Deprotonation reactions of the aminocarbyne complex *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$ (dppe = $Ph_2PCH_2CH_2PPh_2$). Synthesis and properties of the cyano-complexes *trans*-$[Re(CN)L(dppe)_2]$ (L = NCR, N_2, CO or C=CHPh) and crystal structure of *trans*-$[Re(CN)(NCMe)(dppe)_2]Pr^iOH$

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The reaction of the aminocarbyne complex *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$ with NBu_4OH, under N_2 or CO, afforded the cyano-dinitrogen or -carbonyl compound *trans*-$[Re(CN)L(dppe)_2]$ (L = N_2 or CO), respectively, whereas in the presence of an organonitrile or of phenylacetylene (under argon) the nitrile or the vinylidene complexes *trans*-$[Re(CN)L(dppe)_2]$ (L = NCMe, NCPh, NCC_6H_4Me-4 or C=CHPh, respectively) were obtained. Spectroscopic, FAB mass spectrometric and electrochemical data are reported and discussed in terms of the structural and electronic properties of these complexes. Electrochemical parameters which measure the electron richness and the polarizability of the *trans*-$\{Re(CN)(dppe)_2\}$ centre have been estimated and the cyanide ligand shown to present a very low capacity to buffer changes in the electron density at the metal upon changing the *trans* ligand. The crystal structure of *trans*-$[Re(CN)(NCMe)(dppe)_2]\cdot Pr^iOH$ has been determined.

The co-ordination chemistry of the simplest aminocarbyne group CNH_2, together with that of CNH and CN^-, is of particular significance for obtaining an insight into the possible mechanism of the reduction of aqueous cyanide to methylamine, methane and ammonia by nitrogenase.[1] Moreover, and in contrast with the significant number of known complexes with secondary, CNHR (R = alkyl or aryl),[2,3] and tertiary, CNR_2,[3,4] aminocarbyne ligands, only very rare examples of CNH_2 ligating a single metal centre are known.[5,6] In addition, there has been a recent growth of interest[7] in the development of organometallic chemistry based on the cyano and CNH groups which should interconvert into CNH_2. The complex *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$ **1** was the first containing the CNH_2 ligand to be reported and its molecular structure was authenticated by a single-crystal X-ray diffraction analysis.[5] It was prepared[5] by reaction of HBF_4 with *trans*-$[ReCl(CNSiMe_3)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) (upon N–Si bond cleavage to form $SiMe_3F$), in tetrahydrofuran (thf) or toluene, although it could also be obtained by protonation of the hydrogen isocyanide complex *trans*-$[ReCl(CNH)(dppe)_2]$. Moreover, the electrochemical behaviour of **1** was investigated[8] in detail and shown to involve anodically induced deprotonation to give the corresponding oxidized hydrogen isocyanide compound *trans*-$[ReCl(CNH)(dppe)_2]^+$. The acidity of the CNH_2 ligand was promoted by oxidation leading to the formation of CNH; similarly, oxidation of the latter complex also resulted in proton loss to give the oxidized cyano-complex $[ReCl(CN)(dppe)_2]^+$.[8] The mechanism of the electrode process was investigated by digital simulation[8] of the cyclic voltammograms which indicated that the acidity constant of the CNH_2 group increased by a factor of *ca.* 4×10^9 upon single-electron oxidation of **1** in NCMe. Anodically induced CNH_2 to CN conversion was also reported[6] for *trans*-$[MCl(CNH_2)(dppe)_2]$ (M = Mo or W) to give *trans*-$[MCl(CN)(dppe)_2]$.

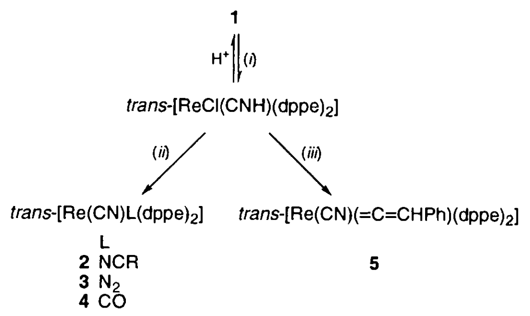
In the present study we have investigated the purely chemical deprotonation (by base) of CNH_2 in complex **1** without involving its activation by electron-transfer (oxidation) and succeeded in obtaining, in the presence of suitable substrates, a variety of cyano-complexes. The crystal structure of one, *trans*-$[Re(CN)(NCMe)(dppe)_2]\cdot Pr^iOH$, is also reported.

Results and Discussion

Syntheses

Treatment of a CH_2Cl_2 solution of *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$ **1** with NEt_3 (either in an equivalent amount or in excess) leads to formation of the hydrogen isocyanide complex *trans*-$[ReCl(CNH)(dppe)_2]$ which, upon addition of HBF_4, undergoes protonation to regenerate the parent **1** [Scheme 1(*i*)]. These reactions can be conveniently monitored by ^{31}P NMR spectroscopy which clearly shows the replacement of the singlet resonance of **1** at δ −114.5, relative to $P(OMe)_3$, by that of the hydrogen isocyanide complex at δ −108.6, upon addition of NEt_3, and the reverse process following acidification by HBF_4.

The use of an excess of NEt_3 does not appear to lead to



Scheme 1 (*i*) B, $-HB^+$; (*ii*) OH^-, L(NCR, N_2 or CO), −HCl; (*iii*) OH^-, HCCPh, argon, −HCl

further deprotonation beyond the hydrogen isocyanide state. However, by treatment of a thf or CH_2Cl_2 solution of **1**, and under N_2, with NBu_4OH (in alcoholic solution) a stronger base than the amine, in the presence of an adequate substrate, deprotonation of the hydrogen isocyanide occurs as well as substitution of the chloride ligand to give a variety of cyano complexes, in particular *trans*-[Re(CN)L(dppe)$_2$] **2** (L = NCMe, NCPh or NCC_6H_4Me-4) and **4** (L = CO) formed in the presence of the appropriate organonitrile or CO, respectively) and *trans*-[Re(CN)(N_2)(dppe)$_2$] **3**, if the reaction is carried out in the absence of any substrate apart from N_2 [Scheme 1(*ii*)]. In addition, by treating the aminocarbyne complex **1** with base in the presence of phenylacetylene, HC≡CPh, in an argon atmosphere, the vinylidene complex *trans*-[Re(CN)(=C=CHPh)(dppe)$_2$] **5** is the obtained product [reaction (*iii*)]. Therefore, the processes depicted in Scheme 1 (*ii*) and (*iii*) involve dehydrochlorination of *trans*-[ReCl(CNH)(dppe)$_2$] with the strong base. A related process occurs for the hydridochloride complex [$WH_2Cl_2(PMe_2Ph)_4$] which dechlorinates with base (NEt_3) in the presence of a suitable substrate L (CO, N_2, CNR, *etc.*) to form a range of complexes of L.[9] However, in our case, the CNH ligand rather than the metal is the site which undergoes deprotonation.

The Re–Cl bond is labilized by deprotonation of the hydrogen isocyanide ligand conceivably forming the anionic intermediate [ReCl(CN)(dppe)$_2$]$^-$ which is known[10] to have a low stability in solution. The related and unstable [$ReCl_2$(dppe)$_2$]$^-$ complex, electrochemically generated by single-electron reduction of the neutral dichloro species, readily undergoes Re–Cl bond cleavage[11] to give the known[12] unsaturated compound [ReCl(dppe)$_2$]. Strong π-electron acceptors are not stabilizing those anionic 18-electron complexes, in contrast with the related (and more stable) cyanide and other pseudohalide complexes [NBu_4][MX(N_2)(dppe)$_2$] (M = Mo or W; X = CN, SCN or N_3), with a dinitrogen ligand, which have been obtained[13] by reaction of *trans*-[M(N_2)$_2$(dppe)$_2$] with NBu_4X.

The labilized chloride ligand in the unstable [ReCl(CN)(dppe)$_2$]$^-$ intermediate is then easily replaced by a π-electron acceptor such as an organonitrile, dinitrogen, CO or an alkyne to give products **2**–**5**, respectively. Hence, the conceivable sequence of reaction steps is [M′ = Re(dppe)$_2$]:

$$[M'Cl(CNH)] \xrightarrow[-H^+]{\text{Base}} [M'Cl(CN)]^- \xrightarrow{-Cl^-} [M'(CN)] \xrightarrow{L} [M'(CN)L]$$

The greater labilization of the Re–Cl relative to the Re–CN bond in [ReCl(CN)(dppe)$_2$]$^-$ is consistent with the expected stronger ability of cyanide, compared to the stronger net electron donor chloride, to stabilize the electron-rich d^6 rhenium centre. Attempts to isolate the five-co-ordinate intermediate [Re(CN)(dppe)$_2$] by performing the reaction with base under argon were not successful. Its generation, although under FAB mass spectrometry conditions, was detected in this work (see below).

Moreover, in the case of the reaction with phenylacetylene [Scheme 1(*iii*)] a 1,2-hydrogen migration from the terminal to the adjacent unsaturated carbon atom of the alkyne has also occurred to form the vinylidene complex **5**. Such a rearrangement has previously been observed in comparable systems, *e.g.* in the reaction of alk-1-ynes (HC≡CPh) with *trans*-[ReCl(N_2)(dppe)$_2$] to give the corresponding vinylidene complexes *trans*-[ReCl(=C=CHPh)(dppe)$_2$];[14] a related 1,3-hydrogen migration process is also known[15] to occur in the reaction of phenylpropyne (PhC≡CMe) with *trans*-[ReCl(N_2)(dppe)$_2$] to form the η^2-allene complex *trans*-[ReCl(CH_2C=CHPh)(dppe)$_2$]. These processes can be rationalized[14–16] by considering the destabilizing interaction between a metal filled d orbital, at the electron-rich d^6 rhenium(I) centre, and the filled $\pi_\perp$ orbital of a binding alkyne, which results in the conversion of the alkyne into an organic ligand (vinylidene or η^2-allene) in which such a destabilizing interaction is no longer present.

The current work indicates that the electron-rich *trans*-{Re(CN)(dppe)$_2$} centre is also capable of inducing hydrogen migration at an alkyne. The present rearrangement occurs at that metal centre rather than at the related *trans*-{ReCl(dppe)$_2$} site in view of the more favourable formation of the former, relatively to the latter, from [ReCl(CN)(dppe)$_2$]$^-$ due to the higher substitution lability of chloride compared with cyanide at the metal site (see above).

Complexes **2** were isolated as green (L = NCMe), orange (L = NCC_6H_4Me-4) or red (L = NCPh) solids, whereas **3** (L = N_2) is yellow, **4** (L = CO) pale yellow and **5** (L = CCHPh) greenish red. They were characterized by IR, ^1H, ^{31}P and ^{13}C NMR spectroscopies, elemental analysis, FAB MS spectrometry and electrochemical studies, as well as, for **2** (L = NCMe), by a single-crystal diffraction study.

Infrared spectroscopic data

Analytical and IR spectroscopic data for these complexes are presented in Table 1. In the solid-state IR spectra (KBr pellets) they show a medium or strong band assigned to C≡N stretching of the cyanide ligand, in the region 2070–1995 cm^{-1}. In addition, the medium or strong band observed at 2220–2145 (complexes **2**), 1995 (**3**), 1825 (**4**) or 1570 and 1550 cm^{-1} (**5**) is attributed to ν(N≡C), ν(N≡N), ν(CO) or ν(C=C) of the nitriles, dinitrogen, carbonyl or vinylidene ligands, respectively.

The wavenumber decrease of the NC stretching vibration of NCR upon co-ordination (between −90 and −80 cm^{-1}) is indicative of a high π-electron releasing ability of the *trans*-{Re(CN)(dppe)$_2$} centre. A similar trend was observed[17] for complexes *cis*-[ReCl(NCR)(dppe)$_2$]. Hence, at such electron-rich metal centres the π-electron effect overcomes that of the σ-electron release from the ligand to the metal [the latter effect leads to an increase in ν(NC) upon co-ordination]. Moreover, ν(N≡N) for complex **3**, ν(CO) for **4** and ν(C=C) for **5** are higher than those observed (1945, 1800 and 1532 cm^{-1}, respectively) for the analogous chloride compounds *trans*-[ReCl(L)(dppe)$_2$] (L = N_2, CO or C=CHPh), suggesting that in the former complexes the unsaturated ligands behave as weaker π-electron acceptors than in the latter, thus supporting that the π-electron-releasing character of the *trans*-rhenium chloride centre exceeds that of the *trans*-rhenium cyanide analogue.

In all the complexes the cyano-ligand exhibits ν(CN) at significantly lower values than that observed for free cyanide (*ca.* 2150 cm^{-1} for NBu_4CN), as a result of its π-electron acceptance from the electron-rich metal centre. Moreover, the ν(CN) values are higher than that (1945 cm^{-1})[10] of the related anionic [ReCl(CN)(dppe)$_2$]$^-$ species with a stonger π-electron-releasing metal site.

Multinuclear NMR data

In the ^1H NMR spectra (in CD_2Cl_2) the phenyl resonances occur as sets of complex multiplets which are resolved only for the phenyl protons of the aromatic nitrile or vinylidene ligands (Table 2). Hence, for **2** (L = NCC_6H_4Me-4) the upfield doublet at δ 6.05 (integrating for two protons) in the phenyl region appears to be the high-field half of an AB or AA′BB′-type pattern resulting from the expected[18] inequivalence of the nitrile aromatic protons; the lower-field half of this pattern being buried under the remaining phenyl signals. Similarly, the doublet at δ 6.13 of the benzonitrile complex is assigned to the phenyl *o*-protons of the nitrile ligand.

The *trans* configuration is assigned to the complexes in view of the observed singlet in the ^{31}P NMR spectra (Table 2). In accord with this geometry, the ^1H NMR spectra of these

Table 1 Physical data for *trans*-[Re(CN)L(dppe)$_2$] **2** (L = NCMe, NCC$_6$H$_4$Me-4 or NCPh), **3** (L = N$_2$), **4** (L = CO) and **5** (L = CCHPh)

	IR/cm^{-1}		Analysis (%)^b		
L	ν(C≡N)^a	ν(N≡C), ν(N≡N)^a or other	C	N	H
NCMe^c	2000m	2220m (br) ν(N≡C)	62.3 (62.9)	3.0 (3.0)	5.2 (4.9)
	1995 (sh)	2210m (br) ν(N≡C)			
NCC$_6$H$_4$Me-4^d	2005s	2140s ν(N≡C)	64.5 (65.1)	2.3 (2.5)	5.6 (5.0)
NCPh^e	2005s	2145s ν(N≡C)	61.5 (61.2)	2.7 (2.3)	5.2 (4.6)
N$_2$^{f}	2015s	1995s ν(N≡N)	61.1 (61.3)	3.5 (3.8)	4.9 (5.2)
CO^g	1995m	1825s ν(CO)	59.1 (59.3)	1.4 (1.2)	4.8 (5.3)
=C=CHPh^g	2070	1570m ν(C=C)	62.8 (63.6)	1.4 (1.2)	5.1 (5.5)
		1550m ν(C=C)			

^{a} In KBr pellets; values ±2.5; s = strong, m = medium, sh = shoulder, br = broad. ^{b} Required values in parentheses. ^{c} With 0.25 NCMe of crystallization. ^{d} With 0.25 thf of crystallization. ^{e} With CH$_2$Cl$_2$ of crystallization. ^{f} With 0.5 thf·0.5Et$_2$O of crystallization. ^{g} With 3MeOH of crystallization.

Table 2 Proton and ^{31}P-{^{1}H} NMR data for *trans*-[Re(CN)L(dppe)$_2$] **2** (L = NCMe, NCC$_6$H$_4$Me-4 or NCPh), **3** (L = N$_2$), **4** (L = CO) and **5** (L = CCHPh)

L	δ(^{1}H)^a	Assignment^a	δ(^{31}P)^b
NCMe	7.56 (br, 6 H)	Ph (dppe)	−106.90
	7.07 (m, br, 28 H)		
	6.41 (br, 6 H)		
	2.69 (br, 4 H)	CH$_2$ (dppe)	
	2.56 (br, 4 H)		
	1.25 (d, 3 H)	Me (nitrile)	
NCC$_6$H$_4$Me-4	7.79 (d, br, 6 H)^c	Ph (dppe + H$_A$ nitrile)	−110.60
	7.22–6.85 (m, 30 H)		
	6.67 (d, br, 6 H)^c		
	6.05 (d, 2 H)^d	H$_B$ (nitrile)	
	2.42 (br, 8 H)	CH$_2$ (dppe)	
	1.15 (s), 1.13 (s) (3 H)	Me (nitrile)	
NCPh	7.76 (br, 6 H)	Ph (dppe + H$_m$ of nitrile + H$_p$ of nitrile)	−110.85
	7.25–6.84 (m, 31 H)		
	6.68 (br, 6 H)		
	6.13 (d, 2 H)^e	H$_o$ (nitrile)	
	2.42 (br, 8 H)	CH$_2$ (dppe)	
N$_2$	7.72 (m, br, 6 H)	Ph (dppe)	−112.80
	7.26–7.01 (m, 28 H)		
	6.61 (m, br, 6 H)		
	2.45 (t, 8 H)^f	CH$_2$ (dppe)	
CO	7.52–6.08 (m, 40 H)	Ph (dppe)	−112.50
	2.45 (m, br, 8 H)	CH$_2$ (dppe)	
=C=CHPh	7.56 (br, 6 H)	Ph (dppe)	−113.95
	7.28–6.94 (m, 34 H)		
	6.66 (t, 2 H)^g	H$_m$	
	6.53 (t, 1 H)^g	H$_p$ (=C=CH*Ph*)	
	5.75 (d, 2 H)^h	H$_o$	
	2.62 (br, 8 H)	CH$_2$ (dppe)	
	0.55 (qnt, 1 H)^i	C=C*H*Ph	

^{a} In CD$_2$Cl$_2$; δ in ppm relative to internal SiMe$_4$; s = singlet, d = doublet, t = triplet, qnt = quintet, m = multiplet, br = broad; subscripts A and B denote part A and B of an AB-type pattern, *o*, *m* and *p* the *o*-, *m*- and *p*-protons of phenyl, respectively. ^{b} In CH$_2$Cl$_2$; δ in ppm relative to external P(OMe)$_3$. ^{c} ^3J(HH) [or ^3J(HP)] = 6.9 Hz. ^{d} ^3J(HH) = 8.1 Hz. ^{e} ^3J(HH) = 7.2 Hz. ^{f} 7.8 Hz (virtual coupling to phosphorus nuclei). ^{g} ^3J(HH) = 7.1 Hz. ^{h} ^3J(HH) = 7.7 Hz. ^{i} ^4J(HP) = 5.3 Hz.

complexes do not show the high-field triplet pattern normally exhibited in the phenyl region by *cis*-dppe complexes.[19] The resonances of the dppe-methylene protons usually appear as broad signals, but for complex **3** they are resolved into a triplet (7.8 Hz) due to coupling to the ^{31}P nuclei.

In the ^{13}C NMR spectra (both ^{1}H-decoupled and the -coupled) of complexes **2** (Table 3) the broad singlet resonances observed at δ *ca.* 115–113 are assigned to the NCR carbon, being slightly upfield (*ca.* 4 ppm) relative to those of the corresponding free nitriles. The other aromatic nitrile carbon resonances were assigned by comparison with those of the free species. For the vinylidene complex **5** the carbene carbon resonance is at δ 316.08, *i.e.* at lower field than those observed (δ 284.7 and 296.9)[14] for the related chloro-complexes *trans*-[ReCl(=C=CHR)(dppe)$_2$] (R = CO$_2$Et and Bu^t, respectively), possibly in accord with the weaker net electron-donor ability of the *trans* cyanide ligand in the former complex compared with chloride in the latter.

The methylene carbon resonance of the diphosphines usually appear as a singlet in the ^{13}C-{^{1}H} NMR spectrum (at δ *ca.* 32), but for **2** (L = NCPh) it is resolved into a quintet (*ca.* 11 Hz) due to coupling to the four ^{31}P nuclei. Two singlet resonances are observed in the ^{13}C-{^{1}H} NMR spectra for each type of dppe aromatic carbon, which, with the exception of the *ipso*-carbons (which appear at the lowest field, δ *ca.* 140 and 137), split into the expected multiplets in the corresponding ^{1}H-coupled spectra [see Fig. 1, for **2** (L = NCC$_6$H$_4$Me-4)]. The appearance of two sets of phenyl-carbon resonances can tentatively associate to the two sets of phenyl rings observed in the solid state (Fig. 4), four of which are situated above the equatorial plane of the molecule, on the side of the acetonitrile ligand, whereas the other four are on the opposite side, towards

Table 3 $^{13}C-\{^1H\}$ and ^{13}C NMR data[a] for *trans*-[Re(CN)L(dppe)$_2$] **2** (L = NCMe, NCC_6H_4Me-4 or NCPh) and **5** (L = CCHPh)

L	δ	$^{13}C-\{^1H\}$	^{13}C	$J(CH)[^2J]$/Hz	Assignment
NCMe	140.73	m, br	br	—	C_i (dppe)
	137.66	m, br	br	—	C'_i (dppe)
	134.74	s	dm	162.5	C_m (or C_p) (dppe)
	132.32	s	dm	160.7	C'_m (or C'_p) (dppe)
	128.84	s	dt	160.7 [5.8]	C_p (or C_m) (dppe)
	128.02	s	dt	169.7 [7.9]	C'_p (or C'_m) (dppe)
	127.73	s	dd	159.4 [7.4]	C_o (dppe)
	127.52	s	dd	160.1 [7.1]	C'_o (dppe)
	32.48	br	tm	156.7	CH_2 (dppe)
	25.57	s	q	125.9	CH_3 (nitrile)
NCC_6H_4Me-4	140.40	s	br	—	C_p (nitrile)
	140.13	br	br	—	C_i (dppe)
	136.94	br	br	—	C'_i (dppe)
	134.59	s	dt	151.9 [6.8]	C_m (or C_p) (dppe)
	132.59	s	dt	153.8 [6.8]	C'_m (or C'_p) (dppe)
	132.06	s, br	n.o.[b]	—	C_o (nitrile)
	129.03	s	n.o.[b]	—	C_m (nitrile)
	128.93	s	dt	160.06 [7.0]	C_p (or C_m) (dppe)
	128.24	s	dt	161.27 [7.5]	C'_p (or C'_m) (dppe)
	128.08	s	dd	161.27 [7.4]	C_o (dppe)
	127.52	s	dd	160.0 [7.5]	C'_o (dppe)
	112.46	s	s, br	—	N*C*R
	32.44	s, br	t, br	134.3	CH_2 (dppe)
	25.58	s	q	128.4	CH_3 (nitrile)
NCPh	140.03	br	br	—	C_i (dppe)
	136.63	br	br	—	C'_i (dppe)
	134.57	s	d, br	153.9	C_m (or C_p) (dppe)
	132.61	s	d, br	158.8	C'_m (or C'_p) (dppe)
	132.10	s	dm	163.8	C_p (nitrile)
	129.51	s	dt	159.9 [7.7]	C_m (nitrile)
	128.99	s	dt	160.1 [7.5]	C_p (or C_m) (dppe)
	128.31	s	dt	157.8 [6.5]	C'_p (or C'_m) (dppe)
	128.12	s	dm	159.5	C'_o (dppe)
	127.56	s	dm	158.8	C_o (dppe)
	115.69	s	s, br	—	N*C*R
	114.00	s	s	—	C_i (nitrile)
	32.42	qnt[c]	tm	131.8	CH_2 (dppe)
=C=CHPh[d]	316.08	s, br	n.o.	—	*C*=CHPh
	138.59–138.18	m	m, br	—	C_i (dppe)
	137.17–136.85	m	m, br	—	C'_i (dppe)
	134.51	s	d, br	161.9	C_m (or C_p) (dppe + vinylidene)
	134.01	s	d, br	165.2	C'_m (or C'_p) (dppe + vinylidene)
	129.53	s	d, br	155.8	C_p (or C_m) (dppe + vinylidene)
	129.32	s	d, br	161.8	C'_p (or C'_m) (dppe + vinylidene)
	127.00	s	d, br	158.9	C_o (dppe)
	32.90	qnt	t, br	141.5	CH_2 (dppe)

[a] In CD_2Cl_2; δ in ppm relative to $SiMe_4$; s = singlet, d = doublet, q = quartet, qnt = quintet, m = multiplet, br = broad, t = triplet, n.o. = not observed; subscripts *i*, *o*, *m* and *p* denote the *ipso*-, *ortho*-, *meta*- and *para*-carbons, respectively, of the phenyl rings. Two sets (one denoted with a prime) of dppe aromatic resonances are observed. [b] Buried under other phenyl carbon resonances. [c] Owing to virtual coupling (11 Hz) to the four equivalent phosphorus nuclei. [d] In the $^{13}C-\{^1H\}$ NMR spectrum other resonances are also observed at δ 144.42 (m, br), 121.45 (s) and 112.40 (s), possibly due to decomposition products.

the CN ligand, although a possible fluxional behaviour in solution can alter this situation.

FAB mass spectra

In the FAB mass spectra of the cyano compounds, run in 3-nitrobenzyl alcohol matrices, the corresponding molecular ions are clearly detected (see Fig. 2 for the cyano carbonyl complex) with the expected metal isotopic pattern. The ions $[Re(CN)(dppe)_2]^{\cdot +}$ and $[ReL(dppe)_2]^+$ are also detected in all the cases and are formed upon loss of the appropriate ligand (L or $CN^{\cdot}$) from the correspondent starting complexes, see the proposed general fragmentation pattern in Scheme 2.

Elimination of the diphosphine ligand can occur either at $[Re(CN)(dppe)_2]^{\cdot +}$ (*m/z* 1009) or $[ReL(dppe)_2]^+$ to give $[Re(CN)(dppe)]^{\cdot \bullet}$ (*m/z* 611) and $[ReL(dppe)]^+$, respectively. Hence, loss of the chelating diphosphine occurs only after elimination of the monodentate ligands (L or $CN^{\cdot}$), as known to occur in other cases[20] in accord with the greater co-ordination lability of the latter relative to the former ligands. The formation of $[Re(CN)(dppe)_2]^{\cdot +}$ from $[Re(CN)L(dppe)_2]^{\cdot \bullet}$ corresponds to the retrosynthetic process of the proposed formation (see above) of the latter complexes from the former.

The diphosphine ligand can undergo partial fragmentation still in the presence of one of the monodentate coligands and of the other diphosphine and its fragmentation processes are analogous for all the complexes, generally being initiated by either phenyl ($Ph^{\cdot}$) or $PPh_2^{\cdot}$ elimination. Loss of ethylene or PPh can be the following step, *e.g.* from $[Re(CN)(Ph_2PC_2H_4PPh)]^+$ (*m/z* 534) to form fragment ions at *m/z* 506 or 426, conceivably due to $[Re(CN)(PPh_2)(PPh)]^+$ and $[Re(CN)Ph_2PC_2H_4)]^+$, respectively. Further fragmentation can lead to rather unsaturated fragment ions such as $[Re(PPh)(PPh_2)]^{\cdot +}$ (*m/z* 480), $[Re(CN)(PPh)]^{\cdot \bullet}$ (*m/z* 321) and derived $[Re(PPh)]^+$ (*m/z* 295) or $[Re(PPh_2)]^{\cdot +}$ (*m/z* 372), as well as $[Re(NCMe)]^+$ (*m/z* 228) in the case of the acetonitrile complex.

Oxygenated rhenium ions are readily detectable as resulting from the molecular ion [for **2** (L = NCC_6H_4Me-4)] or from derived species containing either CN or L. Hence, *e.g.*, the ions at *m*/*z* 1025 and 1041 are possibly due to $[ReO(CN)(dppe)_2]^{\bullet +}$ and $[ReO_2(CN)(dppe)_2]^{\bullet +}$, respectively. Although corresponding species with oxygenated dppe (instead of oxygenated metal), *e.g.* $[Re(CN)(dppe{\cdot}O)(dppe)]^{\bullet +}$ and $[Re(CN)(dppe{\cdot}O)_2]^{\bullet +}$, could also be postulated, the formation of the former oxorhenium-(IV) or -(VI) complexes is well accounted for by the capacity of this metal easily to increase its oxidation state.

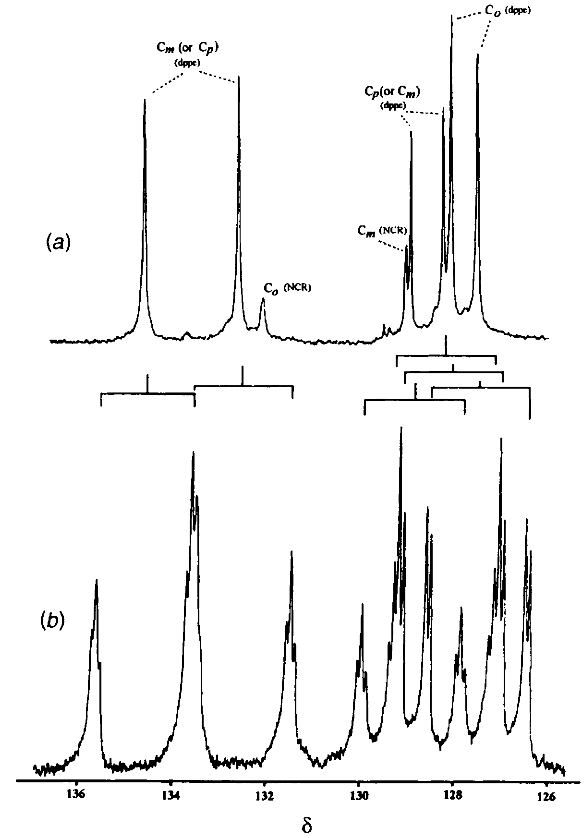


Fig. 1 (*a*) ^{13}C-{^1H} and (*b*) ^{13}C NMR spectra (partial phenyl region) of *trans*-$[Re(CN)(NCC_6H_4Me\text{-}4)(dppe)_2]$ in CD_2Cl_2

Moreover, alternative, but related, formulations could also be postulated instead of some of the others which have been proposed in Scheme 2. Rearrangement processes may be involved in some of the proposed pathways and, *e.g.*, the fragment ion at *m*/*z* 768, tentatively formulated as $[Re(CN)(PPh_2)_3]^+$, can alternatively be $[Re(CN)Ph(PPh)(PPh_2)_2]^+$. The formation of the latter is postulated *via* the transfer of a phenyl group from one of the PPh_2 ligands to the other, in the former ion, a process which can occur *via* the metal, as reported[21] for the complexes $[PtL_2(dppe)_2]$ (L = Me, Et or Ph).

Crystal structure of *trans*-$[Re(CN)(NCMe)(dppe)_2]$ 2 (L = NCMe)

The molecular structure of *trans*-$[Re(CN)(NCMe)(dppe)_2]$ has been confirmed by an X-ray diffraction study. The crystals also contain propan-2-ol molecules of solvation. The structure is depicted in Fig. 3, and selected bond lengths and angles are listed in Table 4.

The Re atom exhibits octahedral co-ordination with the four P atoms in the equatorial positions, whereas the terminal C and N atoms of the cyanide and acetonitrile ligands, respectively, occupy the apical positions. Both the CN^- and the NCMe ligands have essentially linear co-ordination [Re–C(1)–N(1) and Re–N(2)–C(2) 173.4(4) and 174.5(4)°, respectively], and the latter is also linear [N(2)–C(2)–C(3) 178.2(5)°].

The Re–C(1) (cyanide) distance [2.049(4) Å] is shorter than the expected Re–C single-bond length [2.13 Å, evaluated[22] as the sum of the single-bonded covalent radii of Re (1.53 Å) and sp C (0.60 Å)], and is similar to the Re–C (carbene) distance in the complex *trans*-$[ReCl({=}C{=}CHPh)(dppe)_2]$ [2.046(8) Å],[23] consistent (see above) with the expected π-electron release from the metal to the cyanide ligand. Hence, form **b** appears to

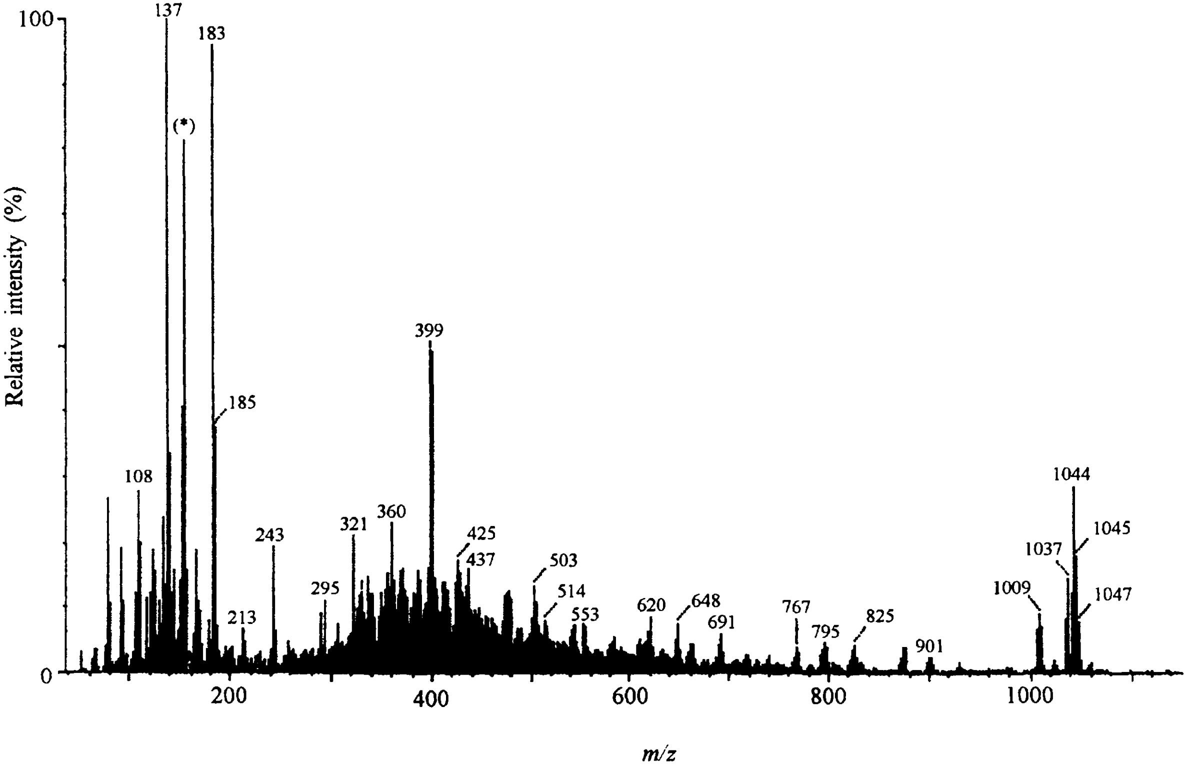
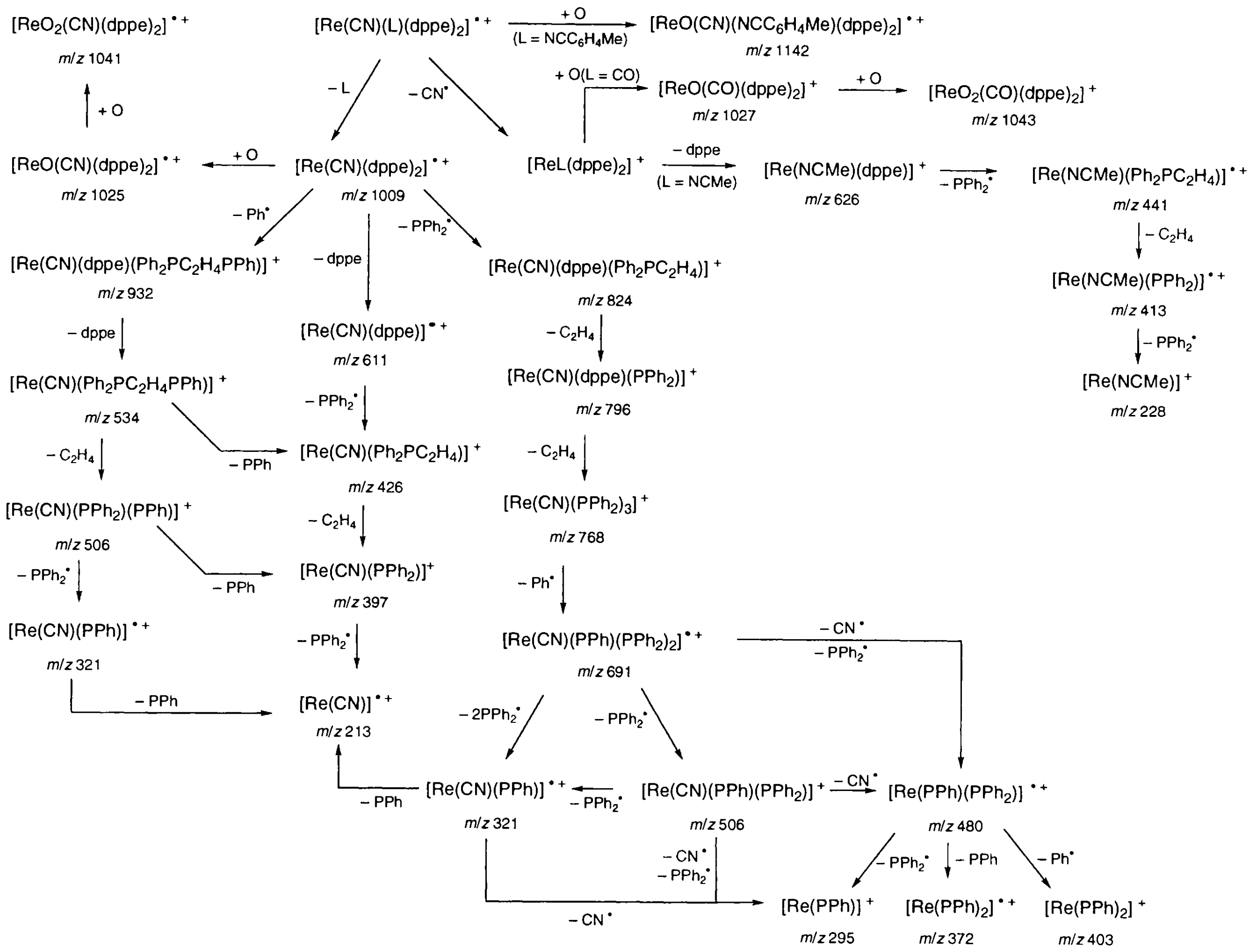


Fig. 2 The FAB mass spectrum of *trans*-$[Re(CN)(CO)(dppe)_2]$ **4**



Scheme 2 Proposed general fragmentation pattern for complexes *trans*-[Re(CN)L(dppe)$_2$] **2** (L = NCMe, NCC$_6$H$_4$Me-4 or NCPh), **3** (L = N$_2$), **4** (L = CO) and **5** (L = CCHPh) under FAB conditions

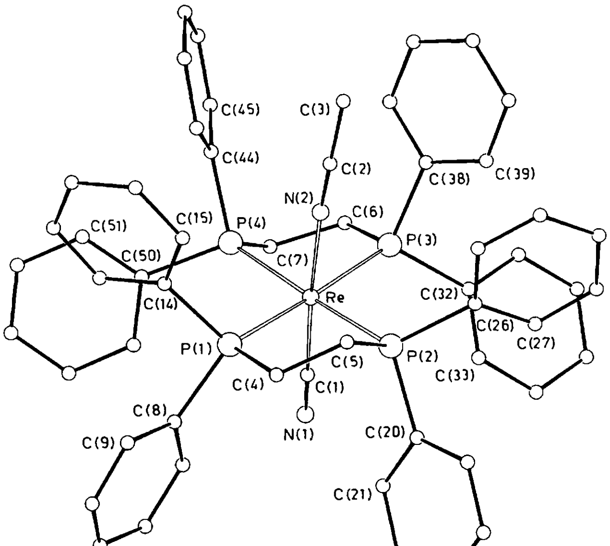


Fig. 3 Molecular structure of *trans*-[Re(CN)(NCMe)(dppe)$_2$]

Table 4 Selected bond distances (Å) and angles (°) with estimated standard deviations in parentheses for *trans*-[Re(CN)(NCMe)(dppe)$_2$]·Pr^{i}OH

About the Re atom			
Re–P(1)	2.393(1)	Re–P(4)	2.380(1)
Re–P(2)	2.392(1)	Re–C(1)	2.049(4)
Re–P(3)	2.371(1)	Re–N(2)	2.085(4)
P(1)–Re–C(1)	97.7(1)	P(1)–Re–N(2)	89.1(1)
P(2)–Re–C(1)	99.6(1)	P(2)–Re–N(2)	82.8(1)
P(3)–Re–C(1)	84.7(1)	P(3)–Re–N(2)	88.4(1)
P(4)–Re–C(1)	84.0(1)	P(4)–Re–N(2)	93.6(1)
N(2)–Re–C(1)	173.1(2)		
In the cyanide ligand			
N(1)–C(1)	1.175(6)	Re–C(1)–N(1)	173.4(4)
In the nitrile ligand			
N(2)–C(2)	1.145(6)	Re–N(2)–C(2)	174.5(4)
C(2)–C(3)	1.457(8)	N2–C(2)–C(3)	178.2(5)

present a significant weight in the valence-bond representation: Re–C≡N (**a**) ⟷ $\overset{+}{\text{Re}}$=C=$\overset{-}{\text{N}}$ (**b**). However, the C≡N bond length [1.175(6) Å] is not significantly different from that known (1.16 ± 0.01 Å) in the free cyanide.[24]

The Re–N (nitrile) distance [2.085(4) Å)] is similar to those observed in both *cis*- and *trans*-[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$]$^+$ [2.065(16) (average)[25] and 2.063(7) Å,[26] respectively], but higher than the unusually short one, 1.978(5) Å, in *trans*-[ReCl(NCMe)(dppe)$_2$].[27] This suggests a higher *trans* influence of the CN$^-$ ligand, relative to Cl$^-$, which is consistent with the IR results discussed above. However, the unsaturated N≡C bond lengths of NCMe for the rhenium cyanide and chloride complexes [1.145(6) and 1.141(9) Å,[27] respectively] are identical and do not reflect such an influence.

The average metal–phosphorus bond length, 2.384(1) Å, is shorter than those observed for the cationic complexes *trans*-

Table 5 Cyclic voltammetric data[a] for *trans*-[Re(CN)L(dppe)$_2$] **2** (L = NCMe, NCC$_6$H$_4$Me-4 or NCPh), **3** (L = N$_2$), **4** (L = CO) and **5** (L = CCHPh)

L	$^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$/V	$^{\mathrm{II}}E_{\frac{1}{2}}^{\mathrm{ox}}$/V
NCMe	−0.10	1.13
NCC$_6$H$_4$Me-4	−0.04	1.13
NCPh	−0.10	1.05
N$_2$[b]	0.57	1.54
CO	0.78	—
=C=CHPh	0.06	1.19

[a] In 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$ at a platinum disc (diameter = 0.5 mm) working electrode and at ambient temperature, except when stated otherwise. Potentials ±0.02 *vs.* SCE, measured by using [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ ($E_{\frac{1}{2}}^{\mathrm{ox}}$ = 0.55 V) as internal standard. [b] At −30 °C.

[Re(NCC$_6$H$_4$Me-4)$_2$(dppe)$_2$]$^+$ [2.401(3) Å][26] and *trans*-[ReCl(CNH$_2$)(dppe)$_2$]$^+$ [2.433(1)–2.478(1) Å],[5] reflecting the stronger π-electron release of the present neutral metal centre in comparison with the others.

Electrochemical behaviour

By cyclic voltammetry, in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$ at a platinum disc electrode, the complexes *trans*-[Re(CN)L(dppe)$_2$] undergo two successive single-electron reversible (or partially reversible) anodic processes to the corresponding rhenium-(II) and -(III) species, respectively. The single-electron transfers were also confirmed by controlled-potential electrolyses. Only the first anodic wave was detected for compound **4** (L = CO), since the second is expected to occur at an oxidation potential too high to be observed, *i.e.* above the detection limit imposed by oxidation of the background electrolyte solution. The study of the dinitrogen complex **3** had to be undertaken at low temperature (−30 °C) due to its instability in the electrolyte solution at higher temperatures. However, no permanent decomposition at ambient temperature was detected, since well defined cyclic voltammograms were obtained upon lowering the temperature.

For the nitrile complexes **2** the values of the oxidation potentials of both anodic waves (Table 5) span very narrow ranges [$^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$ from −0.04 to −0.10 V *vs.* saturated calomel electrode (SCE), and $^{\mathrm{II}}E_{\frac{1}{2}}^{\mathrm{ox}}$ from 1.13 to 1.05 V *vs.* SCE], indicating only a very limited dependence on the R group of the nitrile ligand. The oxidation potentials of the vinylidene complex **5** are only marginally higher than those of the nitrile compounds, but **3** (L = N$_2$) and **4** (L = CO) are oxidized at substantially higher potentials ($^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$ = 0.57 or 0.78 V, respectively) in accord with the stronger π-electron acceptor character of the N$_2$ and CO ligands compared with the nitriles. Moreover, these cyano-complexes exhibit higher oxidation potentials than the analogous compounds with the {ReCl(dppe)$_2$} site, *i.e.* *trans*-[ReCl(L)(dppe)$_2$] [L = NCC$_6$H$_4$Me-4 ($E_{\frac{1}{2}}^{\mathrm{ox}}$ = −0.13),[28] CCHPh (−0.16 V),[14] N$_2$ (0.28 V) or CO (0.62 V)]. The greater stabilization of the highest occupied molecular orbital (HOMO) in the cyano-complexes is in accord with the π-electron acceptor ability of the cyanide ligand in contrast with the electron-releasing character of chloride in the chloro-complexes. In addition and as expected, our neutral compounds **2**–**5** are oxidized at more anodic potentials than that of the anionic complex *trans*-[Re(CN)$_2$(dppe)$_2$]$^-$ ($E_{\frac{1}{2}}^{\mathrm{ox}}$ = −0.49 V),[10] whereas the related isocyanide complex *trans*-[Re(CN)(CNMe)(dppe)$_2$] has an oxidation potential ($E_{\frac{1}{2}}^{\mathrm{ox}}$ = 0.29 V)[10] which is intermediate between those of **2** and **3** thus following the known[29–32] net electron-acceptor ability of the corresponding unsaturated ligands: CO > N$_2$ > CNMe > CCHPh, NCR.

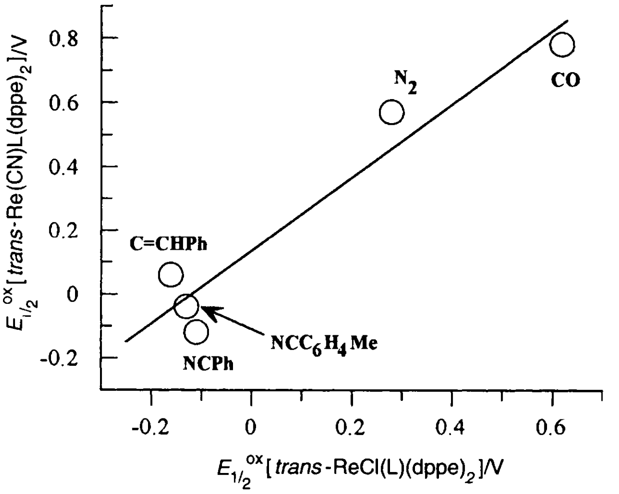


Fig. 4 Plot of $E_{\frac{1}{2}}^{\mathrm{ox}}$ of *trans*-[Re(CN)L(dppe)$_2$] *vs.* $E_{\frac{1}{2}}^{\mathrm{ox}}$ of *trans*-[ReCl(L)(dppe)$_2$] (L = CO, N$_2$, CCHPh, NCPh or NCC$_6$H$_4$Me). Potentials in *vs.* SCE. The values for the chloro complexes were taken from refs. 30–32

A systematic approach to quantify the redox potential–electronic structure relationship was initiated[29] for octahedral 18-electron complexes [M$_S$L] with a square-pyramidal metal site {M$_S$}. A linear relationship (1) was recognized between $E_{\frac{1}{2}}^{\mathrm{ox}}$

$$E_{\frac{1}{2}}^{\mathrm{ox}}(\mathrm{M_SL}) = E_\mathrm{S} + \beta P_\mathrm{L} \qquad (1)$$

and a ligand parameter P_L defined by equation (2), which

$$P_\mathrm{L} = E_{\frac{1}{2}}^{\mathrm{ox}}[\mathrm{Cr(CO)_5L}] - E_{\frac{1}{2}}^{\mathrm{ox}}[\mathrm{Cr(CO)_6}] \qquad (2)$$

constitutes a measure of the net electron π-acceptor/σ-donor character of the ligand L; E_S is the oxidation potential of the carbonyl complex [M$_S$(CO)] [equation (3)] and is considered a

$$E_\mathrm{S} = E_{\frac{1}{2}}^{\mathrm{ox}}[\mathrm{M_S(CO)}] \qquad (3)$$

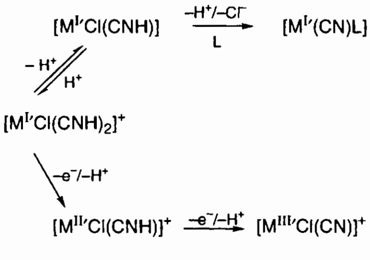
measure of the electron richness of the binding metal site {M$_S$} (a lower E_S value corresponding to a higher electron-rich character). The slope, β (polarizability of the metal centre) corresponds to the sensitivity of the energy of the HOMO to a change of the ligand L.

Hence, by definition [equation (3)],[29] the electron richness E_S of our metal site *trans*-{Re(CN)(dppe)$_2$} is 0.78 V and this value is higher than that (E_S = 0.62 V)[31] for the analogous chloro-centre *trans*-{ReCl(dppe)$_2$}, consistent with the results discussed above which indicate that the former metal centre is electronically poorer than the latter.

Moreover, a comparison between the values of $^{\mathrm{I}}E_{\frac{1}{2}}^{\mathrm{ox}}$ for the cyano complexes and those[30–32] of the rhenium chloride series [ReCl(L)(dppe)$_2$] (L = CO, N$_2$, CCHPh, NCPh or NCC$_6$H$_4$Me) is depicted in Fig. 4, indicating a rough linear variation expressed by equation (4) (correlation coefficient, *r*,

$$E_{\frac{1}{2}}^{\mathrm{ox}}[\mathrm{Re(CN)L(dppe)_2}] = 1.12\,E_{\frac{1}{2}}^{\mathrm{ox}}[\mathrm{ReCl(L)(dppe)_2}] + 0.14 \qquad (4)$$

0.934). Since the slope of this line (*ca.* 1.1 ± 0.1) should be the ratio of the polarizabilities (β) of the *trans*-{Re(CN)(dppe)$_2$} and *trans*-{ReCl(dppe)$_2$} sites [as concluded from the application of expression (1) to the corresponding series of complexes], and considering the known[31] value of the polarizability for the latter centre (β = 3.4), one can estimate the value of *ca.* 3.7 ± 0.5 for the polarizability of the cyanometal site. This is rather high, particularly in comparison with values commonly exhibited by other diphosphine metal centres,[29] indicating that in the cyano-centre the energy of



M′ = *trans*-Re(dppe)$_2$

Scheme 3

the HOMO is rather sensitive to a change in the electronic properties of the L ligand. In other words, the cyanide ligand has a high inability to buffer changes in the electron density at the metal induced by a change in the *trans* L ligand. This behaviour has been previously recognized[31] for the strong electron-donor chloride, whereas strong π-electron acceptors (such as N_2 or CO) behave in the opposite way.

Conclusion

The versatility of the aminocarbyne group at a chlororhenium phosphine centre, towards the generation of a variety of derived cyano species, is evident. Two main complementary routes can be followed [see Scheme 3, in which M′ = *trans*-Re(dppe)$_2$]: (i) a chemical one (presented in this work and apparently more versatile), involving stepwise deprotonation of CNH_2 by base (to form CNH and CN complexes) with concomitant labilization of the *trans*-Re–Cl bond leading to dehydrochlorination of the Cl–M′–CNH species, with ready replacement of the chloride ligand by a suitable π-electron acceptor (such as N_2 or nitrile), to give products in low metal oxidation state, *i.e.*, Re^{I}; (ii) an electrochemical one (discussed previously),[8] involving the anodically induced stepwise deprotonation of the CNH_2 ligand to give derived CNH and CN complexes in medium metal oxidation states, *i.e.* Re^{II} or Re^{III}. The chemically derived cyano-centre *trans*-{Re(CN)(dppe)$_2$}, in comparison with the related chloro site *trans*-{ReCl(dppe)$_2$}, has a less-extensive π-electron-releasing ability towards a π-acceptor substrate, and their complexes exhibit an unusually rather high sensitivity of the HOMO energy to a change of the ligand *trans* to cyanide, the latter ligand presenting a very low buffering ability towards the electron-density change induced by a variation of the ligand in *trans* position.

Experimental

The complex *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] was prepared according to a published method,[5] and the solvents were dried and degassed by using standard techniques. All reactions were performed under an inert atmosphere (N_2). Solid nitriles and the alcoholic solution of NBu_4OH were used as purchased (Aldrich or Lancaster Synthesis).

Infrared spectra were run with a Perkin-Elmer 683 spectrophotometer and NMR spectra on a Varian Unity 300 spectrometer. The FAB mass spectrometric measurements were performed on a Trio 2000 spectrometer. Positive-ion FAB mass spectra were obtained by bombarding 3-nitrobenzyl alcohol matrices of the samples with 8 keV (*ca.* 1.28×10^{-15} J) Xe atoms. Nominal molecular masses were calculated using the most abundant isotope, *i.e.* ^{187}Re (63%), and the expected natural-abundance isotope cluster patterns were observed for various ion clusters. However, further complexity due to addition (from the matrix) or loss of hydrogen was usually not taken into account. Mass calibration for data-system acquisition was achieved with CsI.

The electrochemical experiments were carried out on an EG&G PAR 273 potentiostat/galvanostat connected to a 386-SX personal computer through a GPIB interface. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell, at a platinum-disc working electrode (diameter = 0.5 mm), probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode. The oxidation potentials of the complexes are quoted relative to the SCE by using as internal reference the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ redox couple ($E_{\frac{1}{2}}^{ox}$ = 0.55 V *vs.* SCE in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–CH$_2$Cl$_2$). Controlled-potential electrolysis were carried out in a three-electrode H-type cell with platinum-gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudo-reference electrode.

Syntheses

***trans*-[Re(CN)(NCMe)(dppe)$_2$] 2 (L = NCMe).** The complex *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (88 mg, 0.080 mmol) was dissolved in NCMe (10 cm^3) and a 0.1 mol dm^{-3} solution of NBu_4OH in methanol–propan-2-ol was added dropwise. Upon addition of *ca.* 0.5 cm^3 of this basic solution a suspension was formed, which was filtered, washed with small portions of NCMe and dried *in vacuo*. The IR spectrum of this fraction revealed the previously reported *trans*-[ReCl(CNH)(dppe)$_2$] complex.[5] The addition of the base solution was continued dropwise (0.8 cm^3) to the mother-solution which then turned deep green and a bright yellow suspension appeared. After isolation of the solid (another fraction of this CNH complex) and slight evaporation of the solvent, the solution was left to stand overnight, leading to the formation of crystals of the cyano compound **2** (L = NCMe). This final product was filtered off and dried *in vacuo* (*ca.* 65% yield).

***trans*-[Re(CN)(NCPh)(dppe)$_2$] 2 (L = NCPh).** The complex *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (60 mg, 0.050 mmol) was dissolved in NCPh (10 cm^3) and the above-mentioned basic solution of NBu_4OH (1.30 cm^3, 0.13 mmol) was added dropwise. Pentane was then added to the dark red solution and the mixture left for 72 h at low temperature (−20 °C) leading to the precipitation of a white solid which was filtered off. The filtered solution was then taken to dryness and the dark red residue crystallized from CH_2Cl_2–Et_2O to give a dark red crystalline solid of complex **2** (L = NCPh) which was filtered off and dried *in vacuo* (*ca.* 75% yield).

***trans*-[Re(CN)(NCC$_6$H$_4$Me-4)(dppe)$_2$] 2 (L = NCC$_6$H$_4$Me-4).** The above-mentioned NBu_4OH solution (0.88 cm^3, 0.088 mmol) was added to a solution of *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (40 mg, 0.035 mmol) and NCC$_6$H$_4$Me-4 (4.1 mg, 0.035 mmol) in thf (10 cm^3) and the mixture was left to stir under dinitrogen for 1 h. After addition of pentane and evaporation under vacuum, the mixture was left at low temperature (−20 °C) for *ca.* 8 h, during which an orange crystalline solid of complex **2** (L = NCC$_6$H$_4$Me-4) precipitated. The crystals were filtered off, washed with thf–pentane (1 : 4), then with pentane and dried *in vacuo* (*ca.* 60% yield).

***trans*-[Re(CN)(N$_2$)(dppe)$_2$] 3.** The complex *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (90 mg, 0.086 mmol) was dissolved in thf (10 cm^3), an excess of the above-mentioned NBu_4OH solution (2.4 cm^3, 0.24 mmol) added dropwise, and the mixture left to stir for *ca.* 0.25 h. After concentration *in vacuo* and addition of Et_2O a bright yellow solid of complex **3** precipitated from the greenish solution; it was filtered off, washed with thf–Et_2O (1 : 4) and dried *in vacuo* (*ca.* 60% yield).

***trans*-[Re(CN)(CO)(dppe)$_2$] 4.** The complex *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (36 mg, 0.032 mmol) was dissolved in thf (15 cm^3) and an excess of the base (0.76 cm^3, 0.076 mmol) added while CO was bubbled through the solution. The mixture was left to stir for *ca.* 15 min under a saturated atmosphere of carbon monoxide. Upon evaporation of the solvent under vacuum complex **4** precipitated as a pale yellow solid, which was filtered off, washed with thf and dried under vacuum (*ca.* 55% yield). Further crops of precipitate from the mother-solution consisted of a mixture of **4** with *trans*-[ReCl(CNH)(dppe)$_2$].

***trans*-[Re(CN)(=C=CHPh)(dppe)$_2$] 5.** The complex *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (50 mg, 0.044 mmol) was dissolved in thf (15 cm^3) and HC≡CPh added in slight excess (7.2 μl, 0.066 mmol). Upon addition of the base (0.96 cm^3, 0.096 mmol), the solution became deep red and was left to stir for 0.5 h. Upon concentration of the solution under vacuum and addition of Et$_2$O complex **5** precipitated as a greenish red solid, which was filtered off, washed with thf–Et$_2$O (1:4), then with Et$_2$O and dried under vacuum.

Crystallography

A crystal of *trans*-[Re(CN)(NCMe)(dppe)$_2$]·Pr^{i}OH of approximate dimensions 0.25 × 0.33 × 0.40 mm was used for the X-ray analysis.

Crystal data. $C_{55}H_{51}N_2P_4Re\cdot C_3H_8O$, M = 1110.21, monoclinic, space group $P2_1/c$, a = 13.276(3), b = 19.542(5), c = 20.457(6) Å, β = 98.88(1)°, U = 5244(2) Å^3, $\bar{\lambda}$ = 0.710 73 Å, Z = 4, D_c = 1.406 g cm^{-3}, $F(000)$ = 2256, μ(Mo-Kα) = 24.80 cm^{-1}.

Data were collected at room temperature on Philips PW 1100 single-crystal diffractometer using graphite-monochromated Mo-Kα radiation and the θ–2θ scan mode. All reflections with θ in the range 3–30° were measured; of 15 297 independent reflections, 9308, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analysed according to Lehmann and Larsen.[33] The intensity of one standard reflection was measured after 100 as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A semiempirical absorption correction was applied (maximum and minimum transmission factors 1.000 and 0.759).[34]

The structure was solved by Patterson and Fourier methods and the refinement on F_o was performed first by full-matrix least squares with isotropic thermal parameters and then by blocked full-matrix least squares with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms. The hydrogen atoms, excepting those of the propan-2-ol solvation molecule which were omitted, were placed at their calculated positions (C–H 0.96 Å) and refined 'riding' on the corresponding carbon atoms. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement; at convergence the K and g values were 0.486 and 0.0019, respectively. Final R and R' values were 0.0379 and 0.0443. The SHELX 76 and SHELXS 86 systems of computer programs were used.[35] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 36. All calculations were carried out on the Gould POWERNODE 6040 and ENCORE 91 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/79.

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