	c	6·41 (q) ^{d}	8·25 (s), 8·29 (s), 8·69 (d)	8·78 (t) ^{e}	
[$ReCl(H)_2(S_2CNMe_2)(PMe_2Ph)_3$]Cl	*c*	7·10 (s)	7·90 (d), 7·93 (d), 8·30 (d)		14·20 (dt) ^{g}
[$ReCl(H)_2(S_2CNEt_2)(PMe_2Ph)_3$]Cl	*c*	6·56 (r) ^{d}	7·96 (d), 80·2 (d), 8·23 (d)	8·90 (t) ^{h}	14·20 (dt*t* ^{g}
[$ReBr(H)_2(S_2CNMe_2)(PMe_2Ph)_3$]Br	*c*	7·02 (s)	8·04 (d), 8·10 (d), 8·30 (d)		14·18 (dt) ^{g}
[$ReBr(H)_2(S_2CNEt_2)(PMe_2Ph)_3$]Br	*c*	6·68 (dq) ^{d,i}	8·16 (d), 8·24 (d), 8·38 (d)	8·81 (t) ^{h}	14·15 (dt) ^{g}
[$ReCl(H)(S_2CNMe_2)(PMe_2Ph)_3$]	*b*	7·02 (s)	8·24 (d), 8·29 (d), 8·75 (d)		19·93 (dt) ^{j}
	f	7·42 (s)	8·18 (d), 8·54 (d)		19·97 (dt) ^{j}
	c	7·02 (s)	8·22 (s), 8·76 (s)		*ca.* 20 (w)
	k				19·71 (dt) 19·70 (dt) ^{j,l}
[$ReBr(H)(S_2CNMe_2)(PMe_2Ph)_3$]	*b*	7·00 (s)	8·28 (d), 8·33 (d), 8·77 (d)		20·00 (dt) ^{j}
	f	7·36 (s)	8·12 (d), 8·50 (d)		20·02 (dt) ^{j}
	c	7·00 (s)	8·22 (s), 8·77 (s)		*ca.* 20 (w)
[$ReCl(H)(S_2CNEt_2)(PMe_2Ph)_3$]	*b*	6·44 (dq) ^{d,i}	8·26 (d), 8·32 (d), 8·73 (d)	8·84 (t) ^{h}	19·45 (t) ^{j}
	f	6·61 (dq) ^{d,i}	8·02 (d), 8·40 (d)	8·91 (t) ^{h}	19·81 (dt) ^{j}
	c	6·44 (dq) ^{d,i}	8·22 (s), 8·77 (s)	8·83 (t) ^{h}	*ca.* 20
	k				19·74 19·56 (dt) ^{j,m}
[$ReBr(H)(S_2CNEt_2)(PMe_2Ph)_3$]	*b*	6·42 (dp) ^{d,i}	8·38 (d), 8·45 (d), 8·77 (d)	8·86 (t) ^{h}	20·15 (dt)
	f	6·82 (dp) ^{d,i}	7·99 (d), 8·62 (d)	9·01 (t) ^{h}	20·20 (dt)
	c	6·46 (q) ^{d}	8·36 (s),^{l} 8·82 (s) ^{l}	8·82 (t) ^{h}	*ca.* 20 (w)
[$ReH(S_2CNMe_2)_2(PMe_2Ph)_2$]	*b*		insufficiently soluble		
	f	7·31 (s)	8·08 (d)		18·88 (t) ^{n}
	c	6·89 (s)	8·22 (d)		19·55 (t) ^{n}
[$ReH(S_2CNEt_2)_2(PMe_2Ph)_2$]	*b*	6·34 (q) ^{d}	8·27 (d)	8·81 (t) ^{h}	19·09 (t) ^{n}
	f	6·58 (q) ^{d}	8·00 (d)	8·98 (t) ^{h}	18·72 (t) ^{n}
	c	6·40 ^{d}	8·24 (s)	8·80 (t) ^{h}	*ca.* 19 (w)

[a] Satisfactory integrals were obtained in all cases. Chemical shifts were measured, from centres of multiplets where they occurred, relative to tetramethylsilane as internal standard. Phenyl multiplets at τ 2—3 were omitted. τ Values are ±0·1; s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, r = septet, w = very broad resonance. Typical ranges of coupling constants for the phosphine ligands are: (PCH_3) d, |^2J(PCH)| 8·3—9·6; t, |^2J(PCH) + ^4J(P′RePCH)| 6·0—7·6 Hz. The *O*-ethyl dithiocarbonato- and dithiophosphato-complexes decomposed during attempts to record their spectra. [b] $(D_3C)_2CO$. [c] $CDCl_3$. [d] ABX_3-Type system. [e] |^3J(HCCH)| 7·7 ± 0·1 Hz. [f] C_6D_6. [g] |^2J(PReH)| 53 ± 2, |^2J(P′ReH) 42 ± 2 Hz. [h] |^3J(HCCH) 7 ± 2 Hz. [i] Multiplet separation = 33 ± 3 Hz. [j] |^2J(PReH)| 63 ± 3, |^2J(P′ReH)| 55 ± 3 Hz. [k] CD_2Cl_2. [l] 1 : 0·6 Relative integration. [m] 1 : 0·4 Relative integration. [n] |^2J(PReH)| 66 Hz.

The hydride resonances of these cationic complexes at τ *ca.* 14·1 occurred at the lower end of the region where hydridorhenium complexes absorb {*cf.* [$ReH_5(py)(PPh_3)_2$] (τ 14·56 in thf) and [$ReH_7(PEt_2Ph)_2$] (τ 15·82—16·33 in thf) [8]}, possibly a consequence of their charge. The hydrido-ligands are equivalent, as is commonly found in polyhydrido-complexes [8] and the resonance was a doublet of triplets due to splitting by two equivalent and one unique phosphorus atoms (Table 2).

(ii) The four monohydrido-complexes (III) exhibited hydride resonances at higher field (τ *ca.* 20) than (II). Two isomers are present in CD_2Cl_2 solution since the hydride resonances consisted of two overlapping doublets of triplets. The isomer ratio depended on R (Table 2). In perdeuterioacetone and CD_2Cl_2 solutions, complexes (III) had spectra (PMe region) which resembled those of (II), but in C_6D_6 or $C_6D_5CD_3$ solution no inequivalence of P-*Me* groups was seen. This effect may be due to rapid exchange of these ligands since broadening of the simple doublet signal occurred at −80 °C ($C_6D_5CD_3$ solution).

The N*Me* resonance shifted in benzene solution relative to its constant position in the other solvents used. A similar effect was previously observed and ascribed to the

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[8] J. Chatt and R. S. Coffey, *J. Chem. Soc.* (*A*), 1969, 1963 and refs. therein.

specific interaction of the NCS_2 group with the aromatic ring, leading to additional shielding of the N-*Me* protons.[9] When $CDCl_3$ was used as solvent for complexes (III) these was a loss of fine structure throughout their spectra, probably due to an interaction with the $CDCl_3$, perhaps a hydrogen(deuterium)-bonding effect since the complexes can be recovered unchanged.

The proton-decoupled ^{31}P spectra of these complexes (R = Me or Et) showed, in CD_2Cl_2 solution, the doublet (intensity 2) and triplet (intensity 1) pattern expected for two equivalent and one unique phosphine ligands. [The values were (upfield from trimethyl phosphite, relative integrations in parentheses): (R = Me) $\delta = 173{\cdot}30(2)$, doublet, $|^2J(\mathrm{PReP'})|$ 24·1, $\delta = 178{\cdot}60(1)$, triplet, $|^2J(\mathrm{P'ReP})|$ 24·1; (R = Et) $\delta = 173{\cdot}30(2)$, doublet, $|^2J(\mathrm{PReP'})|$ 24·1, $\delta = 177{\cdot}60(1)$ p.p.m., triplet, $|^2J(\mathrm{P'ReP})|$ 24·1 Hz.]

Since there is a large number of possible isomers for this system, all having little energy difference, speculation on the actual structures in solution is inappropriate at this stage.

(iii) In the ^1H n.m.r. spectra of complex (IV; R = Et) (benzene or CD_2Cl_2 solutions) the equivalent tertiary phosphine ligands gave rise to a doublet at τ *ca.* 2 and the Re*H* resonance at τ *ca.* 20 was a triplet due to coupling with the phosphorus nuclei. Again fine structure was lost in $CDCl_3$, probably due to interaction with the solvent.

(iv) The dinitrogen complexes (I) had, in perdeuterioacetone or benzene solutions, a P*Me*$_2$Ph pattern (Table 2) characteristic of a *mer*-arrangement of these ligands as is found, for example, in *mer*-$[OsCl_2(N_2)(PMe_2Ph)_3]$.[10] As was observed for the hydrido-complexes, this pattern became broader and less distinct in deuteriochloroform solution, again possibly due to a hydrogen(deuterium)-bonding interaction with the solvent.

(v) *The* N-R$_2$ *resonances.* All the complexes where R = Me showed a sharp singlet for the N*Me*$_2$ group whose position is solvent dependent (see above). The N-*CH*$_2$ resonance pattern was more complicated. Complex (I; R = Et) showed an N-*CH*$_2$ quartet in C_6D_6 or $CDCl_3$ solutions but an ABX_3-type pattern in $(D_3C)_2CO$ (Table 2). Complex (IV; R = Et) exhibited a simple N-*CH*$_2$ quartet in C_6D_6 or $CDCl_3$ solutions, but an ABX_3 pattern was seen for the N-*CH*$_2$ resonance of (III; R = Et, X = Cl or Br) whether the solvent was C_6D_6, CD_2Cl_2, or $(D_3C)_2CO$.

An ABX_3 pattern is readily explained in terms of restricted rotation about the $N{=}CS_2$ bond of these chelated ligands, the asymmetric nature of the site to which they are attached, and, probably most important, methyl–methyl interactions of the NEt groups which force the N-CH_2 protons to adopt inequivalent environments. Golding discussed the above effects in detail with reference to $[Co(S_2CNEt_2)_3]$ [11] and observed the collapse of an ABX_3 pattern to a simple quartet on passing from $CDCl_3$ to C_6D_6 solution. He suggested a specific effect of $CDCl_3$ in explanation. Certainly in our spectra fine structure is lost most often in $CDCl_3$ solution, but in view of the variety of effects observed for the various solvents clearly more work on these systems, particularly temperature-variation studies for a range of solvents, is necessary to clarify their behaviour.

(vi) The binding of the dithiocarbamato-ligands appears to be bidentate in all of the complexes studied, since the positions of the N-Me (R = Me) and N-CH_2 (R = Et) resonances (Table 2) were in the region observed for bidentate dithiocarbamato-groups [(δ(Me) *ca.* 2·8, $\delta(CH_2)$ *ca.* 3·6 p.p.m.],[11,12] and secondly the position of the band due to the NCS_2 group vibration in the i.r. spectra (solid state and solution) fell in the range 1 493—1 518 cm^{-1} (Table 1), again in the range found for known bidentate groups.[13]

Conclusion.—Although the introduction of sulphur ligands into rhenium dinitrogen complexes renders them more reactive to hydrogen halides than the parent *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ complex, there is no evidence that the dinitrogen is protonated, but rather that the metal is rendered more susceptible to protonation. The dithiocarbamato-ligands stabilise a new series of hydrido-complexes, but analogous hydrido-complexes are not formed by the *O*-ethyl dithiocarbonato- or diphenyldithiophosphato-ligands.

The dithiocarbamatohydrido-complexes have ^1H n.m.r. spectra which are strongly dependent on solvent. This dependency is probably caused by the fluxionality of these ligands and the large number of possible isomeric structures of similar energies for their complexes. That similar behaviour has been observed in apparently simpler systems [11] indicates that other effects play a part, however, and more detailed studies are necessary to evaluate them.

EXPERIMENTAL

The salts $Na[S_2CNMe_2],3H_2O$, $Na[S_2CNEt_2],3H_2O$, and $K[S_2PPh_2]$ and the complexes *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ and *mer*-$[ReCl(N_2)(py)(PMe_2Ph)_3]$ (py = pyridine) were prepared by established methods; [4] $K[S_2COEt]$ was used as commercially supplied (B.D.H.). ^1H N.m.r. spectra were recorded using Varian T-60, HA 100, of Jeol PS-100 instruments and ^{31}P spectra were measured in the Fourier-transform mode with proton decoupling using the Jeol PS-100 instrument. I.r. spectra were measured with a Unicam SP 1200 instrument. Conductivities were measured with a Portland Electronics conductivity bridge and analyses were by Mr. A. G. Olney of these laboratories. Analytical data, *etc.*, for all new complexes prepared are in Table 1 and examples of each method of preparation are given below.

mer-$[Re(S_2CNR_2)(N_2)(PMe_2Ph)_3]$, (I; R = Me *or* Et).—The complex *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$ (0·8 g) heated under reflux in acetone (20 cm^3) was treated with $Na[S_2CNR_2],3H_2O$

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[10] J. Chatt, G. J. Leigh, and R. L. Richards, *J. Chem. Soc.* (*A*), 1970, 2243.

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(0·8 g) to give, after 45 min, a red solution from which the solvent was removed. The resulting solid was extracted twice with diethyl ether (2 × 25 cm^3), to the combined extracts was added light petroleum (b.p. 100—120 °C, 5 cm^3), and the solution was concentrated to 5 cm^3 *in vacuo* at 60 °C. On cooling the solution to 20 °C *prisms* of the complexes (0·6 g) separated over 24 h.

mer-*Tris(dimethylphenylphosphine)(dinitrogen)(*O-*ethyl dithiocarbonato)rhenium*(I).—The complex *mer*-[ReCl(N$_2$)(py)(PMe$_2$Ph)$_3$] (1 g) was treated with K[S$_2$COEt] (1 g) heated under reflux in acetone (20 cm^3) for 2 h. Removal of the solvent and work-up as above gave only a small quantity of red *prisms* (0·05 g, 5%) after 1 month, since the complex is very soluble.

mer-*Tris(dimethylphenylphosphine)(dinitrogen)(diphenyldithiophosphato*-SS'*)rhenium*(I).—The complex *mer*-[ReCl(N$_2$)(py)(PMe$_2$Ph)$_3$] (0·8 g) heated under reflux in acetone (20 cm^3) was treated with K[S$_2$PPh$_2$] (0·5 g). After 20 min the reaction mixture was cooled to 20 °C and the resulting yellow precipitate filtered off. The solid was washed twice with water (2 × 5 cm^3) and once with ethanol (0·5 cm^3) and then dried.

[ReH$_2$(S$_2$CNR$_2$)X(PMe$_2$Ph)$_3$]X, (II; R = Me *or* Et, X = Cl *or* Br).—Into solutions of the complexes (I) in tetrahydrofuran (thf) (10 cm^3) was passed an excess of the gaseous hydrogen halides HX (0·3 g) in a stream of dry dinitrogen. After 10 min, light petroleum (b.p. 100—120 °C, 3 cm^3) was added and the solvent was gently removed under reduced pressure. The complex salts (II) crystallised from the solution. The products were washed with light petroleum (b.p. 30—40 °C, 3 cm^3) and dried *in vacuo*. In a further experiment, HCl (10 mol) and thf (15 cm^3) were condensed onto (I; R = Me) (0·25 g) at −196 °C *in vacuo*. The vessel was sealed and allowed to warm to 25 °C after which a yellow solution resulted. The vessel was then cooled to −196 °C and dinitrogen (0·95 mol) was recovered using a Töpler pump and identified with an M.S.10 mass spectrometer. Work-up in the usual way gave (II; R = Me) in 80% yield.

[ReCl(H)$_2$(S$_2$CNR$_2$)(PMe$_2$Ph)$_3$][PF$_6$], (II; R = Me or Et).—A saturated aqueous solution of the chloride salts (II; R = Me or Et) was treated with a few drops of saturated aqueous K[PF$_6$]. A yellow precipitate formed at once, and was filtered off, washed with diethyl ether (5 cm^3), and dried *in vacuo*.

[ReH(S$_2$CNR$_2$)X(PMe$_2$Ph)$_3$], (III; R = Me *or* Et, X = Cl *or* Br).—The complex salts (II) (1 g) were suspended in benzene (30 cm^3) and treated with NEt$_3$ (2·5 cm^3). The yellow colour of the solutions deepened and a colourless precipitate of [Et$_3$HN]X was filtered off and identified by its i.r. spectrum. Light petroleum (b.p. 100—120 °C, 10 cm^3) was added to the filtrate. The solution was reduced to half volume under reduced pressure at 60 °C and deep yellow crystals of the complexes separated on cooling. These were filtered off, washed with light petroleum (b.p. 30—40 °C, 2 cm^3), and dried *in vacuo*. When the appropriate hydrogen halide was passed into a benzene solution of these complexes, the salts (II) were regenerated, isolated as above, and identified by their i.r. spectra.

[ReH(S$_2$CNR$_2$)$_2$(PMe$_2$Ph)$_2$] (IV; R = Me *or* Et).—Complexes (III; X = Cl or Br) (0·3 g) in acetone (20 cm^3) at 20 °C reacted with Na[S$_2$CNR$_2$] (0·3 g). (Reaction times: R = Me, X = Cl, 60; R = Me, X = Br, 30; and R = Et, X = Br, 10 s.) Where R = Me and X = Cl the reaction mixture was heated to 40 °C for 1 min. The solvent was removed *in vacuo* at 40 °C, and the residue was washed with water (3 × 5 cm^3) and methanol (1 cm^3) and recrystallised from benzene–methanol as red *prisms*. Where R = Et and X = Cl the oily residue was extracted with methanol (5 cm^3, 40 °C) and the complex allowed to crystallise as red *prisms*.

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