Preparation and Properties of *mer*-[ReCl(N_2)(CNR){P(OMe)$_3$}$_3$] (R = Me, Et, Bu^t, C_6H_4Me-4, or C_6H_4Cl-4) and [ReCl(N_2)(CNMe)(PPh$_3$){P(OEt)$_3$}$_2$]. *X*-Ray Crystal Structure of *mer*-[ReCl(N_2)(CNMe){P(OMe)$_3$}$_3$]† and Reductive Cleavage of the Isocyanide Ligands to Primary Amines upon Protonation

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The complexes [ReCl(N_2)(CNR){P(OMe)$_3$}$_3$] (R = Me, Et, Bu^t, C_6H_4Me-4, or C_6H_4Cl-4) and [ReCl(N_2)(CNMe)(PPh$_3$){P(OEt)$_3$}$_2$] have been prepared by reaction of the corresponding diazenido-species [ReCl$_2$(NNCOPh)(PPh$_3$)$_x${P(OR′)$_3$}$_{3-x}$] (x = 0 or 1; R′ = Me or Et) with the appropriate isocyanide in refluxing methanol, and the *X*-ray crystal structure of *mer*-[ReCl(N_2)(CNMe){P(OMe)$_3$}$_3$] is reported. In these complexes the isocyanide ligand undergoes protic attack with cleavage of the unsaturated NC bond to afford the corresponding primary ammonium salt.

During our studies of the co-ordination and activation of isocyanides by electron-rich dinitrogen-binding transition metal centres, we have prepared several series of isocyanide complexes by replacement of dinitrogen by isocyanide in the parent d^6-metal species *trans*-[M(N_2)$_2$(dppe)$_2$],[1] [M(N_2)$_2$L$_4$] (M = Mo or W; L = PMe$_2$Ph or PMePh$_2$; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$),[2] and *trans*-[ReCl(N_2)(dppe)$_2$].[3] However, we have sought a more convenient general synthetic route for such isocyanide compounds which avoids prior synthesis of the parent dinitrogen complexes. In pursuit of this objective, we have developed a new preparative pathway for isocyanide complexes which also carry dinitrogen as a co-ligand. A preliminary account of this route has appeared[4] and here we describe it in detail.

The compounds [ReCl$_2$(NNCOPh)(PPh$_3$)$_2$] and [ReCl$_2$(NNCOPh)(PPh$_3$)$_x${P(OR′)$_3$}$_{3-x}$] (x = 0 or 1; R′ = Me or Et) are convenient precursors for such a type of mixed dinitrogen–isocyanide complex and the variety of Re^I metal sites thus obtained allows study of the influence of the composition and the structure of the binding centre on the co-ordination and reactivity of the isocyanide and/or the dinitrogen co-ligand.

In our previous studies we have shown that when the isocyanide ligates an octahedral, d^6, N_2-binding centre with chelating diphosphine co-ligands, of the types M(dppe)$_2$ (M = Mo or W)[5] or MCl(dppe)$_2$ (M = Re),[6] it is activated towards electrophilic attack by protic acid to give carbyne-type complexes, *i.e.* the [M≡C–NHR]$^+$ moiety. However, when the Group 6 metal centre carries labile phosphines as co-ligands, *e.g.* in [Mo(CNMe)$_2$(PMe$_2$Ph)$_4$], the protonation of the isocyanide (CNMe) proceeds further to afford primary amine (NH$_2$Me) as the main organic product.[7] In the present work we have extended the scope of this reaction to include alkyl and aryl isocyanides ligating the above rhenium centres.

We should point out that the metalloenzyme nitrogenase causes reduction cleavage of CNMe to give NH$_2$Me,[7] and our work is designed to throw light upon the likely mechanism of this reaction.

Results and Discussion

Preparation and Spectroscopic Properties of the Title Dinitrogen and Isocyanide Complexes.—Treatment of the complex [ReCl$_2$(NNCOPh)(PPh$_3$)$_2$] (1) with an organophosphite P(OR′)$_3$ in refluxing benzene gives the benzoyldiazenido-complexes [ReCl$_2$(NNCOPh)(PPh$_3$)$_x${P(OR′)$_3$}$_{3-x}$] (2, x = 0, R′ = Me;[8] 3, x = 1, R′ = Et), equation (1). Although in these reactions complete displacement of PPh$_3$ in (1) by trimethyl phosphite occurs to form the tris(phosphite) complex (2),[8] only one PPh$_3$ ligand in (1) is replaced by the bulkier triethyl phosphite to give the bis(phosphite) complex (3). Compound (3) exhibits, in the i.r. spectrum (KBr), strong bands at 1 650 and 1 505 cm^{-1} (Table 1) which we assign to ν(CO) and ν(NN) of the benzoyldiazenido-ligand [similar values at 1 653 and 1 507 cm^{-1}, respectively, are observed[8] in Nujol for complex (2)].

$$[\mathrm{ReCl_2(NNCOPh)(PPh_3)_2}] + (3-x)\mathrm{P(OR')_3} \xrightarrow[\mathrm{C_6H_6}]{\text{heat}} [\mathrm{ReCl_2(NNCOPh)(PPh_3)_x\{P(OR')_3\}_{3-x}}] + (2-x)\mathrm{PPh_3} \quad (1)$$

In complex (3) the two triethyl phosphite ligands appear to be non-equivalent in the ^{1}H n.m.r. spectrum which exhibits two triplets for the methyl proton resonances (Table 2).

The benzoyldiazenido-complexes, (2) and (3), undergo NN–C bond cleavage in refluxing methanol to afford, in the presence of isocyanide, the mixed dinitrogen–isocyanide complexes [ReCl(N_2)(CNR)(PPh$_3$)$_x${P(OR′)$_3$}$_{3-x}$] (4, x = 0; R′ = Me; R = Me, Et, Bu^t, C_6H_4Me-4, or C_6H_4Cl-4; 5, x = 1, R′ =

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† *mer*-Chloro(dinitrogen)(methyl isocyanide)tris(trimethyl phosphite)rhenium(I).

Supplementary data available (No. SUP 56272, 2 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Physical data for complexes *mer*-$[ReCl(N_2)(CNR)\{P(OMe)_3\}_3]$ (**4**), *cis*-$[ReCl(N_2)(CNMe)(PPh_3)\{P(OEt)_3\}_2]$ (**5**), $[ReCl_2(NNCOPh)(PPh_3)\{P(OEt)_3\}_2]$ (**3**), and ammonium salts derived from (**4**)

			I. r. data[a]		Found (calc.) (%)		
Compound	Colour	Yield (%)	$\nu(N{\equiv}N)$	$\nu(C{\equiv}N)$	C	H	N
(**4**, R = Me)	White	60	2 020s	2 120s	19.8 (19.9)	4.7 (4.5)	6.5 (6.4)
(**4**, R = Et)	White	30	2 030s	2 120s	24.9 (25.2)	4.9 (4.9)	6.4 (5.9)
(**4**, R = Bu^t)	Pale yellow	20	2 010s	2 097s	24.9 (25.1)	5.1 (5.2)	5.8 (5.9)
(**4**, R = C_6H_4Me-4)[b]	Brown	—	2 027s	2 053s			
(**5**)[c]	Pale yellow	30	2 010s	2 074s	44.7 (44.6)	4.5 (5.4)	4.6 (4.4)
			$\nu(N{=}N)$	$\nu(C{=}O)$			
(**3**)	Orange	70	1 505s	1 650s	46.7 (46.9)	5.2 (5.2)	3.1 (2.8)
			$\nu(NH)$ or $\nu(CH)$	$\delta(NH_3)$			
$[NH_3Me]BF_4$[d]	White	70	3 205w, 3 195w, 2 980—2 960s,br, 2 870—2 850s,br	1 610s 1 510s	11.6 (11.7)	4.6 (5.2)	11.0 (11.4)
$[NH_3Bu^tCl]$[e]	White	50	3 200s,br, 3 040—2 860s,br, 2 790wm, 2 690ms, 2 590s, 2 490ms	2 080s,[f] 1 600ms, 1 500s	42.7 (43.0)	10.0 (11.1)	11.2 (11.2)
$[NH_3C_6H_4Me\text{-}4]Cl$[e]	White	70	3 120w, 3 040w, 2 920—2 800s,br, 2 590m,br, 2 570m,br	1 603w,br, 1 550w,br, 1 500s	56.8 (56.8)	6.7 (7.6)	9.1 (8.8)

[a] In KBr pellet. [b] Not analytically pure. [c] With $\frac{2}{3}$ molecule of C_6H_6 of crystallisation. [d] With $\frac{1}{20}$ molecule of thf of crystallisation. [e] With $\frac{1}{2}$ molecule of MeOH of crystallisation. [f] Deformation + torsion band.

Et, R = Me). Methyl benzoate and hydrochloric acid are other products of these reactions, equation (2).

$$[ReCl_2(NNCOPh)(PPh_3)_x\{P(OR')_3\}_{3-x}] + MeOH + CNR \longrightarrow [ReCl(N_2)(CNR)(PPh_3)_x\{P(OR')_3\}_{3-x}] + PhCOOMe + HCl \quad (2)$$

The alkyl isocyanide complexes (**4**, R = Me, Et, or Bu^t) and (**5**) are white or pale yellow in colour and their i.r. spectra (KBr pellet) exhibit $\nu(N{\equiv}N)$ and $\nu(C{\equiv}N)$ in the ranges 2 010—2 030 and 2 074—2 120 cm^{-1}, respectively (Table 1). The lowest frequencies for the dinitrogen and the alkyl isocyanide ligand are observed, as expected, for the bis(phosphite) complex (**5**) [$\nu(N_2)$ = 2 010, ν(CN) = 2 074 cm^{-1}] where presence of the stronger net electron-donor PPh_3 co-ligand favours π-electron release from rhenium to the N_2 and CNR π-acceptor ligands.

The aryl isocyanide complexes (**4**, R = C_6H_4Me-4 or C_6H_4Cl-4) were not isolated in an analytically pure state (see below). They are darker coloured (brown) than the alkyl isocyanide compounds, with $\nu(N_2)$ at 2 027 (R = C_6H_4Me-4) and 2 030 cm^{-1} (R = C_6H_4Cl-4), and ν(CN) at 2 053 (R = C_6H_4Me-4) and 1 995 cm^{-1} (R = C_6H_4Cl-4).

In the ^1H n.m.r spectrum of complex (**4**, R = Bu^t) (Table 2), the phosphite Me proton resonance pattern consists of a doublet and a somewhat broad singlet (δ 3.68 and 3.76 p.p.m. relative to $SiMe_4$ respectively) which integrate for 9 and 18 protons. We assign the singlet to the two *trans* $P(OMe)_3$ ligands whereas the doublet of half the intensity is assigned to the unique methyl phosphite ligand ($^3J_{PH}$ = 3 Hz) in a meridional arrangement. In the related complexes (**4**, R = Me or Et) this phosphite proton resonance pattern is not so clearly observed.

Complex (**4**, R = Me) exhibits in its ^{31}P n.m.r. spectrum a triplet:doublet pattern [δ −14.6 and −19.1 p.p.m. relative to $P(OMe)_3$, respectively, ^2J(PP) = 96 Hz], with a 1:2 relative intensity, consistent with the meridional phosphite arrangement which was confirmed by its *X*-ray crystal structure (see below).

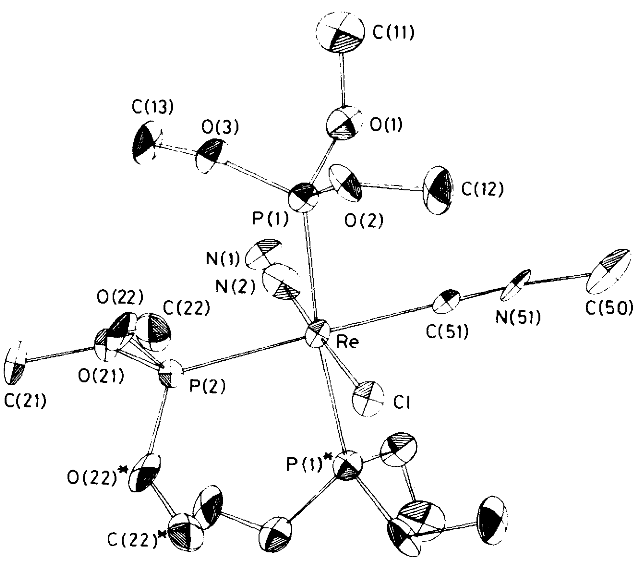

Figure. Structure of *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$

In complex (**4**, R = Me) the Re–NN bond is stabilised by electron release from the *trans* Cl ligand. The same *trans*-$ClRe(N_2)$ group is believed to occur in all the N_2 complexes of the present study, so that the ReN_2 bond is stable despite the competition of the RNC co-ligand for metal π-electron density.

In the preparation of the mixed dinitrogen–isocyanide complexes, mainly on prolonged heating and mostly for the aryl isocyanide compounds, the corresponding ammonium salts $[NH_3R]Cl$ were also obtained and their formation is believed (see below) to result from attack at the isocyanide by hydrochloric acid which is formed in the reaction, see equation (2).

X-Ray Structural Analysis of mer-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$ (**4**, R = Me).—A schematic view of compound

Table 2. Hydrogen-1 n.m.r. data for complexes *mer*-$[\mathrm{ReCl(N_2)(CNR)\{P(OMe)_3\}_3}]$ (**4**), *cis*-$[\mathrm{ReCl(N_2)(CNMe)(PPh_3)\{P(OEt)_3\}_2}]$ (**5**), $[\mathrm{ReCl_2(NNCOPh)(PPh_3)\{P(OEt)_3\}_2}]$ (**3**), and ammonium salts derived from (**4**)

Compound	δ[a]	Integration	Assignment	$^3J_{HH}$ or $^3J_{PH}$ (Hz)
(**4**, R = Me)[b,c]	3.62 (s,br)	27 (27)	$\mathrm{P(OMe)_3}$	
	3.43 (s)[d]			
	1.26 (s)	3 (3)	CNMe	
(**4**, R = Et)[b]	3.9—3.4 (m)[e]	29 (27 + 2)	$\mathrm{P(OMe)_3 + CNC\mathit{H}_2CH_3}$	
	1.30 (t)	3 (3)	$\mathrm{CNCH_2C\mathit{H}_3}$	7
(**4**, R = $\mathrm{Bu^t}$)[f]	3.76 (s,br)	18 (18)	2 *trans* $\mathrm{P(OMe)_3}$	
	3.68 (d)	9 (9)	$\mathrm{P(OMe)_3}$ *trans* to CNR	3
	1.40 (s)	9 (9)	$\mathrm{CNBu^t}$	
(**4**, R = $\mathrm{C_6H_4Me}$-4)[f]	7.6—7.3 (m)	4 (4)	$\mathrm{CNC_6\mathit{H}_4Me}$-4	
	3.8—3.7 (m)	27 (27)	$\mathrm{P(OMe)_3}$	
	2.1 (s)	3 (3)	$\mathrm{CNC_6H_4\mathit{Me}}$-4	
(**5**)[g,h]	8.0—7.1 (m)	19 (15 + 4)	$\mathrm{PPh_3 + \tfrac{2}{3}C_6\mathit{H}_6}$	
	4.0 (q)	12 (12)	$\mathrm{2\ P(OC\mathit{H}_2CH_3)_3}$	7
	3.8 (q)			
	3.00 (s)	3 (3)	CNMe	
	1.25 (t)	9 (9)	$\mathrm{2\ P(OCH_2C\mathit{H}_3)_3}$	7
	1.03 (t)	9 (9)		
(**3**)[b]	8.0—7.3 (m)	20 (15 + 5)	$\mathrm{P\mathit{Ph}_3 + NNCO\mathit{Ph}}$	
	4.2—3.5 (m)	12 (12)	$\mathrm{2\ P(OC\mathit{H}_2CH_3)_3}$	
	1.3 (t)	9 (9)	$\mathrm{2\ P(OCH_2C\mathit{H}_3)_3}$	7
	1.1 (t)	9 (9)		
$\mathrm{[NH_3Me]BF_4}$[g]	7.28 (t,br)[i,j]	3 (3)	$\mathrm{MeN\mathit{H}_3^+}$	
	7.86 (s)	3 (3)	$\mathrm{\mathit{Me}NH_3^+}$	
$\mathrm{[NH_3Bu^t]Cl}$[k]	8.30 (s,br)[i]	3 (3)	$\mathrm{Bu^tN\mathit{H}_3^+}$	
	1.35 (s)	9 (9)	$\mathrm{\mathit{Bu^t}NH_3^+}$	
$\mathrm{[NH_3C_6H_4Me\text{-}4]Cl}$[k]	10.52 (s,br)[i]	3 (3)	$\mathrm{4\text{-}MeC_6H_4N\mathit{H}_3^+}$	
	7.38 (s,br)	4 (4)	$\mathrm{4\text{-}MeC_6\mathit{H}_4NH_3^+}$	
	2.41 (s)	3 (3)	$\mathrm{4\text{-}\mathit{Me}C_6H_4NH_3^+}$	

[a] Relative to internal $\mathrm{SiMe_4}$. [b] In $\mathrm{CDCl_3}$. [c] In the $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ n.m.r. spectrum, the observed triplet:doublet pattern ($^2J_{PP}$ = 96 Hz), with relative intensity of 1:2 and centred at δ = 14.6 and 19.1 p.p.m. upfield from $\mathrm{P(OMe)_3}$, respectively, is assigned to the $\mathrm{\mathit{P}(OMe)_3}$ *trans* to CNMe (triplet) and to the two *trans* $\mathrm{\mathit{P}(OMe)_3}$ (doublet). [d] This singlet, with *ca.* one quarter the intensity of the main one at δ 3.62 is probably the upper-field half of a doublet which corresponds to the unique phosphite (*trans* to CNMe) proton resonance: see complex (**4**, R = $\mathrm{Bu^t}$). [e] A broad singlet at δ 3.60 is probably due to the phosphite proton resonance. [f] In $\mathrm{(CD_3)_2CO}$. [g] In $\mathrm{CD_2Cl_2}$. [h] With $\tfrac{2}{3}$ molecule of $\mathrm{C_6H_6}$ of crystallisation. [i] Disappears upon addition of $\mathrm{D_2O}$. [j] J_{NH} = 50 Hz (gross 1:1:1 triplet). [k] In $\mathrm{(CD_3)_2SO}$.

Table 3. Final positional parameters for (**4**, R = Me) with estimated standard deviations (e.s.d.s) on the last figure in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	0.129 69(2)	0.178 21(6)	0.25	O(22)	0.0608(3)	0.5189(10)	0.1512(7)
P(1)	0.1335(1)	0.1670(3)	0.4378(2)	C(11)	0.1243(6)	−0.0481(16)	0.5921(10)
P(2)	0.0621(2)	0.3999(5)	0.25	C(12)	0.2507(6)	0.1589(18)	0.4810(12)
Cl	0.2206(2)	0.3619(5)	0.25	C(13)	0.0252(5)	0.2355(17)	0.5057(13)
N(1)	0.0240(7)	−0.0500(18)	0.25	C(21)	−0.0550(7)	0.4615(26)	0.25
N(2)	0.0601(6)	0.0292(17)	0.25	C(22)	0.1120(6)	0.5957(15)	0.1098(10)
O(1)	0.1262(3)	−0.0119(9)	0.4791(6)	C(51)	0.1914(7)	−0.0057(20)	0.25
O(2)	0.1922(3)	0.2312(9)	0.4986(6)	C(50)	0.2781(8)	−0.2072(23)	0.25
O(3)	0.0887(3)	0.2622(9)	0.5149(6)	N(51)	0.2253(6)	−0.1038(18)	0.25
O(21)	−0.0071(4)	0.3468(12)	0.25				

Table 4. Some relevant bond distances (pm) and angles (°) with e.s.d.s on the last figure in parentheses

Re–P(1)	235.7(2)	N(1)–N(2)	103.8(21)	P(1)–O(1)	160.0(8)	O(1)–C(11)	145.0(14)
Re–P(2)	238.7(4)	C(51)–N(51)	111.3(21)	P(1)–O(2)	159.4(8)	O(2)–C(12)	144.4(15)
Re–Cl	253.0(4)	N(51)–C(50)	145.4(22)	P(1)–O(3)	159.8(8)	O(3)–C(13)	142.3(13)
Re–N(2)	198.0(14)			P(2)–O(21)	158.9(10)	O(21)–C(21)	143.1(21)
Re–C(51)	206.0(16)			P(2)–O(22)	159.2(9)	O(22)–C(22)	140.1(15)
P(1)–Re–P(1)*	173.81(9)	P(2)–Re–C(51)	177.3(4)	Re–P(1)–O(1)	110.9(3)	O(21)–P(2)–O(22)	99.1(4)
P(1)–Re–P(2)	93.09(10)	Cl–Re–N(2)	178.4(4)	Re–P(1)–O(2)	119.6(3)	O(22)–P(2)–O(22)*	102.1(4)
P(1)–Re–Cl	89.77(10)	Cl–Re–C(51)	86.3(4)	Re–P(1)–O(3)	124.2(3)	P(1)–O(1)–C(11)	121.1(7)
P(1)–Re–N(2)	90.1(3)	N(2)–Re–C(51)	92.0(5)	Re–P(2)–O(21)	112.3(3)	P(1)–O(2)–C(12)	120.6(8)
P(1)–Re–C(51)	86.9(4)	Re–N(2)–N(1)	179.3(12)	Re–P(2)–O(22)	120.2(3)	P(1)–O(3)–C(13)	118.7(8)
P(2)–Re–Cl	90.96(11)	Re–C(51)–N(51)	179.2(12)	O(1)–P(1)–O(2)	104.3(4)	P(2)–O(21)–C(21)	121.3(8)
P(2)–Re–N(2)	90.7(4)	C(51)–N(51)–C(50)	168.9(14)	O(1)–P(1)–O(3)	102.3(4)	P(2)–O(22)–C(22)	124.3(8)
				O(2)–P(1)–O(3)	92.4(4)		

* Refers to the symmetry operation *x*, *y*, 0.5 − *z*.

(**4**, R = Me) is shown in the Figure; atomic co-ordinates are listed in Table 3, and a selection of bond distances and angles in Table 4.

The complex exhibits crystallographic mirror symmetry with Re, P(2), O(21), C(21), Cl, and all atoms of both the N_2 and the CNMe ligand in the mirror plane. Around the central rhenium atom the chloride and the dinitrogen ligand are mutually *trans*, as well as the isocyanide and P(2). Meridional arrangement of the three bulky phosphite ligands causes angular deviations from an ideal octahedral symmetry within the Re, P(1),P(1)*,P(2),C(51) plane: the angles P(1)–Re–P(2) are increased to 93.1° at the cost of the angles P(1)–Re–C(51), which are reduced to 86.9°. The remaining bond angles at rhenium are close to 90°.

Within the phosphite ligands, differences between the various Re–P–O and O–P–O angles can be attributed to the orientation of the methyl substituents. If a methyl group is bent towards the metal [atoms C(12), C(13), C(22)], the corresponding Re–P–O angle is between 120 and 124°; however, if the methyl group is bent away from the metal [atoms C(11), C(21)], Re–P–O is *ca.* 10° smaller.[9] The average Re–P–O angle (117.9°) and the average O–P–O angle (99.9°) are the same as in other phosphite complexes.[10]

There are two distinctly different Re–P distances. While Re–P(1) is 235.7 pm for the mutually *trans* phosphite ligands, Re–P(2) is 3.0 pm longer due to the *trans* influence of the isocyanide ligand. This lengthening is indicative of some π back-bonding component in the Re–C(51) bond of (**4**, R = Me). On the other hand, Re–C(51) [206(2) pm] is considerably longer than in the related compound *mer*-[Re(σ-S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)$_3$] (**6**),[11] in which the stronger net electron-donor character of the other ligands, particularly the *trans* ligand, renders the isocyanide a better π-acceptor ligand. Consequently, the C(51)–N(51) distance [111(2) pm] is shorter and ν(CN) occurs at higher wavenumbers (2 120 cm^{-1}) for (**4**, R = Me) than in the dithiophosphinato-complex (**6**) [C–N 120(2) pm, ν(CN) 1 980 cm^{-1}].

Within the standard deviations the Re–Cl, Re–N, and N–N bond lengths in (**4**, R = Me) [253.0(4), 198(1), and 104(2) pm] are the same as those observed for *trans*-[ReCl(N_2)(PMe_2Ph)$_4$][12] [252.1(4), 197(2), and 106(3) pm, respectively]. This observation implies that the binding of the N_2 ligand is mainly determined by the electron-releasing character of the Cl ligand in the *trans* position, while the electronic influence of the *cis* ligands seems to be less important. Compared with these two complexes, the better electron-donating dithiophosphinato-ligand *trans* to N_2 in compound (**6**) causes a distinct shortening of its Re–N distance [182.9(9) pm] and lengthening of its N–N distance [113(1) pm].

The Re–Cl bond is similarly influenced by the electronic nature of the corresponding *trans* ligand. Thus if the π-accepting properties of the N_2 ligand are increased by co-ordination of a second metal complex moiety to it, the *trans* Re–Cl bond becomes much shorter, as might be expected. Thus *trans*-[ReCl(PMe_2Ph)$_4${$N_2MoCl_4(OMe)$}][13] has Re–N 181.5(15) and Re–Cl 241.8(6) pm and *trans*-[{ReCl(PMe_2Ph)$_4$(N_2)}$_2$-$MoCl_4$][14] has Re–N 189(2) and Re–Cl 244.9(7) pm, compared to the values Re–N 197(2) and Re–Cl 252.1(4) for the parent *trans*-[ReCl(N_2)(PMe_2Ph)$_4$].

Reductive Cleavage of the Isocyanide Ligand to Amine by the Action of Protic Acids.—When bound to an electron-rich, d^6, Mo^0 or W^0 metal centre with labile monophosphine co-ligands, *e.g.* MoL_4 or WL_3 (L = PMe_2Ph), methyl isocyanide has a very low value of ν(CN) {*e.g.* 1 780 cm^{-1} in *trans*-[Mo(CNMe)$_2$L$_4$]} and is susceptible to protonation leading to complete CN bond cleavage to afford methylamine as the major organic product.[7]

In the present study a similar protonation reaction (by HBF_4 or HCl) is observed for both alkyl and aryl isocyanide bound to the ReCl(N_2){P(OMe)$_3$}$_3$ centre in complexes (**4**), although a weaker degree of isocyanide activation towards electrophilic attack might be expected at this Re^I site (compared to the above mentioned Mo^0 or W^0 centres) in view of the much higher ν(CN) values observed for these isocyanide complexes of Re^I (1 995—2 120 cm^{-1}). Nevertheless these ν(CN) values are lower than those of the free ligands and there is considerable Re → isocyanide π back-bonding (see above).

In the ReCl(N_2){P(OMe)$_3$}$_3$ centre, the presence of labile ligands (phosphite and, possibly, also N_2) undoubtedly plays a fundamental role in the reaction with protic acid (HA) due to their facile replacement by the stronger electron-donor anion A^-, which promotes further protonation at the isocyanide co-ligand and concomitant oxidation of the metal to give complete reduction to amine. In agreement with this explanation, the isocyanide, when bound to the robust ReCl(dppe)$_2$ centre with a chelating diphosphine, does not undergo protonation beyond the first single protic attack, although ν(CN) occurs at a very low value, *e.g. ca.* 1 800 cm^{-1} in [ReCl(CNMe)(dppe)$_2$].[6]

A similar behaviour towards reduction induced by protonation was observed for the N_2 ligand at Mo^0 or W^0 centres.[15] Mechanistic studies[16] of the N_2-protonation reaction at metal centres carrying labile phosphines indicate that replacement of monophosphines by more strongly donating anionic ligands induces proton attack at ligating N_2 to give ammonia.

In the present work, the formation of amines from the isocyanide ligands was detected using 2,4-dinitrofluorobenzene.[17] Moreover, the amines were isolated as their ammonium salts ([NH_3R]A) and identified by comparison of their physical properties with those of the authentic salts prepared independently (Tables 1 and 2; Experimental section).

In the ^1H n.m.r. spectra of these ammonium salts, the NH_3R^+ resonance occurs at a low field (in the range δ *ca.* 10.5 to 7.3 p.p.m.) as a broad singlet (for R = Bu^t or C_6H_4Me-4) or as a broad gross 1:1:1 triplet (for R = Me) due to coupling to the ^{14}N nucleus ($J_{NH} \simeq 50$ Hz). The assignment was confirmed by addition of D_2O with resulting disappearance of the signal.

The reduction of isocyanide ligand to amine is also observed during the preparation of complexes (**4**) as a result of the liberation of HCl in the reaction [see equation (2)] which protonates the isocyanide. Thus the salts [NH_3R]Cl were isolated in the preparation of the corresponding complexes (**4**), and their amount increases upon prolonged heating of the reaction solution in MeOH. The ease of amine salt formation appears to parallel the decrease of the observed ν(CN) of the isocyanide ligand: whereas the methyl isocyanide complex [with ν(CN) at 2 120 cm^{-1}] may be prepared without appreciable formation of [NH_3Me]Cl for short refluxing times, [NH_3Bu^t]Cl and [$NH_3C_6H_4Me$-4]Cl are formed in fairly large amounts during the preparation of the corresponding isocyanide complexes which display ν(CN) at 2 097 and 2 053 cm^{-1}. Moreover, the isolation of the analytically pure aryl isocyanide complexes [with the lowest ν(CN) values] has not yet been achieved. Although these compounds were detected in solution by i.r. spectroscopy during their attempted preparation, protonation readily occurred on working-up the reaction mixture and, *e.g.* in the case of the *p*-tolyl isocyanide reaction, the corresponding salt, [$NH_3C_6H_4Me$-4]Cl was the main isolated product.

We have, as yet, been unable to isolate metallic products from the protonation reactions nor do we know the fate of the terminal CNR carbon atom. Without further information it is inappropriate to speculate on the mechanism of the CNR cleavage step, although species involving carbon hydrides ligating Re seem likely intermediates.

Conclusions

A convenient synthesis for mixed dinitrogen–isocyanide complexes of Re^I with organophosphites as co-ligands has been developed through reaction of the isocyanides with the appropriate organodiazenido-compounds, the Re–NN bond being stabilised by the strong electron-donor Cl co-ligand in the *trans* position.

The bond of the isocyanide to the ReCl(N$_2$){P(OMe)$_3$}$_3$ centre has some degree of π character as shown by *X*-ray data, and the alkyl or aryl isocyanide ligands, although having ν(CN) values which are not greatly below those observed in the free ligands, are activated towards electrophilic attack by protic acid. The lability of the phosphite co-ligand is believed to play a fundamental role in the production of amine upon protonation at the isocyanide ligand. The ease of isocyanide reduction to amine appears to be greater the greater the lowering of ν(CN) on co-ordination.

Experimental

All reactions were carried out in the absence of air, by standard inert-gas and vacuum techniques, using purified and dried solvents. I.r. spectra were recorded on a Perkin-Elmer 683 spectrometer, ^{1}H n.m.r. data were obtained using JEOL FX-90Q and Bruker CXP spectrometers, and the ^{31}P n.m.r. spectra were recorded on a JEOL FX-90Q spectrometer. [ReCl$_2$(NNCOPh)(PPh$_3$)$_2$] was prepared by literature methods,[18] as were the isocyanides CNMe,[19] CNBu^t,[20] and CNC$_6$H$_4$Me-4.[21] The organophosphites P(OMe)$_3$ and P(OEt)$_3$ were purchased from Merck and BDH, respectively, whereas [Et$_2$OH]BF$_4$ was obtained from Aldrich.

Preparation of the Complexes.—[ReCl(N$_2$)(CNMe){P(OMe)$_3$}$_3$] (**4**, R = Me). A solution of [ReCl$_2$(NNCOPh){P(OMe)$_3$}$_3$] (**2**) (0.200 g, 0.262 mmol) and CNMe (0.04 cm^3, 0.85 mmol) in MeOH (25 cm^3) was refluxed for two hours. The resulting pale yellow solution was then evaporated under reduced pressure to approximately 5 cm^3 and the *complex* (**4**, R = Me) precipitated upon slow addition of Et$_2$O (5 cm^3) and recrystallised from tetrahydrofuran–diethyl ether (1:5) (60% yield).

[ReCl(N$_2$)(CNEt){P(OMe)$_3$}$_3$] (**4**, R = Et). A suspension of complex (**2**) (0.500 g, 0.656 mmol) and CNEt (0.10 cm^3, 1.6 mmol) in MeOH (30 cm^3) was refluxed for 2 h. The solvent was evaporated and acetone (10 cm^3) was added to the orange residue. A white solid residue was then separated by filtration, the solution concentrated to 1–2 cm^3 and n-pentane (20 cm^3) was added slowly. Complex (**4**, R = Et) precipitated as a *white solid* and was recrystallised from thf–Et$_2$O (1:8) (30% yield).

[ReCl(N$_2$)(CNBu^t){P(OMe)$_3$}$_3$] (**4**, R = Bu^t). t-Butyl isocyanide (0.20 cm^3, 2.0 mmol) was added to the orange suspension of (**2**) (0.500 g, 0.656 mmol) in MeOH (45 cm^3) and the mixture refluxed for 3 h. The solvent was evaporated under reduced pressure to 2—3 cm^3, acetone (5 cm^3) was then added and a white crystalline solid ([NH$_3$Bu^t]Cl) was filtered off. The solution was again concentrated and *complex* (**4**, R = Bu^t) precipitated upon slow addition of n-pentane (15 cm^3) (20% yield).

[ReCl(N$_2$)(CNC$_6$H$_4$Me-4){P(OMe)$_3$}$_3$] (**4**, R = C$_6$H$_4$Me-4). A solution of (**2**) (0.200 g, 0.262 mmol) and CNC$_6$H$_4$Me-4 (120 mg, 1.03 mmol) in MeOH (34 cm^3) was refluxed for 2 h. The solvent was reduced under vacuum to 5 cm^3 and C$_6$H$_6$ (16 cm^3) was then added. The resulting white precipitate ([NH$_3$C$_6$H$_4$Me-4]Cl) was filtered off and the solution was concentrated to a *brown oil* (**4**, R = C$_6$H$_4$Me-4).

[ReCl$_2$(NNCOPh)(PPh$_3$){P(OEt)$_3$}$_2$] (**3**). Triethyl phosphite (1.6 cm^3, 9.22 mmol) was added to a suspension of [ReCl$_2$(NNCOPh)(PPh$_3$)$_2$] (2.00 g, 2.18 mmol) in C$_6$H$_6$ (50 cm^3) and the mixture refluxed for 2 h. The solution was then concentrated with heating to 10 cm^3 and MeOH (40 cm^3) was added. Complex (**3**) precipitated as an *orange crystalline solid* which was filtered off and thoroughly washed with Et$_2$O (6 × 10 cm^3) (70% yield).

[ReCl(N$_2$)(CNMe)(PPh$_3$){P(OEt)$_3$}$_2$] (**5**). Methyl isocyanide (0.09 cm^3, 1.9 mmol) was added to a suspension of [ReCl$_2$(NNCOPh)(PPh$_3$){P(OEt)$_3$}$_2$]·0.5C$_6$H$_6$ (0.620 g, 0.605 mmol) in MeOH (60 cm^3) and the system was stirred overnight at room temperature. The resulting *pale yellow precipitate* of (**5**) was then filtered off and a further crop was obtained upon concentration of the mother-liquor to 5 cm^3 and addition of Et$_2$O (10 cm^3) (30% yield).

Reduction of the Isocyanide Ligand to Amine.—The general formation of amine upon protonation of isocyanide ligand in the above mentioned dinitrogen–isocyanide complexes is illustrated for [ReCl(N$_2$)(CNMe){P(OMe)$_3$}$_3$] as follows.

Diethyloxonium tetrafluoroborate (0.07 cm^3, 0.5 mmol) was added to a solution in tetrahydrofuran (thf) (25 cm^3) of [ReCl(N$_2$)(CNMe){P(OMe)$_3$}$_3$] (0.110 g, 0.166 mmol) and the system was stirred for 30 min. The solution was concentrated under reduced pressure to 10 cm^3 and Et$_2$O (5 cm^3) was added slowly. The precipitated *white salt*, [NH$_3$Me]BF$_4$, was filtered off and washed with Et$_2$O (*ca.* 70% yield).

Preparation of the Ammonium Salts.—The general technique is illustrated for a BF$_4^-$ and a Cl$^-$ salt as follows.

[NH$_3$Me]BF$_4$. Tetrafluoroboric acid (9.90 cm^3, 50% aqueous solution, 159 mmol) was added to a solution of NH$_2$Me (5.5 cm^3, 40% aqueous solution, 159 mmol) in water (10 cm^3). The solution was allowed to cool to room temperature with stirring. The solvent was then evaporated, and the white solid obtained ([NH$_3$Me]BF$_4$) was filtered off, thoroughly washed with diethyl ether and dried *in vacuo*.

[NH$_3$Bu^t]Cl. A solution of NH$_2$Bu^t (2.00 g, 27.4 mmol) and HCl (37% aqueous solution, 2.70 cm^3, 32.6 mmol) was allowed to cool to room temperature with stirring. The solvent was then evaporated off and the resulting white solid ([NH$_3$Bu^t]Cl) was filtered off, thoroughly washed with diethyl ether (3 × 5 cm^3) and dried *in vacuo*.

X-Ray Crystallography.—Crystals of compound (**4**, R = Me) were grown from thf–Et$_2$O as described above. A crystal of approximate dimensions 0.2 × 0.2 × 0.3 mm was used for data collection.

Crystal data. C$_{11}$H$_{30}$ClN$_3$O$_9$P$_3$Re, M = 663.0, orthorhombic, space group *Pnam*, a = 2 204.0(6), b = 841.3(2), c = 1 253.6(4) pm, U = 2 324 × 10^6 pm^3, Z = 4, D_c = 1.89 g cm^{-3}, F(000) = 1 304, μ(Mo-K_α) = 59.0 cm^{-1}.

Data collection. Unit-cell parameters were obtained by least-squares fit of the 2θ values of 15 reflections (2θ > 15°) from different parts of the reciprocal space. The data were collected with an automated four-circle diffractometer (Syntex $P2_1$) using graphite-monochromated Mo-K_α radiation (λ = 71.069 pm). Using the ω scan technique, 1 914 independent reflections were measured ($2 \leqslant 2\theta \leqslant 50°$; $h,k,l \geqslant 0$). During the data collection two check reflections were measured every 50 reflections and no significant variations were detected. Reflections were corrected for Lorentz and polarisation factors and an empirical absorption correction was applied.

Structure analysis. The structure was solved by the Patterson method and refined by full-matrix least-squares (Syntex XTL). Hydrogen atoms were located partly from difference Fourier maps and partly by calculation according to idealised geometry. Their contributions were taken into account but not refined. The final R factors were $R = 0.058$ and $R' = 0.058$ ($1/w = \sigma^2 + 0.000\,025\, F_o^2$) for all reflections.

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