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FULL PAPER

Aminocarbyne and isocyanide complexes of rhenium. Crystal structures of *trans*-$[ReCl(CNR)(Ph_2PCH_2CH_2PPh_2)_2]$ (R = H or $SiMe_3$)

M. Fátima C. Guedes da Silva,[a,b] M. Amélia N. D. A. Lemos,[a] João J. R. Fraústo da Silva,[a] Armando J. L. Pombeiro,*[a] Maria A. Pellinghelli[c] and Antonio Tiripicchio[c]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. E-mail: pombeiro@alfa.ist.utl.pt*
[b] *Universidade Lusófona de Humanidades e Tecnologias, Campo Grande 376, 1749-024 Lisboa, Portugal*
[c] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Vialle delle Scienze 78, I-43100 Parma, Italy*

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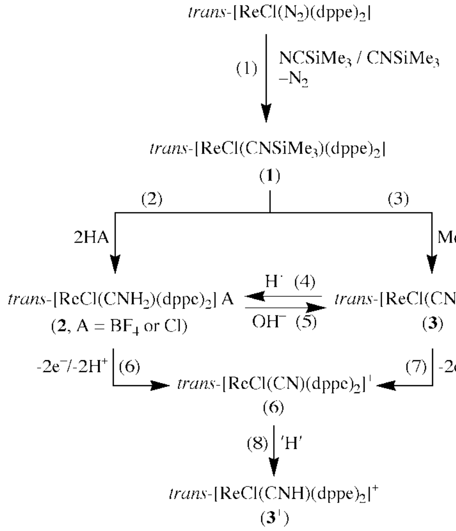
Treatment of a thf solution of *trans*-$[ReCl(N_2)(dppe)_2]$ with an excess of $NCSiMe_3$ in sunlight led to the formation of *trans*-$[ReCl(CNSiMe_3)(dppe)_2]$ **1** in which the trimethylsilyl isocyanide ligand undergoes desilylation by acid or MeOH to give the aminocarbyne *trans*-$[ReCl(CNH_2)(dppe)_2]A$ **2** (A = BF_4 or Cl) upon treatment with an excess of HBF_4 or HCl or the isocyanide *trans*-$[ReCl(CNH)(dppe)_2]$ **3** upon treatment with a stoichiometric amount of HCl or with MeOH. Complexes **2** convert into **3** by reaction with $[NBu_4]OH$ or NEt_3 (a more convenient route for **3** than the above), and conversely are obtained from the reaction of **3** with HBF_4 or HCl. Anodic controlled potential electrolysis of a solution of **2** (A = BF_4) in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–NCMe, until the consumption of 2 F mol^{-1}, resulted in complete deprotonation of the aminocarbyne ligand to give the cyano-complex *trans*-$[ReCl(CN)(dppe)_2][BF_4]$ **4** which, upon hydrogen abstraction from the electrolytic medium, converts into the isocyanide compound $\mathbf{3}^+$ isolated as *trans*-$[ReCl(CNH)(dppe)_2][BF_4]\cdot 2[NBu_4][BF_4]$. The detailed syntheses and spectroscopic properties of all these complexes are reported, as well as the crystal structures of **1** and **3**, and are discussed in terms of electronic and stereochemical properties of the ligands and binding metal centres.

Introduction

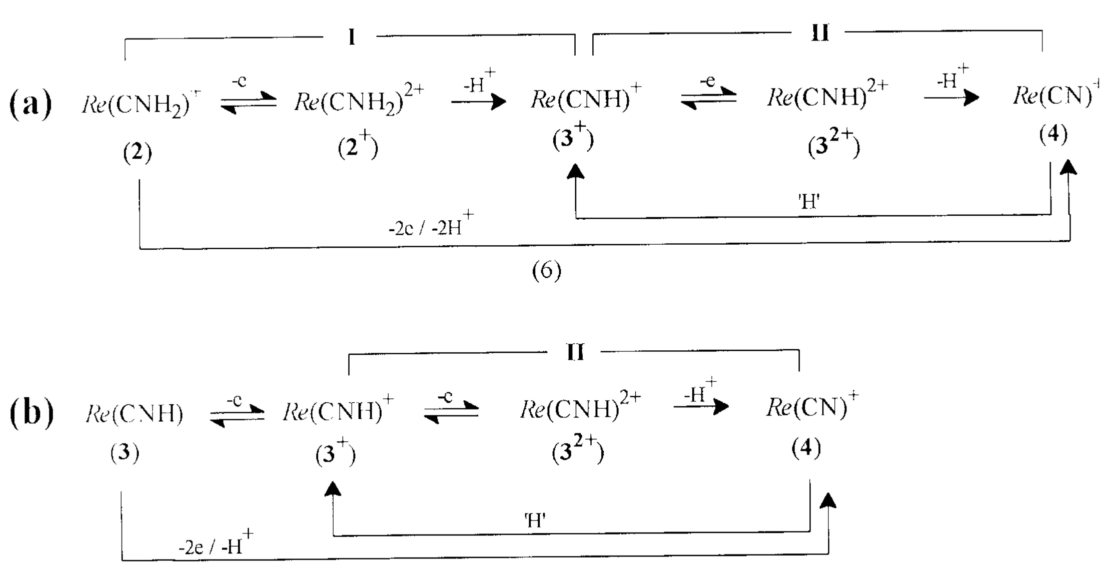
In contrast with the well established chemistry[1] of carbyne complexes with Group 6 transition metals, that of rhenium, particularly with phosphine coligands,[2,3] is still a field to be developed. Moreover, a diversity of routes and of types of carbyne ligands has been reported,[1–3] but the simplest aminocarbyne ligand, CNH_2, is almost unknown.[4] The investigation of the reactivity and activation by electron transfer of this ligand may be of significance towards the understanding of the biological reduction[5] of aqueous cyanide by nitrogenase and can also provide an entry into the emergent CNH (isocyanide) and CN based organometallic chemistry.[6]

In the present work, we show that an organosilane, trimethylsilyl cyanide, $NCSiMe_3$, can be a convenient starting material for the syntheses of CNH_2 and CNH complexes of rhenium, and also report on their chemical interconversion and electrochemical activation towards hydrogen transfer.

The possibility of overall interconversion of the cyano and the aminocarbyne ligands has been shown electrochemically at Mo or W and the complexes *trans*-$[MCl(CNH_2)(dppe)_2]$ (M = Mo[7] or W,[8] dppe = $Ph_2PCH_2CH_2PPh_2$) were electrosynthesized cathodically from *trans*-$[MCl(CN)(dppe)_2]$. Moreover, we have demonstrated the fundamental role of CNH in such a type of interconversion by showing electrochemically[9] that the aminocarbyne ligand in *trans*-$[ReCl(CNH_2)(dppe)_2][BF_4]$ **2** can be anodically converted into the hydrogen isocyanide (CNH) species in *trans*-$[ReCl(CNH)(dppe)_2]^+$ $\mathbf{3}^+$ which appears to generate, also anodically, the cyano product *trans*-$[ReCl(CN)(dppe)_2]^+$ **4** (Scheme 1). Neither the CNH complex $\mathbf{3}^+$ nor the CN compound **4** was then isolated and their formation was proposed[9] mainly on the basis of a mechanistic study. We now present further evidence for the formation of this cyano-complex and show that it converts into the new isocyanide complex $\mathbf{3}^+$ which we have now succeeded in isolating. The crystal structures of the neutral CNH complex **3** and of its parent trimethylsilyl isocyanide compound **1** are also reported, with their detailed syntheses and spectroscopic properties which are also indicated for the aminocarbyne complexes *trans*-$[ReCl(CNH_2)(dppe)_2]A$ **2** (A = BF_4 or Cl). The preparation of some of these compounds has been briefly indicated[4] (improved synthetic procedures are now described in detail), together with the crystal structure of the aminocarbyne complex **2** (A = BF_4) which therefore will not be included herein.



Scheme 1



(6)

(7)

Scheme 2

The synthetic interest of the isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$] **3** which forms a variety of cyano-complexes has been revealed[10] by preparing the series *trans*-[Re(CN)L(dppe)$_2$] (L = N_2, NCR, CO or C=CHPh) upon dehydrochlorination in the presence of suitable substrates (dinitrogen, organonitrile, carbon monoxide or phenylacetylene, respectively).

Results and discussion

Syntheses

Treatment of a thf solution of the dinitrogen complex *trans*-[ReCl(N_2)(dppe)$_2$] with an excess of trimethylsilyl cyanide (which is known[11] to contain *ca.* 5% of the isocyanide isomer) in sunlight leads to the formation (reaction 1 in Scheme 1) of the isocyanide complex *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] **1** which has been isolated, after *ca.* 6 h, in high yield (*ca.* 85%), as a light green solid. The reaction involves displacement of N_2 which is promoted by sunlight in accord with some π-MO schemes[12,13] which indicate that the HOMO in the dinitrogen complex has a M–N_2 bonding character; hence, photochemical electron removal from this orbital should result in labilisation of the N_2 ligand. Reaction (1) also proceeds without sunlight, in solvent refluxing conditions, under argon, but rather more slowly (takes a few days to completion).

The co-ordination of the isocyanide CNSiMe$_3$ in preference to the cyanide NCSiMe$_3$, in spite of the predominance of the latter (see above), shifts the isomeric equilibrium towards the former which is thus further generated, and is in accord with the stronger net π-electron acceptor/σ-donor character of isocyanides, compared with organocyanides, with a resulting more effective stabilisation of the binding electron-rich {ReCl(dppe)$_2$} centre. Consistent with this, isocyanide complexes with this metal site are known[13,14] to undergo oxidation at a higher (by *ca.* 0.4–0.5 V) potential than those of the corresponding organonitrile complexes.

The CNSiMe$_3$ ligand in complex **1** undergoes desilylation on treatment of its solution (in toluene or thf) with HBF$_4$, HCl or MeOH to give the aminocarbyne or the isocyanide products *trans*-[ReCl(CNH$_2$)(dppe)$_2$]A **2** (A = BF$_4$ or Cl) (formed by using an excess of acid) or *trans*-[ReCl(CNH)(dppe)$_2$] **3** (use of MeOH or a stoichiometric amount of HCl) (reactions 2 and 3, Scheme 1). The formation of these complexes is in accord with the high tendency of Si to form stable Si–F, Si–Cl or Si-O bonds, and Me$_3$SiF, Me$_3$SiCl or Me$_3$SiOMe are the other possible products of the reactions. The conceivable cyano-intermediate [see below for a related iron(II) system] is protonated by methanol to form the isocyanide CNH in **3**. However, double protonation occurs by using an excess of HBF$_4$ (or HCl), a stronger acid, to form the aminocarbyne CNH$_2$ in **2**, a reaction which is assisted by another driving force, the susceptibility to protonation of the isocyanide when ligating the electron-rich {ReCl(dppe)$_2$} centre. In fact, complex **2** is readily formed by reaction of **1** with HBF$_4$ (or HCl) (reaction 4), a process that can be conveniently monitored by ^{31}P-{^{1}H} NMR spectroscopy, in CH$_2$Cl$_2$. Moreover, the alkyl isocyanide CNR (R = Me or Bu^t) in *trans*-[ReCl(CNR)(dppe)$_2$] is known[3b] to undergo rapid β-protonation by acid, HBF$_4$, to afford, in high yields, the derived aminocarbyne complexes *trans*-[ReCl(CNHR)(dppe)$_2$][BF$_4$].

The protonation of the isocyanide ligand does not occur in *trans*-[FeH(CNH)(dppe)$_2$][BF$_4$] which is formed either by reaction[15] of *trans*-[FeH(Cl)(dppe)$_2$] with NCSiMe$_3$ in the presence of Tl[BF$_4$] and of HBF$_4$ or by protonation (by this acid)[16] of the cyano-complex *trans*-[FeH(CN)(dppe)$_2$]. The lower electron-richness of the iron(II) centre compared to the rhenium(I) one of the current study is not sufficient to activate the CNH ligand towards further protonation.

The protonation reaction (4) of the isocyanide complex **3** to form the aminocarbyne **2** can be reversed by base (NEt$_3$ or [NBu$_4$]OH) and, in fact, the former compound is better prepared in this way, from the latter one (reaction 5), than *via* the above mentioned desilylation of complex **1** by MeOH (reaction 3). If the deprotonation reaction of **2** is carried out in NCMe or at low temperature (−60 °C) in thf on addition of [NBu$_4$]OH the isocyanide complex **3** precipitates spontaneously from the solution. Hence, chemical deprotonation of the aminocarbyne ligand CNH$_2$ in **2**, under those experimental conditions, involves loss of a single proton, *i.e.* does not proceed beyond the CNH stage. However, full deprotonation to the CN ligand is achieved electrochemically, upon two-electron anodic oxidation either of the aminocarbyne **2** or the isocyanide **3** complex (reaction 6 or 7, respectively, Scheme 1). The increase of acidity of the CNH$_2$ or the CNH ligand upon oxidation of their complexes (*e.g.*, by a factor of at least *ca.* 10^9 on single-electron oxidation of the aminocarbyne complex **2**)[9] leads to ready deprotonation even in a weakly basic solvent such as NCMe.

In fact, controlled potential electrolysis, at a platinum-gauze electrode, of a solution of *trans*-[ReCl(CNH$_2$)(dppe)$_2$]-[BF$_4$] **2** in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–NCMe, at a potential (1.70 V *vs.* SCE) on the plateau of its second anodic wave [wave

II, Scheme 2(a)] until the consumption of 2 F mol^{-1} results in the complete deprotonation of the complex to give a violet product which we formulate (see below) as the cyano-complex *trans*-[ReCl(CN)(dppe)$_2$]$^+$ **4**. The protons liberated during this electrolysis have been detected by a cathodic sweep of the cyclic voltammogram of the electrolysed solution (as an irreversible cathodic wave at $E_p{}^{red}$ *ca.* −0.7 V at a platinum electrode, which shifts to a much more cathodic value, *ca.* −2.0 V, on replacement of the Pt by a vitreous carbon electrode), and quantified by potentiometric titration. Other examples of anodically promoted deprotonation of unsaturated ligands have been quoted, namely for the isocyanide iron complex *trans*-[FeH(CNH)(dppe)$_2$]$^+$ (N–H bond cleavage),[15] for some carbene complexes of Pd or Pt (N–H and C–H bond cleavage),[17] for vinylidene-rhodium complexes (C–H bond cleavage)[18a] and for Ir complexes of Rh or Ir with a benzothiophene-derived ligand (C–H bond cleavage).[18b]

As discussed previously,[9] the cyclic voltammogram of a solution of the aminocarbyne complex **2** in the above electrolyte medium exhibits [Scheme 2(a)] two single-electron irreversible anodic waves at $^{I}E° = 0.84$ and $^{II}E° = 1.58$ V *vs.* SCE, the former (wave I) involving the oxidation of the complex followed by proton loss to give the cationic isocyanide complex *trans*-[ReCl(CNH)(dppe)$_2$]$^+$ **3**$^+$ which is the species being oxidised at wave II. On the basis of the analysis, by digital simulation, of the cyclic voltammograms, the occurrence at wave II of a process related to that of wave I was proposed[9] but involving the electrogenerated complex **3**$^+$, *i.e.* its anodically induced deprotonation to give the cyano-complex *trans*-[ReCl(CN)(dppe)$_2$]$^+$ **4**. Accordingly, equations (6) and (7) can be detailed as shown in Scheme 2 in which (I) and (II) denote the redox processes at the anodic waves I and II, respectively.

Although the electrochemical generation of **4** upon anodically induced deprotonation of the aminocarbyne complex **2** or of the isocyanide compound **3** appears to succeed, the isolation and full characterisation of **4** could not be achieved because this violet complex is highly unstable. Upon working up (even at low temperature, −50 °C) of its solution, a paramagnetic red crystalline species was isolated and shown to contain the isocyanide *trans*-[ReCl(CNH)(dppe)$_2$]$^+$ **3**$^+$ moiety as the redox active species, on the basis of its cyclic voltammetric behaviour which is the expected one for the singly oxidised derivative of *trans*-[ReCl(CNH)(dppe)$_2$] **3**; in fact, it exhibits a reversible single-electron cathodic wave at $E° = 0.45$ V to form **3**, and a chemically irreversible single-electron anodic wave at $E° = 1.58$ V to regenerate **4** [see Scheme 2(b) and Fig. 1]. This isolated red compound consists of the $BF_4{}^-$ salt of **3**$^+$ with two molecules of electrolyte of crystallisation as shown by an X-ray diffraction analysis (the very poor quality of all crystals prevented sufficiently accurate structural results). Thus it can be formulated as *trans*-[ReCl(CNH)(dppe)$_2$][BF$_4$]·2[NBu$_4$][BF$_4$]. The cocrystallisation of the electrolyte was also observed[19] in the isolation of *trans*-[MoCl$_2$(dppe)$_2$][BF$_4$]·2[NBu$_4$][BF$_4$], obtained by anodic controlled potential electrolysis of *trans*-[MoCl$_2$(dppe)$_2$] in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–thf.

The spontaneous conversion of complex **4** into **3**$^+$ (reaction 8, Scheme 1) was monitored by cyclic voltammetry and involves hydrogen abstraction conceivably from the electrolytic medium, since the presence of *trans*-[ReCl(CNH$_2$)(dppe)$_2$]$^+$ **2**, which in principle could behave either as a reducing agent of **4** (to give the corresponding neutral cyano-complex which would be susceptible to protonation to give **3**$^+$) or as a hydrogen source for **4**, did not appear to accelerate the formation of **3**$^+$ from **4**. This conversion is also not affected significantly by addition of water or by replacement of the electrolyte (use of LiClO$_4$ instead of [NBu$_4$][BF$_4$]). However, the use of another solvent (*e.g.*, CH$_2$Cl$_2$) resulted in different electrochemical behaviour without formation of **3**$^+$. These observations suggest that acetonitrile is the conceivable source of hydrogen in reaction (8). Other cases of hydrogen-transfer reactions of electrogenerated radical complexes with unspecified hydrogen donors or acceptors have been reported.[20]

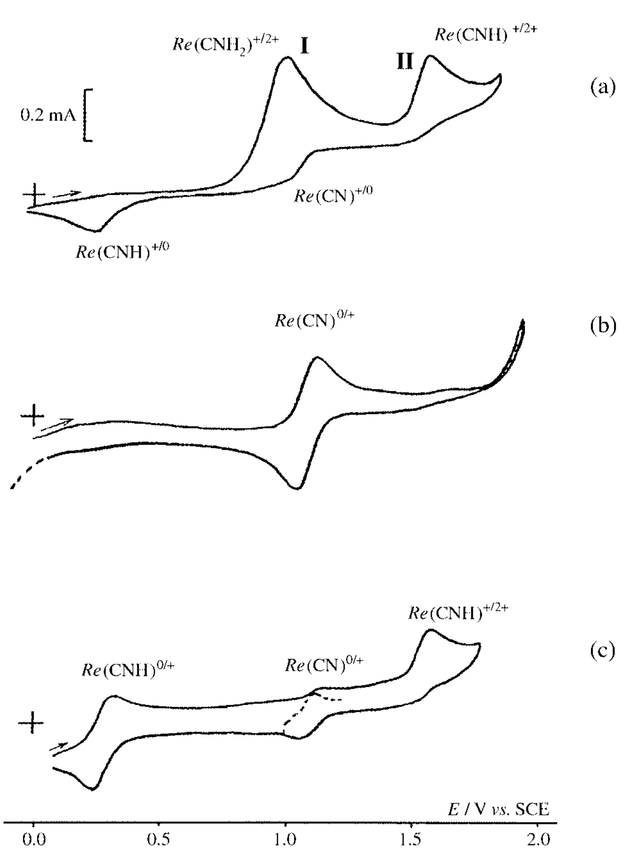


Fig. 1 Cyclic voltammograms, in NCMe with 0.2 mol dm^{-3} [NBu$_4$][BF$_4$], at a platinum gauze working electrode, of (a) *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] **2** (3.95 mM); (b) *trans*-[ReCl(CN)(dppe)$_2$]$^+$ **4** (violet solution) obtained upon exhaustive controlled potential electrolysis (CPE) at wave II of complex **2**; (c) *trans*-[Re(CNH)(dppe)$_2$]$^+$ **3**$^+$ (red solution) obtained upon decomposition in solution of complex **4**. Scan rate of 0.2 V s^{-1}.

The complexes **1**, **2**, **3** and **3**$^+$ have been characterised by IR spectroscopy, ^{1}H, ^{31}P-{^{1}H} and ^{13}C NMR (see Experimental section), FAB-mass spectrometry, elemental analyses and, for **1** and **3**, by X-ray diffraction analyses, which are discussed below (the crystal structure of **2**, A = BF$_4$, has been reported[4] and will not be included herein).

Spectroscopic properties

For complex **1** the IR band (KBr pellet) at 1840 cm^{-1} (very strong and broad) is assigned to ν(C≡N) of the trimethylsilyl isocyanide ligand. This value is comparable with those found[3b,14] for related isocyanide complexes, *e.g.* 1830 and 1800, or 1920 cm^{-1}, for *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me or Bu^t, respectively), being much lower than for free isocyanide in agreement with the strong π-electron release of the electron-rich rhenium(I) centre.

For the CNH complex **3**, the IR bands observed at 1725 (strong) and 1685 (strong) cm^{-1} are assigned to δ(NH) rather than to ν(C≡N) in view of the pronounced isotopic shift to lower wavenumbers (1580 and 1520 cm^{-1}) of the deuteriated analogue. For the aminocarbyne CNH$_2$ **2** complexes, only a slight shift in the strong band at 1585 cm^{-1} assigned to ν(C=N) occurs on deuteriation (1575 cm^{-1} for the CND$_2$ analogue). In the latter complexes, the frequency of the ν(NH) band (with medium intensity and broad) depends on the counter ion ($BF_4{}^-$ or Cl$^-$) in the following way: although in the $BF_4{}^-$ case it appears at *ca.* 3260 cm^{-1}, within the usual range, in the case of Cl$^-$ as the counter ion it is shifted to a lower wavenumber (*ca.* 2680 cm^{-1}) suggesting the occurrence of the hydrogen bond

Table 1 ^{13}C-{^1H} and ^{13}C NMR data for *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] **1** and [ReCl(CNH$_2$)(dppe)$_2$]A **2** (A = BF$_4$)[a]

Complex	δ	^{13}C-{^1H}	J(CP) [b][^3J]	^{13}C	J(CH) [^2J]	Assignment
1	139.83	qt	10.5	m, br	—	C_i (dppe)
	137.62	qt	9.6	m, br	—	C'_i (dppe)
	134.15	s	—	d	159.8	C_p (dppe)
	129.04	s	—	dt	159.8 [6.9]	C_m (dppe)
	128.75	s, br	—	n.o.	—	*C*NSiMe$_3$
	128.44	s	—	dt	159.4 [6.9]	C'_m (dppe)
	127.81	qt	2.3	dm	159.4	C_o (dppe)
	127.03	qt	1.8	dm	158.4	C'_o (dppe)
	32.70	qt	11.5	tm	131.9	CH$_2$
	1.69	s	—	q	118.8	CNSi(*C*H$_3$)$_3$
2	222.38	qt	13.4[c]	br	—	CNH$_2$
	135.45	qt	11.8	n.o.	—	C_i (dppe)
	134.52	qt	2.5	dm	161.9	C_o (dppe)
	133.77	qt	11.5	n.o.	—	C'_i (dppe)
	132.86	qt	2.5	dm	158.8	C'_o (dppe)
	131.16	s	—	dt	162.6 [7.1]	C_p (dppe)
	130.74	s	—	dt	162.6 [7.1]	C'_p (dppe)
	129.39	d	[2.5]	dm	163.2	C_m (dppe)
	128.36	d	[2.4]	dm	162.6	C'_m (dppe)
	31.37	qt	10.8	tm	134.3	CH$_2$

[a] In CD$_2$Cl$_2$; δ in ppm; J in Hz; s = singlet, d = doublet, q = quartet, qt = quintet, m = multiplet, br = broad, dt = doublet of triplets, dm = doublet of multiplets, tm = triplet of multiplets, n.o. = not observed; reliable data could not be collected for *trans*-[ReCl(CNH)(dppe)$_2$] **3** due to decomposition. [b] Owing to virtual coupling to the four equivalent phosphorus nuclei, except the values in square brackets which refer to ^3J(CP). [c] J(CP).

CNH···Cl$^-$ [for the analogous deuteriated complex, the band at 2010 cm^{-1} is assigned to ν(ND···Cl$^-$)].

The *trans* configuration is assigned to the complexes **1**, **2** and **3** in view of the observed singlet in their ^{31}P-{^1H} NMR spectra, and of the absence, in the ^1H NMR spectra, of the high-field triplet pattern normally exhibited[21] in the phenyl region by *cis*-dppe complexes. For compounds **1**–**3** and **3**$^+$ the *trans* geometry has been confirmed by X-ray diffraction analyses although for the last complex this technique did not differentiate between the cyanide or the isocyanide ligand (see below).

In the ^{13}C-{^1H} NMR spectra (Table 1) of complexes **1** and **2**, the isocyanide *C*NSiMe$_3$ and the aminocarbyne *C*NH$_2$ resonances are detected as a singlet (broad) at δ 128.75 or low-field quintet [^2J(CP) = 13.4 Hz] at δ 222.38, respectively. For the related methylaminocarbyne complex *trans*-[ReCl(CNHMe)(dppe)$_2$][BF$_4$] the *C*NHMe resonance is an unresolved and broad multiplet centred at δ 222.7.[3b] The *ortho*, *meta* and *ipso* aromatic carbons of dppe exhibit two sets of resonances (see Fig. 2 for complex **1**) which, with the exception of those due to the *ipso* carbons, split into the expected multiplets in the corresponding ^1H-coupled spectra. The detection of these sets can tentatively be accounted for by considering two sets of phenyl rings: one of them (four phenyls) on the side of the equatorial plane of the molecule with the chloro-ligand, and the other one (the remaining phenyls) on the opposite side towards the isocyanide (**1**) or the aminocarbyne (**2**) ligand (see Fig. 3) although a possible fluxional behaviour can change this arrangement. Similar features have been recognised[10] for the related cyano-complexes *trans*-[Re(CN)L(dppe)$_2$] (L = organonitrile or phenylvinylidene).

The paramagnetism of the isocyanide complex of rhenium(II) *trans*-[ReCl(CNH)(dppe)$_2$][BF$_4$].2[NBu$_4$][BF$_4$] **3**$^+$ is indicated by its ^1H NMR spectrum (in CD$_2$Cl$_2$) which consists of a set of resonances spread over a wide chemical shift range (δ *ca.* 4–19) (see Experimental section), similar to what was observed[22] for the isoelectronic complex *trans*-[ReCl(CNMe)(dppe)$_2$]$^+$; a value of $\mu_{eff} = 2.5\ \mu_B$ (corrected for the diamagnetism) was estimated by application of the Evans method.[23] No reliable magnetic behaviour was observed in the solid state by using a Faraday balance, or by ESR spectrometry, due to decomposition.

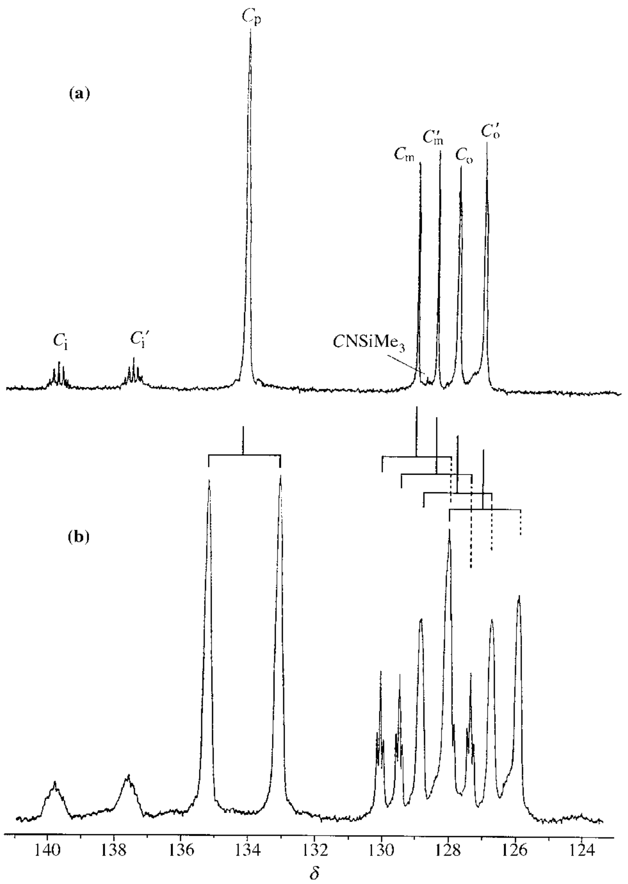


Fig. 2 (a) ^{13}C-{^1H} and (b) ^{13}C NMR spectra (phenyl region) of *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] **1** in CD$_2$Cl$_2$.

In the FAB mass spectra of all the complexes, run in 3-nitrobenzyl alcohol matrices, the corresponding molecular ions are detected with the expected metal isotopic pattern, except for the trimethylsilyl isocyanide complex **1** in which the ion derived from desilylation of the ligand, [ReCl(CN)(dppe)$_2$]$^+$ (m/z 1044), has been observed, in accord with the easy cleavage of the Si–N bond recognised in the chemical studies.

Table 2 Selected intramolecular distances (Å) and angles (°) for *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] **1** and *trans*-[ReCl(CNH)(dppe)$_2$] **3**, with e.s.ds in parentheses[a]

Complex	Re–C$_\alpha$	C$_\alpha$–N	Re–Cl	Re–P	Other	Re–C$_\alpha$–N	Cl–Re–C$_\alpha$	P–Re–C$_\alpha$	P–Re–Cl	Other
1 *A*	1.950(22)	1.128(28)	2.524(6)	2.386(6)	1.724(20) [N–Si]	176.7(18)	178.4(6)	97.4(6)	82.6(2)	171.9(18) [C(1)–N(1)–Si(1)]
				2.393(5)				97.4(5)	84.2(2)	
				2.395(5)	1.866(34)			84.9(6)	95.1(2)	
				2.426(6)	1.773(36) [Si–C]			86.8(5)	91.6(2)	
					1.735(33)					
B	1.833(23)	1.232(29)	2.520(6)	2.373(6)	1.708(19) [N–Si]	173.1(19)	176.2(7)	99.6(7)	83.5(2)	174.4(19) [C(1)–N(1)–Si(1)]
				2.373(6)				98.8(7)	83.8(2)	
				2.411(6)	1.813(36)			82.9(7)	94.0(2)	
				2.418(6)	1.901(39) [Si–C]			87.0(7)	90.4(2)	
					1.747(34)					
3	2.007(38)	1.157(43)	2.532(9)	2.420(2)	—	171.0(29)	178.1(10)	100.3(11)	81.5(2)	
				2.431(2)				94.9(11)	85.8(2)	

[a] For complex **1**, two independent molecules, *A* and *B*. Subscript α for C denotes the atom co-ordinated to the metal.

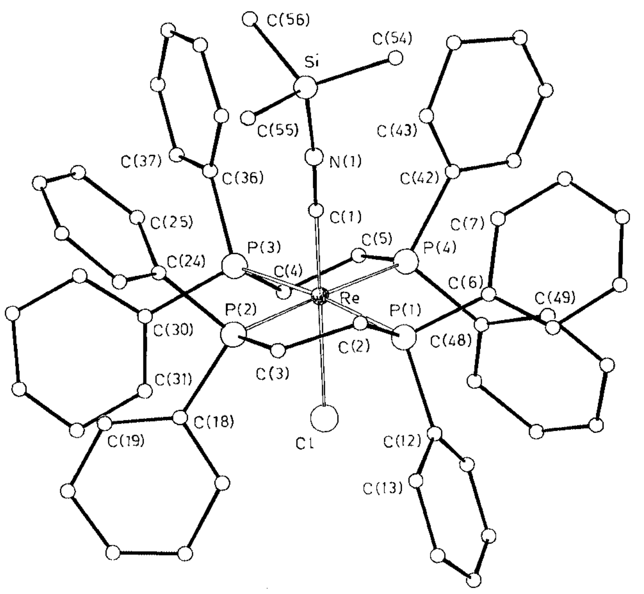


Fig. 3 View of the structure of the complex *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] **1**·thf with the atomic numbering system.

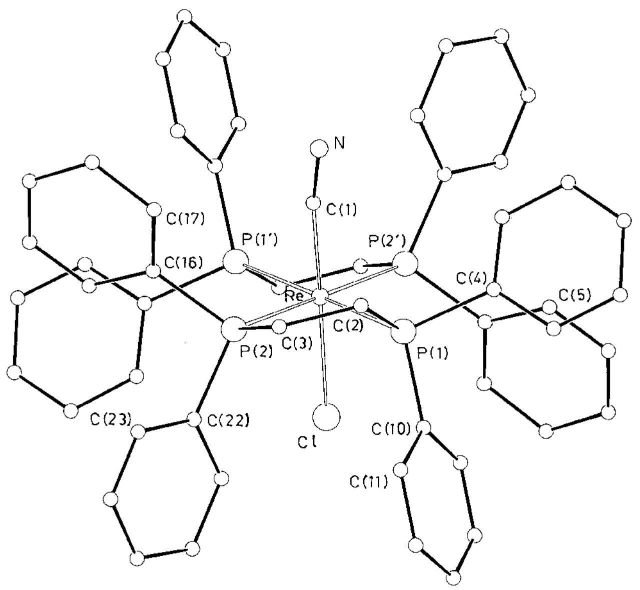


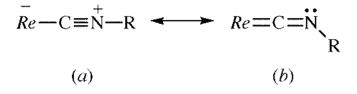
Fig. 4 View of the structure of the complex *trans*-[ReCl(CNH)(dppe)$_2$] **3**·2thf with the atomic numbering system.

Crystal structures of *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$]·C$_4$H$_8$ 1·thf and *trans*-[ReCl(CNH)(dppe)$_2$]·2C$_4$H$_8$O 3·2thf

The crystal structures of the compounds **1** and **3** were obtained by X-ray diffraction studies which indicated that the crystals also contain one and two thf molecules of solvation per molecule of complex, respectively. The molecular structures are depicted in Figs. 3 and 4, and selected bond lengths and angles are listed in Table 2.

In both complexes the Re atom exhibits octahedral-type co-ordination with the four P atoms in the equatorial positions, whereas the Cl atom and the terminal C atom of its *trans* ligand occupy the apical positions (disordered and interchanged in **3**). The isocyanide ligands have essentially linear co-ordination [Re–C(1)–N(1) angle in the 171.0(3)–176.7(2)° range] and the isocyanide in **1** is also linear [C(1)–N(1)–Si angle of 171.9(2) and 174.4(2)°].

For complex **1**, two independent molecules, *A* and *B*, were found, one of them (*B*) presenting a shorter Re–C(1) and a longer C(1)–N(1) bond length: 1.833(23) (*B*) *vs.* 1.950(22) (*A*), 1.232(29) (*B*) *vs.* 1.128(28) (*A*) Å, respectively. In both cases, as well as in complex **3** [Re–C(1) 2.007(38) Å], the Re–C(1) distance is shorter than the expected Re–C single bond length [2.13 Å, evaluated[24] as the sum of the single-bonded covalent radii of Re (1.53 Å) and sp–C (0.60 Å)], and is comparable with those found 1.861(12)[25] and 1.926(9) Å[26] in the methyl- and *tert*-butyl-isocyanide complexes *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me or Bu^t), respectively. However, as expected, it is longer than those exhibited by the aminocarbyne complexes *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$ (1.802(4) Å, R = H;[4] 1.798(30) Å, R = Me[3b]). These results indicate that the carbene form (*b*) has a significant weight in the valence-bond representation of the isocyanide ligand. Moreover, the isocyanide ligand would be expected to present a bent geometry at the N atom (see form *b*), on the basis of electronic arguments associated with the extensive π-electron release from the electron-rich metal to a C≡N π* orbital (with resulting strengthening of the metal–carbon bond, which then presents some carbene character, weakening of the unsaturated C–N bond and a localisation of electronic charge at the N atom), and rationalisations by extended Hückel calculations[3a,27] and by simplified π-MO schemes.[12,13] In fact, the methyl isocyanide ligand in *trans*-[ReCl(CNMe)(dppe)$_2$] is strongly bent [C–N–C angle of 139.4(10)°].[25] However, in contrast with this expectation, in our complex **1** the trimethylsilyl isocyanide is linear (see above) as observed[26] for the analogous *tert*-butyl isocyanide [C–N–C angle of 174.0(9)°] in *trans*-[ReCl(CNBu^t)(dppe)$_2$]. Hence, the tendency for bending of the isocyanides when ligating an electron-rich metal centre, which is electronic in origin, is overcome by steric hindrances in the isocyanides with bulky substituents, such as CNSiMe$_3$ and CNBu^t.



$$\overset{-}{Re}\text{—}C\equiv\overset{+}{N}\text{—}R \longleftrightarrow Re=C=\ddot{N}\diagdown_{R}$$

(*a*) (*b*)

In addition to the metal–carbon distance discussed above, the other metal–ligand bond lengths (Re–Cl and Re–P) also reflect the electronic properties of the metal centre. Hence, complexes **1** and **3**, as well as the analogous *trans*-[ReCl(CNR)(dppe)$_2$] (R = Me[25] or Bu^t[26]), exhibit Re–Cl and Re–P bond lengths (in the 2.520(6)–2.532(9) and 2.373(6)–2.426(6) Å ranges, respectively) which are significantly longer and shorter than the corresponding ones observed in the cationic aminocarbyne compounds *trans*-[ReCl(CNHR)(dppe)$_2$]$^+$ [R = H[4] or Me;[3b] Re–Cl of 2.485(1) or 2.484(6) and Re–P in the range 2.433(1)–2.478(1) or 2.435(7)–2.470(6) Å, respectively]. This can be accounted for by considering that the electron richer rhenium(I) centre in the former complexes is a stronger π-electron releaser for the phosphine ligands than the cationic rhenium site in the latter compounds in which, however, the chloro-ligand behaves as a stronger σ- and π-electron donor in view of the higher metal oxidation state and, in the case of the aminocarbyne complexes, to compensate electronically the metal for the rather high π-electron withdrawing ability of the CNHR carbyne ligands in comparison with that of the ligating isocyanides in the former complexes.

Final comments

Treatment of the isocyanide ligand CNSiMe$_3$ (which has a removable SiMe$_3$ group), activated by an electron-rich metal centre, with a suitable proton source presenting a silyl group abstractor, such as HBF$_4$, allows the generation *in situ* of the very rare and simplest aminocarbyne CNH$_2$ species at a single metal site. This can undergo chemical or electrochemical deprotonation to give the derived isocyanide (CNH) or cyanide (CN) ligands. The CNH$_n$ (n = 2, 1 or 0) species are interconvertible and the system (which can be of biological significance for understanding of the mechanism of cyanide reduction by nitrogenases) can open an *entrée* into the still rather underdeveloped field of the CNH-based organometallic chemistry and electrochemistry.

The problems associated with the generation of the unstable CNH and CNH$_2$ species and with their unambiguous characterisation, in part resulting from the difficult detection of the N*H* proton(s), require the use of indirect synthetic strategies and of a variety of analytical techniques including IR and multinuclear NMR spectroscopies, electrochemistry, mass spectrometry and X-ray diffraction analysis.

Experimental

General

All the manipulations and reactions were performed in the absence of air, using standard inert-gas flow and vacuum techniques. Solvents were purified by standard procedures and *trans*-[ReCl(N$_2$)(dppe)$_2$] was prepared by a published method.[28]

Infrared spectra were run on a Perkin-Elmer 683 spectrophotometer, NMR spectra on a Varian Unity 300 spectrometer and ESR spectra on a Bruker 300E X-band ESR spectrometer equipped with a ESR900 helium flux (Oxford Instruments Ltd.). Solid state magnetic susceptibility was measured on a Faraday system (Oxford Instruments Ltd.) equipped with a Sartorius microbalance. 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 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, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode. Controlled-potential electrolyses 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. The oxidation potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–NCMe in the presence of ferrocene as the internal standard, and the redox potential values are quoted relative to the SCE by using the [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ couple ($E_{1/2}{}^{ox}$ = 0.42 V *versus* SCE, in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]–NCMe). The use, as reference electrode, of the SCE or other electrode in an aqueous medium was avoided due to the sensitivity of the systems to water. The CPE experiments were monitored regularly by CV, thus assuring that no significant potential drift occurred during the electrolysis.

The acid–base potentiometric titrations of the electrochemically oxidised solutions were carried out by using a solution of NaOH in MeOH which was standardised by titration against benzoic acid in NCMe. The results have been corrected for background effects by using the procedure indicated previously.[9]

Standard solutions of anhydrous HCl or (DCl) were prepared in thf under dinitrogen by mixing equimolar amounts of MeOH (or MeOD) and SiMe$_3$Cl.

Syntheses

***trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] 1.** The complex *trans*-[ReCl(N$_2$)(dppe)$_2$] (0.40 g, 0.38 mmol) was dissolved in 250 cm^3 of thf under an N$_2$ atmosphere and an excess of NCSiMe$_3$ was added (2 cm^3, 15 mmol). The mixture was left with stirring in sunlight for *ca.* 6 h and during this period the clean yellow solution gradually turned to pale green. Upon extensive evaporation of the solvent under vacuum and addition of n-pentane, complex **1** precipitated as a pale green crystalline solid which was isolated by filtration, washed with thf–pentane (1 : 4), then with pentane and dried under vacuum (*ca.* 85% yield). One of the crystals was analysed by X-ray diffraction. Longer reaction times in sunlight led to non-identified products. Complex **1** can also be prepared without sunlight, in a much slower way, by refluxing under argon the thf solution of the dinitrogen complex with NCSiMe$_3$, for *ca.* 6 d (0.37 g, 86% yield). IR (KBr pellet): 1840 cm^{-1} [s, br; ν(C≡N)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.56–6.86 (br, 40 H, Ph of dppe), 2.66 (br, 4 H, CH$_2$ of dppe), 2.17 (br, 4 H, CH$_2$ of dppe) and −0.24 (s, 9 H, CNSi*Me*$_3$); ^{31}P-{^{1}H} (CD$_2$Cl$_2$, standard P(OMe)$_3$), δ −106.3. FAB mass spectrum: *m*/*z* 1082 ([*M* − Cl]$^+$) and 1044 ([*M* − SiMe$_3$]$^+$) (Found: C, 60.0; H, 5.4; N, 0.9. C$_{56}$H$_{57}$ClNP$_4$ReSi requires C, 60.2; H, 5.1; N, 1.3%).

***trans*-[ReCl(CNH$_2$)(dppe)$_2$]A 2 (A = BF$_4$).** The complex *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] **1** (0.21 g, 0.19 mmol) was dissolved in *ca.* 30 cm^3 of toluene and a twofold molar amount of HBF$_4$ [in a 1 : 10 diluted diethyl ether solution of the commercially available ether complex [Et$_2$OH][BF$_4$] solution (85%)] was added dropwise and with stirring. The previously pale green solution gradually faded to almost colourless. The mixture was left stirring for 3 h during which complex **2** precipitated as a white solid. Upon evaporation under vacuum of up to *ca.* 1/2 of the solvent volume the solid was isolated by filtration, washed with small portions of toluene, then with n-pentane, and dried in vacuum (0.16 g, *ca.* 75% yield). IR (KBr pellet): 3260 [m, br; ν(NH)], 1585 [m, br; ν(C=N)] and 1050 cm^{-1} [s, br; ν(BF)]. NMR (298 K): ^{1}H (CD$_2$Cl$_2$), δ 7.39–7.01 (m, br, 40 H, Ph of dppe), 3.54 (br, 2 H, CNH$_2$), 2.81 (m, 4 H, CH$_2$ of dppe) and 2.65 (m, 4 H, CH$_2$ of dppe); ^{31}P-{^{1}H}

(CD_2Cl_2, standard $P(OMe)_3$), δ −116.6. FAB mass spectrum: *m*/*z* 1010 [$M - Cl]^+$) (Found: C, 59.3; H, 4.9; N, 1.0. $C_{53}H_{50}BClF_4NP_4Re$ requires C, 58.8; H, 4.8; N, 1.1%).

***trans*-[ReCl(CNH$_2$)(dppe)$_2$]A 2 (A = Cl).** Complex **1** (0.073 g, 0.067 mmol) was dissolved in toluene (10 cm^3) and an excess of HCl (1.4 cm^3, 0.14 mmol, of a solution prepared by addition of 0.10 cm^3 of MeOH and 0.32 cm^3 of Me_3SiCl to 25 cm^3 of thf) was added dropwise and with stirring. After less than 15 min complex **2** precipitated as a greenish white solid which was filtered off, washed with toluene and dried *in vacuo* (0.053 g, *ca.* 75% yield). IR (KBr pellet): 2680 [s, br; ν(NH ··· Cl)] and 1585 cm^{-1} [m, br; ν (C=N)].

***trans*-[ReCl(CND$_2$)(dppe)$_2$]Cl.** The procedure was identical to that followed for the analogous non-deuteriated compound *trans*-[ReCl(CNH_2)(dppe)$_2$]Cl but MeOD was used instead of MeOH (0.030 g, *ca.* 40% yield). IR (KBr pellet): 2010 [s, br; ν(ND ··· Cl)] and 1575 cm^{-1} [m, br; ν(C=N)].

***trans*-[ReCl(CNH)(dppe)$_2$] 3.** This complex is more conveniently prepared from the aminocarbyne complex *trans*-[ReCl(CNH_2)(dppe)$_2$]A **2** (A = BF_4) [route (i)] although it can also be obtained from *trans*-[ReCl($CNSiMe_3$)(dppe)$_2$] **1** [route (ii)].

Route (i). The complex *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (0.060 g, 0.050 mmol) was dissolved in *ca.* 15 cm^3 of thf and the temperature of the solution lowered in a cryostatic bath to −60 °C. Upon addition of base (1.1 cm^3 of a 0.1 M solution of [NBu_4]OH in alcohol, 0.11 mmol), the isocyanide complex **3** precipitated spontaneously as a yellow solid which was immediately isolated by filtration, washed with small volumes of cold thf and dried in vacuum (0.040 g, 73% yield).

Route (ii). The complex *trans*-[ReCl($CNSiMe_3$)(dppe)$_2$] (0.18 g, 0.16 mmol) was dissolved in thf (30 cm^3) and MeOH added with stirring (1.5 cm^3, 37 mmol). The solution turned to greenish yellow and the system were left stirring overnight. The yellow precipitate which was formed (complex **3** contaminated with a paramagnetic impurity) was isolated by filtration, washed with thf (3 × 1 cm^3) and dried under vacuum. Recrystallisation from CH_2Cl_2–n-pentane led to the formation of crystalline crops of the isocyanide complex **1** which were isolated by filtration, washed with CH_2Cl_2–n-pentane (1 : 4), then with n-pentane and dried in vacuum (0.076 g, 45% yield). One of the crystals was analysed by X-ray diffraction. IR (KBr pellet): 3240 [w, br, ν(NH)], 1725 (s) and 1685 (s) cm^{-1} [δ(NH)]. NMR (298 K): ^{1}H (CD_2Cl_2), δ 7.45–6.62 (br, 40 H, Ph of dppe) and 3.04–2.12 (br, 8 H, CH_2 of dppe); ^{31}P-{^{1}H} (CD_2Cl_2, standard $P(OMe)_3$), δ −107.9. FAB mass spectrum: *m*/*z* 1010 ([$M - Cl]^+$) (Found: C, 61.7; H, 5.5; N, 1.0. $C_{53}H_{49}ClNP_4Re$ requires C, 61.4; H, 5.2; N, 1.2%).

***trans*-[ReCl(CND)(dppe)$_2$].** The complex *trans*-[ReCl($CNSiMe_3$)(dppe)$_2$] (0.080 g, 0.071 mmol) was dissolved in thf (20 cm^3) and a stoichiometric amount of DCl added with stirring (0.72 cm^3, 0.070 mmol, of a solution prepared by addition of 0.10 cm^3 of MeOD and 0.32 cm^3 of Me_3SiCl to 25 cm^3 of thf). The system was left stirring for 15 min. Evaporation of the solvent led to spontaneous precipitation of a pale yellow solid which was isolated by filtration, washed with thf–pentane (1 : 4) then with pentane and dried in vacuum (0.008 g, 10% yield). IR (KBr pellet): 1580 and 1520 cm^{-1} [s, δ(ND)].

***trans*-[ReCl(CNH)(dppe)$_2$][BF$_4$]·2[NBu$_4$][BF$_4$] 3$^+$.** The complex *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] (0.060 g, 0.050 mmol), dissolved in a 0.2 mol dm^{-3} [NBu_4][BF_4]–NCMe electrolyte solution (15 cm^3), was oxidised by controlled potential electrolysis at a sufficiently high potential (1.70 V *vs.* SCE), until the consumption of 2 F mol^{-1} and complete disappearance of the two anodic waves of the complex. The electrolysed violet solution was then transferred from the working compartment to a Schlenk tube and the solvent evaporated under vacuum until half of its volume. The solution changed to red. Upon addition of Et_2O, a partial precipitation of the electrolyte was observed and the corresponding white solid (0.15 g) was isolated by filtration. Sequential addition of n-pentane and concentration of the solution under vacuum led to the formation of a pink solid which was filtered off, washed with n-pentane and dried under vacuum. Recrystallisation from thf–n-pentane led to the formation of dark red crystals of complex **3**$^+$ in low yield, which were separated from the mother solution by decantation, washed with a few portions (0.5 cm^3) of thf–n-pentane (1 : 4), then with n-pentane, and dried under vacuum. An X-ray diffraction study on one of these crystals showed the presence of 3[BF_4]$^-$ and 2[NBu_4]$^+$ ions per complex cation, but as already pointed out the poor quality of the structural results prevented further discussion. A further crop, although contaminated with electrolyte, was obtained upon further addition of n-pentane to the mother solution (it was isolated by filtration, washed with thf–n-pentane and dried under vacuum). IR (KBr pellet): 1050 cm^{-1} [s, br, ν(BF)]. NMR (298 K): ^{1}H (CD_2Cl_2), δ 18.5 (m, br, 4 H), 12.73 (t, *J* 7.4, 5 H), 11.79 (d, *J* 7.8, 5 H), 10.74 (t, *J* 7.2, 4 H), 10.60 (t, *J* 7.5, 4 H), 9.66 (t, *J* 7.8, 5 H), 9.02 (br, 4 H), 5.66 (m, 3 H), 5.41 (qt, *J* 7.2, 6 H) (Ph of dppe), 5.12 (m, 9 H), 3.95 (s, 5 H), 3.79–3.34 (m, 35 H), 3.13 (t, *J* 6.6, 7 H), 2.99 (t, *J* 7.5 Hz, 18 H) and −14.30 (m, 6 H) (CH_2 of dppe + NBu_4^+). μ_{eff} (CH_2Cl_2, Evans method) = 2.5 μ_B (corrected for the diamagnetism).

Table 3 Crystallographic data for complexes **1**·thf and **3**·2thf

	1·thf	**3**·2thf
Molecular formula	$C_{60}H_{65}ClNOP_4ReSi$	$C_{61}H_{65}ClNO_2P_4Re$
M	1189.81	1189.74
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	13.612(3)	11.557(3)
b/Å	16.922(5)	13.353(2)
c/Å	24.098(6)	17.284(5)
α/°	91.01(2)	—
β/°	91.34(2)	96.42(2)
γ/°	93.42(2)	—
V/Å^3	5538(2)	2651(1)
Z	4	2
D_c/g cm^{-3}	1.427	1.491
μ(MoKα)/cm^{-1}	24.20	25.09
Unique reflections	15712	5776
Reflections with $I > 2\sigma(I)$	6481	2946
$R(F_o)$	0.0688	0.0364
$R'(F_o)$	0.0968	0.0485

X-Ray data collection, structure determination and refinement of complexes 1·thf and 3·2thf

The measurements were made on a Nonius ENRAF CAD4 (**1**·thf) or a Philips PW 1100 (**3**·2thf) diffractometer with Mo-Kα graphite-monochromated radiation (λ = 0.71073 Å).

The poor quality of the crystals of complex **1**·thf prevented accurate structure determination. Crystallographic data are summarised in Table 3. One standard reflection was monitored every 100 measurements; decay was observed over the time of data collection for both crystals, 68% (**1**·thf) and 23% (**3**·2thf). An empirical correction for absorption was applied to the data of **3**·2thf (maximum and minimum transmission factor values 1.000–0.864).[29]

The structures were solved by Patterson and Fourier methods and refined first by full-matrix least squares procedures with isotropic thermal parameters, and then in the last cycles of refinement by blocked-matrix least squares procedures, with anisotropic thermal parameters for the Re, Cl, P, Si, N and

C1–C5 atoms of complex **1**·thf, and by full-matrix least squares procedures with anisotropic thermal parameters for all the non-hydrogen atoms for **3**·2thf. Two crystallographically independent molecules (*A* and *B*) were found in the structure of **1**·thf, whereas in that of **3**·2thf the Cl and C1 atoms were disordered and interchanged. All hydrogen atoms (except those of the thf molecules) were placed at their geometrically calculated positions (C–H 0.96 Å) and refined "riding" on the corresponding carbon atoms, isotropically. All atoms of the thf molecules were considered as C atoms. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" del C.N.R, Parma, using SHELX 76 and SHELXS 86 systems of crystallographic computer programs.[30]

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