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Syntheses and properties of dinitrogen, diazenido and derived isocyanide complexes of rhenium with phosphite or phosphonite ligands

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Abstract

The dinitrogen complexes $[ReCl(N_2)(PPh_3)L_3]$ (**1**, $L = P(OMe)_3$, $P(OEt)_3$ or $PPh(OEt)_2$) and $[ReCl(N_2)\{PPh(OMe)_2\}_4]$ (**2**), and the benzoyldiazenido compounds $[ReCl_2(NNCOPh)(PPh_3)_x\{PPh(OR)_2\}_{3-x}]$ (**3**, $x = 0$, $R = Et$; **4**, $x = 2$, $R = Me$) have been prepared by reaction of $[ReCl_2(NNCOPh)(PPh_3)_2]$ with the appropriate phosphite $[P(OMe)_3$ or $P(OEt)_3]$ or phosphonite $[PPh(OEt)_2$ or $PPh(OMe)_2]$, in benzene (usually under reflux), followed in the case of the dinitrogen complexes by treatment with hot methanol. They react with isocyanides to give $[ReCl(CNR)_3L_2]$ (**5**; $R = C_6H_4Me$-**4** or $C_6H_2Pr^i_3$-2,4,6, $L = P(OMe)_3$; $R = Me$, $L = PPh(OMe)_2$).

Introduction

The chelate benzoylhydrazido(3–)rhenium(V) complex $[ReCl_2(NNCOPh)(PPh_3)_2]$ is a known key precursor for a variety of benzoyldiazenido and dinitrogen complexes, particularly those of the types $[ReCl_2(NNCOPh)L_3]$ [1–4], *trans*-$[ReCl(N_2)L_4]$ ($L = PR_3$ or $P(OMe)_3$) [2], $[ReCl(N_2)(CO)_2L_2]$ [2,3], *trans*-$[ReCl(N_2)(LL)_2]$ ($LL = R_2PCH_2CH_2PR_2$) [2] or *mer*-$[ReX(N_2)(PMe_2Ph)_3]$ ($X = \eta^2$-S_2PPh_2 or S_2CNEt_2) [5].

Furthermore, the dinitrogen complexes of rhenium(I) with phosphine ligands were shown to be suitable predecessors for low oxidation state isocyanide compounds, namely *trans*-$[ReCl(CNR)(dppe)_2]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) [6a], *trans*-$[Re(CNR)_2(dppe)_2]^+$ [6b], *mer*-$[ReX(N_2)(CNMe)L_3]$ ($X = Cl$ or S_2PPh_2, $L = PMe_2Ph$) [7], $[Re(S_2PPh_2)(N_2)(CNMe)_2L_2]$ [7], $[Re(S_2CNEt_2)(CNMe)L_3]$ [7] and $[Re(S_2CNEt_2)(CNMe)_2L_2]$ [7], derived from the parent complexes *trans*-$[ReCl(N_2)(dppe)_2]$, *trans*-$[ReCl(N_2)L_4]$, *mer*-$[Re(S_2PPh_2)(N_2)L_3]$ or *mer*-$[Re(S_2CNEt_2)(N_2)L_3]$, respectively. At the electron-rich rhenium(I)-chloro centres

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(Re) the isocyanides are activated towards protonation to give aminocarbyne-type species Re≡C–NHR [8,9], or amines [10] formed upon reductive C–N bond cleavage.

In contrast to the well documented chemistry of rhenium phosphine complexes [11], that of phosphite or phosphonite complexes of rhenium is relatively underdeveloped. We therefore decided to investigate the reactions of phosphites with the above-mentioned benzoyldiazenido complex [10] and its parent species, $[ReOCl_3(PPh_3)_2]$ [12a], as well as the chemistry of the derived products. Hence, e.g., treatment of $[ReCl_2(NNCOPh)(PPh_3)_2]$ with an organophosphite (L) in refluxing benzene was shown to give the benzoyldiazenido complexes $[ReCl_2(NNCOPh)(PPh_3)_xL_{3-x}]$ ($x = 0$, $L = P(OMe)_3$ [2]; $x = 1$, $L = P(OEt)_3$ [10]), which, in refluxing methanol, undergo NN–C bond cleavage to afford, in the presence of isocyanide, the mixed dinitrogen-isocyanide compounds $[ReCl(N_2)(CNR)(PPh_3)_xL_{3-x}]$ ($x = 0$; R = Me, Et, Bu^t, C_6H_4Me-4 or C_6H_4Cl-4; $L = P(OMe)_3$, $x = 1$; R = Me; $L = P(OEt)_3$) [10].

Moreover, the oxophosphonato complexes $[ReOClX\{P(O)(OMe)_2\}(PPh_3)_2]$ (X = Cl or OMe) were, respectively, obtained [12a] by reaction of $[ReOCl_3(PPh_3)_2]$ with $P(OMe)_3$ or with $P(OMe)_2OH$/MeOH in the presence of a base; the formation of the phosphonato ligand in the former product involves dealkylation of trimethylphosphite, possibly through a Michaelis–Arbuzov type rearrangement [12a].

In the present work, we have examined the use of $[ReCl_2(NNCOPh)(PPh_3)_2]$ to the synthesis of novel phosphite complexes of dinitrogen, and extended such a route to the preparation of diazenido or dinitrogen compounds of rhenium with phosphonite ligands. In addition, the dinitrogen or diazenido products, with labile phosphite or phosphonite ligands, have been shown to undergo replacement reactions with isocyanides to give triisocyanide complexes of rhenium(I). A preliminary report has appeared [12b].

Results and discussion

Dinitrogen and diazenido complexes

The dinitrogen complexes $[ReCl(N_2)(PPh_3)L_3]$ (**1**, $L = P(OMe)_3$, $P(OEt)_3$ or $PPh(OEt)_2$) and $[ReCl(N_2)\{PPh(OMe)_2\}_4]$ (**2**) are obtained by treatment of $[ReCl_2(NNCOPh)(PPh_3)_2]$ with the appropriate phosphite or phosphonite ($P(OMe)_3$, $P(OEt)_3$, $PPh(OEt)_2$ or $PPh(OMe)_2$, respectively), in refluxing benzene followed by reaction with hot methanol (eq. 1 and 2).

$$[ReCl_2(NNCOPh)(PPh_3)_2] + 3L + MeOH \rightarrow [ReCl(N_2)(PPh_3)L_3] + PPh_3 + PhCOOMe + HCl \quad (1)$$

$$[ReCl_2(NNCOPh)(PPh_3)_2] + 4PPh(OMe)_2 + MeOH \rightarrow [ReCl(N_2)\{PPh(OMe)_2\}_4] + 2PPh_3 + PhCOOMe + HCl \quad (2)$$

This one-pot method is the most convenient one for their preparation, but they can also be made by reaction of the diazenido compounds of the type $[ReCl_2(NNCOPh)(PPh_3)_xL_{3-x}]$ ($x = 0$–2) with hot methanol (which promotes NN–C bond cleavage to generate ligating N_2) in the presence of L or PPh_3, see,

e.g., eq. 3 for the case of **1**, (L = $P(OMe)_3$).

$$[ReCl_2(NNCOPh)\{P(OMe)_3\}_3] + MeOH + PPh_3 \rightarrow$$
$$mer\text{-}[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3] + PhCOOMe + HCl \quad (3)$$

The diazenido compounds may be prepared by reaction of $[ReCl_2(NNCOPh)(PPh_3)_2]$ with an excess of L in benzene; the use of hot methanol should be avoided, otherwise the reaction proceeds further to give the final dinitrogen complexes. Thus, the novel benzoyldiazenido compounds with phosphonite ligands $[ReCl_2(NNCOPh)(PPh_3)_x\{PPh(OR)_2\}_{3-x}]$ (**3**, $x = 0$, R = Et; **4**, $x = 2$, R = Me) have been prepared in this way (eq. 4), which is similar to that used for the synthesis of the related phosphite complexes $[ReCl_2(NNCOPh)(PPh_3)_xL_{3-x}]$ ($x = 0$ or 1; L = $P(OMe)_3$ [2] or $P(OEt)_3$ [10]).

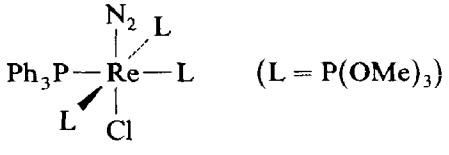
$$[ReCl_2(NNCOPh)(PPh_3)_2] + (3-x)PPh(OR)_2 \rightarrow$$
$$[ReCl_2(NNCOPh)(PPh_3)_x\{PPh(OR)_2\}_{3-x}] + (2-x)PPh_3 \quad (4)$$

The dinitrogen compounds are yellow (**1**, L = $P(OMe)_3$ or **2**, L = $P(OEt)_3$) or light brown (**1**, L = $PPh(OEt)_2$), whereas the benzoyldiazenido complexes **3** and **4** are orange. They are stable in air at room temperature for considerable periods, except for **1** (L = $P(OEt)_3$ or $PPh(OEt)_2$) which readily undergo decomposition in the air with loss of N_2.

The IR spectra (KBr pellets) of the dinitrogen complexes exhibit (Table 1) strong bands in the 2010–1985 cm^{-1} range due to $\nu(N_2)$. The strong bands at 1650–1620 and 1530–1510 cm^{-1} displayed by the benzoyldiazenido compounds are assigned to $\nu(CO)$ and $\nu(NN)$ of the NNCOPh ligand as was the case for related diazenido complexes [1].

In the case of the phosphonite complexes of dinitrogen, $\nu(N_2)$ appears at slightly lower wavenumbers than those for the related phosphite compounds, in keeping with the considerably stronger net electron-donor character of the phosphonite relative to a related phosphite ligand, which favours π-electron release from Re to N_2. Hence, $\nu(N_2)$ for **2** (1985 cm^{-1}) is lower than for $[ReCl(N_2)\{P(OMe)_3\}_4]$ (2013 cm^{-1}) [2], whereas, for compounds **1**, the lowest $\nu(N_2)$ frequency, is observed for the phenyldiethylphosphonite complex. Moreover, complexes **1** have $\nu(N_2)$ at moderately lower wavenumbers than $[ReCl(N_2)\{P(OMe)_3\}_4]$, in accord with the slightly stronger electron-releasing ability of PPh_3 relative to $P(OMe)_3$.

The dinitrogen complexes are believed to have the Cl ligand *trans* to N_2 because of the expected stabilization of the Re–N_2 bond by the electron release from the anionic ligand, as known to be the case for related complexes such as *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$ [10] or *mer*-$[Re(S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]$ [7]. In agreement with this belief, compound **1** (L = $P(OMe)_3$) appears to have a meridional arrangement of the phosphite ligands, as discussed below, with its proposed structure as follows:



(L = $P(OMe)_3$)

Table 1

Physical data for complexes $[ReCl(N_2)(PPh_3)L_3]$ (**1**), $[ReCl(N_2)\{PPh(OMe)_2\}_4]$ (**2**), $[ReCl_2(NNCOPh)(PPh_3)_x\{PPh(OR)_2\}_{3-x}]$ (**3**, **4**) and $[ReCl(CNR)_3L_2]$ (**5**)

Compound	Colour	Yield (%)	Infrared (cm^{-1}) [a]				Analysis (Found (calcd.) (%))		
			ν(N≡N)	ν(C=O)	ν(N=N)	ν(C≡N)	C	H	N
1 (L = $P(OMe)_3$) [b]	Yellow	40	2010 s [c]				37.5	4.6	3.3
			1980 m				(37.5)		(3.1)
			1975 m						
1 (L = $P(OEt)_3$) [d]	Yellow	10	2000 m						
1 (L = $PPh(OEt)_2$) [e]	Light brown	10	1990 m				54.0	5.5	2.0
							(54.1)	(5.5)	(2.4)
2	Yellow	70	1985 s				41.6	4.6	3.1
							(41.3)	(4.7)	(3.0)
3 (x = 0, R = Et)	Orange	30		1650 m	1530 s		47.0	5.2	2.4
							(46.9)	(5.2)	(2.5)
4 (x = 2, R = Me) [f]	Brownish	30		1640 m [g]	1510 m		61.1	4.7	2.2
	orange			1620 m			(61.0)	(4.7)	(2.3)
5 (R = C_6H_4Me-4, L = $P(OMe)_3$) [h]	Redish	50				2116 s			
	brown					2065 sh			
5 (R = $C_6H_2Pr^i_3$-**2**,**4**,**6**, L = $P(OMe)_3$) [i]	Pale	20				2115 sh	54.6	7.5	3.5
	yellow					2045 s	(54.9)	(7.7)	(3.4)
5 (R = Me, L = $PPh(OMe)_2$) [j]	Brown	40				2190 s	36.1	4.2	5.7
							(36.5)	(4.0)	(5.6)

[a] In KBr pellets, unless stated otherwise; relative intensities, s = strong, m = medium, sh = shoulder. [b] With $\frac{1}{6}C_6H_6$ of crystallisation. [c] A single band at 2010 cm^{-1} observed in THF solution. [d] No reliable microanalytical data were obtained due to rapid loss of N_2. [e] With $\frac{1}{4}C_6H_6$ of crystallisation. [f] With $2C_6H_6$ of crystallisation. [g] In Nujol mull. [h] Not obtained in an analytically pure condition. [i] With 2MeOH of crystallisation. [j] With $\frac{3}{4}CH_2Cl_2$ of crystallisation.

Table 2

^{1}H- and ^{31}P-{^{1}H} NMR data for complexes [ReCl(N_2)(PPh_3)L_3] (**1**), [ReCl(N_2){$PPh(OMe)_2$}$_4$] (**2**), [$ReCl_2$(NNCOPh)(PPh_3)$_x$ {$PPh(OR)_2$}$_{3-x}$] (**3**, **4**) and [ReCl($CNR)_3L_2$] (**5**)

Complex	^{1}H NMR		
	δ [a]	Integration	Assignment
1 (L = $P(OMe)_3$) [b,c]	8.0–7.2(m)	16	PPh_3 + 1.6 C_6H_6 [d]
	3.81(d) [e]	9	Unique $P(OMe)_3$
	3.50(t) [f]	18	2 *trans*-$P(OMe)_3$
1 (L = $P(OEt)_3$) [g]	7.9–7.2(m)	15	PPh_3
	4.3–3.0(m)	26	$P(OCH_2CH_3)_3$ + 2 *MeOH* [d]
	1.4–1.1(m)	27	$P(OCH_2CH_3)_3$
2 [i,j]	7.8–7.1(m)	20	$PPh(OMe)_2$
	3.44(s,br)	24	$PPh(OMe)_2$
3 (x = 0, R = Et) [b]	7.8–7.1(m)	20	$PPh(OEt)_2$ + NNCO*Ph*
	4.2–3.7(m)	12	$PPh(OCH_2CH_3)_2$
	1.4–1.1(m)	18	$PPh(OCH_2CH_3)_2$
4 (x = 2, R = Me) [i,k]	7.4–7.3(m)	46	PPh_3 + *Ph*$(OMe)_2$) NNCO*Ph* + C_6H_6 [d]
	3.3(d,br) [l]	6	$PPh(OMe)_2$
5 (R = C_6H_4Me-4, L = $P(OMe)_3$) [i]	7.4–7.0(m)	12	CNC_6H_4Me-4
	3.7–3.6(m)	9	$P(OMe)_3$
	2.3–2.2(m)	18	$P(OMe)_3$ + CNC_6H_4*Me*-4
5 (R = $C_6H_2Pr^i_3$-2,4,6, L = $P(OMe)_3$) [b]	7.4–6.9(m)	6	$C_6H_2Pr^i_3$-2,4,6
	3.8–3.7(m)	12	$P(OMe)_3$ + C*H*($CNC_6H_2Pr^i_3$-2,4,6)
	3.55(sp) [m]	2	C*H*(2$CNC_6H_2Pr^i_3$-2,4,6)
	3.35(sp) [m]	2	
	3.0–2.9(m)	2	
	1.3–1.1(m)	63	$P(OMe)_3$ + CH_3($CNC_6H_2Pr^i_3$-2,4,6)
5 (R = Me, L = $PPh(OMe)_2$) [b]	7.9–7.3(m)	10	$PPh(OMe)_2$
	3.8–3.5(m)	18	$PPh(OMe)_2$ + 2CN*Me*
	3.29(s)	3	CN*Me*

[a] δ values in ppm relative to internal $SiMe_4$; s, singlet; d, doublet; t, triplet; sp, septet; m, multiplet; br, broad. [b] In$(CD_3)_2CO$. [c] ^{31}P{^{1}H}NMR (δ in ppm relative to trimethylphosphite): doublet (^2J(PP) 295 Hz) of triplets (^2J(PP) 33 Hz) at δ −23.4 (unique phosphite), triplet (^2J(PP) 33 Hz) at δ −21.9 (2 *trans*-phosphites), and doublet (^2J(PP) 295 Hz) of triplets (^2J(PP) 33 Hz) at δ −129.3 (phosphine), with relative integrations of 1/2/1 (see text). [d] Solvent of crystallisation. [e] ^3J(PH) 9 Hz. [f] $|{}^3J(PH) + {}^5J(PH)|$ = 2×4.5 Hz. [g] In C_6D_6. [i] In CD_2Cl_2. [j] ^{31}P{^{1}H} NMR: δ −3.5 ppm rel. $P(OMe)_3$. [k] ^{31}P{^{1}H} NMR: δ −26.5(s,br)(phosphonite), −135.0(s,br)(2 phosphines) ppm rel. $P(OMe)_3$, with relative integrations of 1/2. [l] ^3J(PH) 11 Hz. [m] ^3J(HH) 4.5 Hz.

In the ^{1}H NMR spectrum of complex **1**, (L = $P(OMe)_3$) ($(CD_3)_2CO$, 298 K) (Table 2) the phosphite methyl proton resonance pattern consists of a doublet and a triplet, at δ 3.81 and 3.50 ppm rel. $SiMe_4$, respectively, integrating for 9 and 18 protons. We assign the doublet to a unique methylphosphite (^3J(PH) 9 Hz) and the triplet to two *trans*-methylphosphite ligands ($|{}^3J(PH) + {}^5J(PH)|/2 = 4.5$ Hz), in a meridional arrangement.

In the ^{13}P{^{1}H} NMR spectrum of **1** (L = $P(OMe)_3$) (Table 2), a doublet (^2J(PP) 295 Hz) of triplets (^2J(PP) 33 Hz) centred at δ −23.4 ppm rel. $P(OMe)_3$ is assigned to the unique phosphite; it arises from coupling of this phosphite to the phosphine in *trans* position (doublet) and to the two *trans*-$P(OMe)_3$ ligands (triplet). A triplet (^2J(PP) 33 Hz) at δ −21.9 ppm with double intensity of the above-mentioned

resonance pattern is assigned to these two *trans* phosphite ligands, whereas the resonance of the ligating phosphine occurs as a doublet (^2J(PP) 295 Hz) of triplets (^2J(PP) 33 Hz) (centred at δ −129.3 ppm and with the expected intensity) because of coupling to the unique phosphite in *trans* position (doublet) and to the two *trans*-$P(OMe)_3$ ligands (triplet).

In contrast with *mer*-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$ (**1**, L = $P(OMe)_3$), the other complexes **1** (L = $P(OEt)_3$ or $PPh(OEt)_2$) readily decompose in common solvents, and so clear NMR spectra were not obtained, particularly for the phosphonite complex.

In keeping with the expected *trans* geometry for complex $[ReCl(N_2)\{PPh(OMe)_2\}_4]$ (**2**) (CD_2Cl_2, 298 K), the signal from the phosphonite methyl protons is observed as a broad singlet at δ 3.44 ppm.

The ^1H NMR spectra (Table 2) of the benzoyldiazenido complexes $[ReCl_2(NNCOPh)(PPh_3)_x\{PPh(OR)_2\}_{3-x}]$ (**3**, $x = 0$, R = Et; **4**, $x = 2$, R = Me) exhibit the expected resonances, usually as unresolved complex multiplets with normal chemical shifts. However, for compound **4** (CD_2Cl_2), the phosphonite methyl resonances occur as a broad doublet (J(PH) 11 Hz) at δ 3.3 ppm, whereas in the $^{31}P\{^1H\}$ NMR spectrum the $PPh(OMe)_2$ and the PPh_3 resonances are observed as broad singlets with a 1/2 relative integration, at δ −26.5 and −135.0 ppm, respectively. These data are insufficient for assignment of the geometry of these complexes.

Isocyanide complexes

Treatment of a tetrahydrofuran (THF) solution of *mer*-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$ (**1**, L = $P(OMe)_3$) or *trans*-$[ReCl(N_2)\{PPh(OMe)_2\}_4]$ (**2**) with an excess of the isocyanide CNC_6H_4Me-4 or CNMe (In a molar ratio of 5 ~ 6/1) gives the triisocyanide complexes $[ReCl(CNR)_3L_2]$ (**5**, L = $P(OMe)_3$ or $PPh(OMe)_2$) (eq. 5 or 6, respectively).

$$mer\text{-}[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3] + 3CNC_6H_4Me\text{-}4 \rightarrow [ReCl(CNC_6H_4Me\text{-}4)_3\{P(OMe)_3\}_2] + N_2 + PPh_3 + P(OMe)_3 \quad (5)$$

$$trans\text{-}[ReCl(N_2)\{PPh(OMe)_2\}_4] + 3CNMe \rightarrow [ReCl(CNMe)_3\{PPh(OMe)_2\}_2] + N_2 + 2PPh(OMe)_2 \quad (6)$$

These reactions occur at room temperature and involve the facile replacement of both N_2 and two P ligands. However, the ligating dinitrogen can be retained in a less extensive substitution reaction, and the known [10] mixed N_2/CNMe complex *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}]_3]$ is obtained if only a slight excess of the isocyanide relatively to **1** (L = $P(OMe)_3$] is used.

$$mer\text{-}[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3] + CNMe \rightarrow mer\text{-}[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3] + PPh_3 \quad (7)$$

The latter complex was previously synthesized by reaction of $[ReCl_2(NNCOPh)\{P(OMe)_3\}_3]$ with CNMe in refluxing methanol [10]. Such a route, which involves the NN–C bond cleavage of the benzoyldiazenido ligand upon nucleophilic attack by MeOH, has also been utilized in the present study for the synthesis of $[ReCl(CNR)_3\{P(OMe)_3\}_2]$ (**5**, L = CNC_6H_4Me-4 or $CNC_6H_2Pr^i_3$-2,4,6) from the

reactions of the parent benzoyldiazenido complex with the isocyanide in methanol at reflux (eq. 8).

$$[ReCl_2(NNCOPh)\{P(OMe)_3\}_3] + 3CNR + MeOH \rightarrow$$
$$[ReCl(CNR)_3\{P(OMe)_3\}_2] + N_2 + P(OMe)_3 + PhCOOMe + HCl \quad (8)$$

Methyl benzoate and hydrochloric acid are other products of these reactions, which may proceed further through protonation of ligating isocyanide by the liberated HCl to give the corresponding ammonium salt $[NH_3R]Cl$, formed by reductive isocyanide CN bond cleavage, a reaction which is known to occur at electron-rich d^6Re^I [10], Mo^0 or W^0 [13] centres bearing labile phosphite or phosphine ligands. The formation of the ammonium salt is particularly relevant in the case of CNC_6H_4Me-4 and the corresponding complex **5** prepared by this procedure was not obtained analytically pure, always being contaminated with the salt.

Thus, the route to the isocyanide complexes **5** based on the use of a benzoyldiazenido parent compound is less convenient than the alternative one, described above involving only replacement reactions of the dinitrogen complexes **1** and **2**. Moreover, the latter reaction sequence proceeds at room temperature, and so, involves milder experimental conditions. Such mild conditions also contrast with those required [6a] for the preparation of *trans*-$[ReCl(CNR)(dppe)_2]$ by reaction of isocyanide with *trans*-$[ReCl(N_2)(dppe)_2]$ under argon in refluxing THF for extended periods (a few days) or under irradiation from a W-filament light.

The reactions of isocyanides with the N_2 complexes **1** and **2** which contain labile phosphite or phosphonite ligands could conceivably occur by initial replacement of these ligands to give mixed dinitrogen-isocyanide and dinitrogen-diisocyanide complexes of the types obtained in related systems (e.g., $[ReX(N_2)(CNR)L_3]$ (X = Cl or S_2PPh_2, L = $P(OMe)_3$ or PMe_2Ph) [7,10] and $[Re(S_2PPh_2)(N_2)(CNMe)_2(PMe_2Ph)_2]$ [7]) in which the Re–N_2 bond is labilized by the isocyanide co-ligand which is a strong π electron acceptor and competitor for the available metal *d* electrons. Thus further replacement of N_2 by isocyanide can readily occur with those mixed N_2–CNR complexes to give the final triisocyanide compounds **5**. In contrast, the displacement of N_2 at *trans*-$[ReCl(N_2)(dppe)_2]$ [6a], containing strongly-bound chelating diphosphine ligands, highly resistent to replacement reactions, requires relatively drastic experimental conditions.

The described routes for complexes **5** are quite different from that used [14] for the preparation of the related phosphinic compound $[ReCl(CNMe)_3(PMePh_2)_2]$, involving formal loss of $HSbF_6$ in THF from the aminocarbyne complex $[ReCl(CNHMe)(CNMe)_2(PMePh_2)_2][SbF_6]$.

The complexes $[ReCl(CNR)_3L_2]$ (**5**, R = C_6H_5Me-4 or $C_6H_2Pr^i_3$-2,4,6, L = $P(OMe)_3$; R = Me, L = $PPh(OMe)_2$) were isolated as reddish-brown, pale yellow or brown solids, with strong IR bands (Table 1) at 2116 (with a shoulder at 2065), 2045 (with a shoulder at 2115) and 2190 cm^{-1}, respectively, which are assigned to ν(CN). In these complexes, the ν(CN) bands appear at higher wavenumbers than those for related monoisocyanide compounds of Re^I, such as *trans*-$[ReCl(CNR)(dppe)_2]$ (e.g., ν(CN) 1880 cm^{-1} for R = C_6H_5Me-4) [6a], *mer*-$[ReCl(N_2)(CNMe)(PMe_2Ph)_3]$ (2080 cm^{-1}) [7] and *mer*-$[ReCl(N_2)(CNC_6H_4Me\text{-}4)\{P(OMe)_3\}_3]$ (2053 cm^{-1}) [10], in keeping with the competition, in the former, of the various isocyanide ligands for

the metal *d* electrons and with the weaker net electron donor ability of the phosphite and phosphonite ligands relative to that of phosphines.

In the ^1H NMR spectra of complexes **5** (Table 2) the resonance of the methyl protons of the isocyanides usually overlap with those for the $P(OMe)_3$ or $PPh(OMe)_2$ ligands. However, in the case of **5** ($R = C_6H_2Pr^i_3$-2,4,6; $L = P(OMe)_3$), four isopropyl-C*H* protons are clearly observed as two septets ($^3J(HH)$ 4.5 Hz) at δ 3.55 and 3.35 ppm, whereas for **5** ($R = CNMe$, $L = PPh(OMe)_2$), a singlet at δ 3.29 ppm is assigned to the methyl group of one of the isocyanide ligands.

Final comments

This study has demonstrated the utility of a route to benzoyldiazenido or dinitrogen complexes of Re with phosphonites as co-ligands from a chelating benzoyldiazenido precursor, a route previously established [1–4] for complexes with ligating phosphines or, rarely, phosphite ligands. It has also extended this route to preparation of novel phosphite/phosphine complexes of N_2.

The dinitrogen complexes can be synthesized by a one-pot method from $[ReCl_2(NNCOPh)(PPh_3)_2]$ in the presence of hot methanol, the intermediate benzoyldiazenido complexes being isolated if the use of hot methanol is avoided. In spite of the usually low lability of N_2 towards displacement reactions in neutral Re^I–N_2 complexes [6,7], the dinitrogen complexes involved in this study, containing labile phosphonite or phosphite co-ligands, serve as convenient precursors for triisocyanide complexes of Re^I, containing these co-ligands, these complexes being formed readily at room temperature possibly following an initial replacement of such ligands by isocyanide. Therefore, the reactions of dinitrogen complexes of rhenium(I) with isocyanides, which were previously known to give mono- [6a] and di-isocyanide [6b,7] compounds, have now been extended to provide a convenient route to triisocyanide complexes of Re^I.

Experimental

All the reactions were carried out by standard inert-gas flow and vacuum techniques. Solvents were purified by standard techniques. IR spectra were recorded on a Perkin Elmer 683 spectrometer. NMR spectra were recorded on a JEOL EC 100 or a Bruker CXP-300 spectrometer.

$[ReCl_2(NNCOPh)(PPh_3)_2]$ was prepared by literature methods [2,3], as were the isocyanides CNMe [15] and CNC_6H_4Me-4 [16], whereas $CNC_6H_2Pr^i_3$-2,4,6 was a gift from Dr. R. Herrmann (University of Munich). The organophosphites, $P(OMe)_3$ and $P(OEt)_3$, were purchased from Merck and BDH, respectively, and the organophosphonites $PPh(OMe)_2$ and $PPh(OEt)_2$ from Aldrich.

[ReCl(N$_2$)(PPh$_3$){P(OMe)$_3$}$_3$](1, L = P(OMe)$_3$). Trimethylphosphite (2.00 cm^3, 16.9 mmol) was added to a suspension of $[ReCl_2(NNCOPh)(PPh_3)_2]$ (2.00 g, 2.19 mmol) in C_6H_6 (80 cm^3) and the mixture was refluxed for 2 h. The orange-yellow solution was then concentrated under reduced pressure to leave an oil (ca. 2 cm^3), MeOH (80 cm^3) was added, and the mixture heated. The solution was again concentrated at a temperature close to the boiling point of MeOH. Complex **1** ($L = P(OMe)_3$) separated as yellow crystals which were filtered off, washed with a 1/4 mixture of MeOH and Et_2O (4×1 cm^3), and dried in vacuo (ca. 40% yield).

Complex **1** (L = $P(OMe)_3$) was also obtained, by a less convenient route, from the reaction of the benzoyldiazenido compound $[ReCl_2(NNCOPh)\{P(OMe)_3\}_3]$ (0.200 g, 0.026 mmol) with PPh_3 (10 mg, 0.038 mmol) in refluxing MeOH (30 cm^3) for ca. 1 h; concentration of the solution to ca. 1 cm^3 followed by addition of Et_2O gave a precipitate of **1** (L = $P(OMe)_3$).

$[ReCl(N_2)(PPh_3)\{P(OEt)_3\}_3]$ (1, L = $P(OEt)_3$). Triethylphosphite (1.00 cm^3, 5.76 mmol) was added to a suspension of $[ReCl_2(NNCOPh)(PPh_3)_2]$ (0.50 g, 0.54 mmol) in C_6H_6 (30 cm^3) and the mixture was refluxed for 2 h. The solution was then concentrated under reduced pressure to ca. 3 cm^3, EtOH (25 cm^3) and MeOH (10 cm^3) were added, and the mixture was heated. The solution was again concentrated, with heating. Complex **1** (L = $P(OEt)_3$) separated as a yellow crystals, which were filtered off, washed with $MeOH/Et_2O$ (2 × 1 cm^3), and dried in vacuo (ca. 10% yield).

$[ReCl(N_2)(PPh_3)\{PPh(OEt)_2\}_3]$ (1, L = $PPh(OEt)_2$). $PPh(OEt)_2$ (1.00 cm^3, 5.20 mmol) was added to a suspension of $[ReCl_2(NNCOPh)(PPh_3)_2]$ (0.50 g, 0.54 mmol) in C_6H_6 (30 cm^3) and the mixture was refluxed for 2 h. The solution was then concentrated under reduced pressure to ca. 5 cm^3, MeOH (30 cm^3) was added, and the mixture was heated. The solution was again concentrated, with heating, and complex **1** (L = $PPh(OEt)_2$) separated as a light brown solid, which was filtered off, washed with a 1/4 mixture of MeOH and Et_2O (2 × 1 cm^3), and dried in vacuo (ca. 10% yield).

$[ReCl(N_2)\{PPh(OMe)_2\}_4]$ (2). $PPh(OMe)_2$ (0.50 cm^3, 3.15 mmol) was added to a suspension of $[ReCl_2(NNCOPh)(PPh_3)_2]$ (0.50 g, 0.54 mmol) in C_6H_6 (50 cm^3) and the mixture was refluxed for 5 min. The orange solution was then concentrated under reduced pressure to ca. 5 cm^3, MeOH (50 cm^3) was added, and the mixture was heated. The solution was again concentrated, with heating, to ca. 10 cm^3, and complex **2** separated as a yellow crystalline solid on addition of Et_2O (20 cm^3). It was filtered off, washed with Et_2O, dried in vacuo, then recrystallized from THF/Et_2O (ca. 70% yield).

$[ReCl_2(NNCOPh)\{PPh(OEt)_2\}_3]$ (3). $PPh(OEt)_2$ (1.3 cm^3, 6.54 mmol) was added to a suspension of $[ReCl_2(NNCOPh)(PPh_3)_2]$ (1.00 g, 1.09 mmol) in C_6H_6 (25 cm^3) and the mixture was refluxed for 1–2 h. The final orange solution was then concentrated under reduced pressure to ca. 5 cm^3 and MeOH (20 cm^3) was added without heating. The solution was concentrated without heating a complex **3** separated as an orange solid, which was filtered off, thoroughly washed with Et_2O (6 × 5 cm^3), and dried in vacuo (ca. 30% yield).

$[ReCl_2(NNCOPh)(PPh_3)_2\{PPh(OMe)_2\}]$ (4). $PPh(OMe)_2$ (0.50 cm^3, 3.15 mmol) was added to a suspension of $[ReCl_2(NNCOPh)(PPh_3)_2]$ (0.55 g, 0.60 mmol) in $C_6H_5CH_3$ (50 cm^3) and the mixture was stirred at room temperature for 1 h. The orange solution was then concentrated under reduced pressure, MeOH was added and the solution was again concentrated, without heating. Complex **4** separated as an orange solid which was filtered off, washed with Et_2O (2 × 5 cm^3), and dried in vacuo (ca. 30% yield).

$[ReCl(CNR)_3L_2]$ (5, R = C_6H_4Me-4 or $C_6H_2Pr^i_3$-2,4,6, L = $P(OMe)_3$; R = Me, L = $PPh(OMe)_2$). These complexes were best prepared by the reactions of the parent dinitrogen compounds **1** (L = $P(OMe)_3$, for the synthesis of **5** (R = C_6H_4Me-4 or $C_6H_2Pr^i_3$-2,4,6, L = $P(OMe)_3$) or **2** (for the synthesis of **5** (R = Me, L = $PPh(OMe)_2$)) with an excess (4.5/1 to 6/1) of the appropriate isocyanide. A typical

procedure for the preparation of **5** (R = Me, L = $PPh(OMe)_2$) was carried out as follows.

CNMe (0.10 cm^3, 2.1 mmol) was added to a solution of $[ReCl(N_2)\{PPh(OMe)_2\}_4]$ (0.34 g, 0.36 mmol) in THF (35 cm^3) and the mixture was stirred for 2 h at room temperature, then filtered and concentrated under reduced pressure to leave a brown oil. CH_2Cl_2 or THF (ca. 1 cm^3) was added, followed by Et_2O, which gave a precipitate of complex **5** (R = Me, L = $PPh(OMe)_2$) as a brown solid. This was filtered off, washed with Et_2O, and dried in vacuo (ca. 40% yield).

Complexes **5** (R = C_6H_4Me-4 or $C_6H_2Pr^i_3$-2,4,6, L = $P(OMe)_3$) were also obtained, though less conveniently, by reaction of the benzoyldiazenido complex $[ReCl_2(NNCOPh)\{P(OMe)_3\}_3]$ with the appropriate isocyanide (in a 4 to 5 molar excess) in refluxing MeOH. In a typical example, CNC_6H_4Me-4 (0.135 g, 1.15 mmol) was added to a suspension of $[ReCl_2(NNCOPh)\{P(OMe)_3\}_3]$ (0.18 g, 0.23 mmol) in MeOH (20 cm^3) and the mixture was refluxed for 2 h. The yellow solution was then concentrated under reduced pressure to leave a brown oil. Addition of Et_2O followed by 40–60 °C/of petroleum ether caused precipitation of impure $[ReCl(CNC_6H_4Me\text{-}4)_3\{P(OMe)_3\}_2]$ contaminated with $[NH_3C_6H_4Me\text{-}4]Cl$. The rhenium complex was recrystallized from CH_2Cl_2/Et_2O (ca. 20% yield).

mer-[ReCl(N$_2$)(CNMe){P(OMe)$_3$}$_3$]. This complex was previously [10] prepared by reaction of $[ReCl_2(NNCOPh)\{P(OMe)_3\}_3]$ with CNMe in boiling MeOH. In the present study it was obtained in the following way.

A solution of *mer*-$[ReCl(N_2)(PPh_3)\{P(OMe)_3\}_3]$ (0.25 g, 0.28 mmol) in THF (35 cm^3) was treated with CNMe (0.020 cm^3, 0.40 mmol) and the mixture was stirred at room temperature for 5 h then concentrated in vacuo to ca. 15 cm^3, and 30–40 °C petroleum ether (ca. 30 cm^3) was added, to give a precipitate of *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$, which was filtered off and recrystallized from THF/Et_2O (ca. 0.11 g, 59% yield).

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