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Cyanide and methylisocyanide complexes of rhenium(I) $[NBu_4][ReX(CN)(dppe)_2]$ (X = Cl or CN; dppe = $Ph_2PCH_2CH_2PPh_2$) and *trans*-$[ReX(CNMe)(dppe)_2]$ (X = H, F, Cl or CN): crystal structures of *trans*-$[ReX(CNMe)(dppe)_2]$ (X = H or Cl)

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Abstract

Reaction of *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with $[NBu_4]CN$ gives $[NBu_4][ReCl(CN)(dppe)_2]$ (**1**) which, upon further reaction with $[NBu_4]CN$, forms $[NBu_4][$*trans*-$Re(CN)_2(dppe)_2]$ (**2**) which is readily oxidized to $[Re(CN)_2(dppe)_2]$ (**3**). Treatment of **1** with $Me_3SiCF_3SO_3$ affords $[ReH(CNMe)(dppe)_2]$ (**4**) which is also obtained by reaction of *trans*-$[ReCl(CNMe)(dppe)_2]$ (**5**) with $Li[BEt_3H]$. Compound **5** reacts with $[NBu_4]CN$ (in the presence of $Tl[BF_4]$) or $[NBu_4]F$ to give *trans*-$[Re(CN)(CNMe)(dppe)_2]$ (**6**) or *trans*-$[ReF(CNMe)(dppe)_2]$ (**7**) respectively. The crystal structures of **4** and **5** have been determined by X-ray diffraction analyses which indicate very bent isocyanide ligands (CNC angles of 147.7(7)° and 139.4(10)° respectively) and rather short Re–C bond lengths (1.947(6) Å and 1.861(12) Å respectively). Cyclic voltammetry shows that in aprotic solvent these complexes undergo two successive single-electron reversible oxidations. The oxidation potential of the first oxidation, for **7**, allows the estimation of the electrochemical parameter P_L of fluoride as −1.3 V.

Key words: Rhenium; Cyanide; Isocyanide; Crystal structure; Electrochemistry

1. Introduction

In contrast with carbonyl and isocyanides, which are strong π-electron acceptors and can stabilize low oxidation state metal centres, nitriles and cyanide are much weaker net electron acceptors and commonly do not coordinate to transition metals in low oxidation states unless other ligands which can behave as strong π acids are present. This is illustrated by some polycarbonyl–nitrile and polycarbonyl–cyanide complexes of Cr, Mo, W [1] or Re [2]. However, we have previously synthesized nitrile complexes with electron-rich rhenium(I) centres, $[ReCl(NCR)(dppe)_2]$ (R = alkyl or aryl; dppe = $Ph_2PCH_2CH_2PPh_2$) [3] and $[Re(NCR)_2(dppe)_2][BF_4]$ [4], formed by reaction of the appropriate nitrile with *trans*-$[ReCl(N_2)(dppe)_2]$ and these can undergo unusual geometrical isomerization processes [5].

We now report the extension of this study to cyanide, a stronger net electron donor than organonitriles. Moreover, isocyanides and nitriles are activated by the $\{ReCl(dppe)_2\}$ moiety towards protonation to form aminocarbynes or methyleneamide complexes, *trans*-$[ReCl(CNHR)(dppe)_2]^+$ [6] or $[ReCl(NCHR)(dppe)_2]^+$ [7], and the susceptibility and extent of electrophilic attack at cyanide needs to be explored, in particular for the synthesis of isocyanide or aminocarbyne products. At an electron-rich rhenium site, isocyanide would be expected (see below) to be bent owing to electronic effects, but this is not certain; the X-ray analysis of *trans*-$[ReCl(CN^tBu)(dppe)_2]$ [8] has indicated linear geometry for the *tert*-butyl isocyanide ligand. The dependence of the geometry of ligated isocyanide on the *trans* influence of a co-ligand has yet to be investigated. This work aims to provide an insight into such matters, through the preparation of cyanide or iso-

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cyanide complexes containing $\{ReX(dppe)_2\}$ (X = CN, H, F, or Cl) moieties.

2. Results and discussion

2.1. Syntheses and reactivity

Treatment of *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) in toluene with $[NBu_4]CN$ (in an approximately twofold molar ratio) results in the separation of a yellow powder which is a mixture of $[NBu_4][ReCl(CN)(dppe)_2]$ (**1**) and $[NBu_4]$[*trans*-$Re(CN)_2(dppe)_2$] (**2**) (eqns. (1) and (2)):

$$trans\text{-}[ReCl(N_2)(dppe)_2] + [NBu_4]CN \rightarrow [NBu_4][ReCl(CN)(dppe)_2] + N_2 \quad (1)$$

$$trans\text{-}[ReCl(N_2)(dppe)_2] + 2[NBu_4]CN \rightarrow [NBu_4][trans\text{-}Re(CN)_2(dppe)_2] + [NBu_4]Cl + N_2 \quad (2)$$

TABLE 1. IR and analytical [a] data for $[NBu_4][ReX(CN)(dppe)_2]$ (X = Cl or CN), *trans*-$[ReX(CNMe)(dppe)_2]$ (X = H, F or CN) and *trans*-$[Re(CN)_2(dppe)_2]$

Complex	Microanalysis (calculated) (%)			IR [b]: ν (CN) (cm^{-1})
	C	N	H	
$[NBu_4][ReCl(CN)(dppe)_2]$ (**1**)	65.0 (64.4)	2.9 (2.2)	6.5 (6.5)	1945s
$[NBu_4]$[*trans*-$Re(CN)_2(dppe)_2$] (**2**)	65.2 (65.8)	3.4 (3.3)	6.8 (6.6)	1995s
trans-$[Re(CN)_2(dppe)_2]$ [c] (**3**)	58.4 (58.9)	2.5 (2.5)	4.7 (4.5)	2020s
trans-$[Re(CN)(CNMe)(dppe)_2]$ [d] (**6**)	61.2 (61.0)	2.7 (2.6)	5.2 (4.8)	2020s, 1950br [e]
trans-$[ReH(CNMe)(dppe)_2]$ [f] (**4**)	60.3 (60.2)	1.2 (1.3)	5.0 (5.0)	1915s
trans-$[ReF(CNMe)(dppe)_2]$ [g] (**7**)				1800s

[a] Required values in parentheses.
[b] In KBr pellets: s, strong, br, broad.
[c] With CH_2Cl_2 of crystallization.
[d] With $\frac{1}{2}CH_2Cl_2$ of crystallization.
[e] Attributed to the isocyanide.
[f] With $\frac{1}{5}$ pentane of crystallization.
[g] Not obtained analytically pure.

TABLE 2. ^1H and ^{31}P NMR data [a] for cyanide and isocyanide complexes

Complex	^1H NMR			^{31}P NMR
	δ [b] (ppm)	Integration	Assignment	δ [c] (ppm)
trans-$[Re(CN)_2(dppe)_2]^-$ [d] (**2**)	7.3–7.0 (m)	40	C_6H_5 (dppe)	−107.0 (s)
	2.05 (s, br)	8	CH_2 (dppe)	
trans-$[Re(CN)(CNMe)(dppe)_2]$ (**6**)	7.7–6.6 (m)	40	C_6H_5 (dppe)	−108.4 (s)
	2.5–2.3 (m)	8	CH_2 (dppe)	
	2.32 (s)	3	CH_3NC	
trans-$[ReH(CNMe)(dppe)_2]$ (**4**)	7.4–7.0 (m)	40	C_6H_5 (dppe)	−91.9 (s)
	2.76 (m)	4	CH_2 (dppe)	
	2.75 (m)	4	CH_2 (dppe)	
	1.52 (s)	3	CH_3NC	
	−7.67 (q) [e]	≈ 1	Re–H	
trans-$[ReF(CNMe)(dppe)_2]$ (**7**)	7.7–6.8 (m)	40	C_6H_5 (dppe)	−104.7 (d) [f]
	2.7–2.3 (m)	8	CH_2 (dppe)	
	2.29 (s)	3	CH_3NC	

[a] In CD_2Cl_2.
[b] Relative to internal $SiMe_4$: m, multiplet; s, singlet; q, quintet; b, broad.
[c] Relative to $P(OMe)_3$, assigned to 4P (dppe).
[d] The characteristic ^1H resonances of the $[N(CH_2CH_2CH_2CH_3)_4]^+$ counter-ion are observed at $\delta \approx 3.1$ (m, 8H$^+$, α-CH_2); 1.5 (m, 8H$^+$, β-CH_2); 1.3 (8H$^+$, γ-CH_2) and 1.0 (m, 12H$^+$, CH_3) ppm, and have been assigned by spin-decoupling experiments.
[e] $^2J(HP) = 21.2$ Hz.
[f] $^2J(PF) = 23.4$ Hz.

The formation of **2** relative to **1** is promoted, by a larger excess of the cyanide salt and extended reaction time. Complexes **1** and **2** were separated using their different solubilities in CH_2Cl_2, in which the latter complex is much more soluble than the former.

The displacement of N_2 is promoted by light (particularly sunlight) and parallels those reported for the syntheses of [ReCl(L)(dppe)$_2$] (L = CNR [6,9], NCR [3], vinylidene [10] or η^2-phenylallene [11]) from the reactions of the same dinitrogen complex with isocyanides, nitriles, 1-alkynes or phenylpropyne respectively. The replacement of chloride by cyanide in **1** parallels the preparation of *trans*-[Re(CNMe)(L)(dppe)$_2$][BF$_4$] (L = CNR [12], NCMe [12] or NCNH$_2$ [13]) by reaction of *trans*-[ReCl(CNMe)(dppe)$_2$] with the appropriate L in the presence of Tl[BF$_4$] as chloride abstractor. However, in the present case the reactions do not require the thallium salt and yield anionic complexes rather than neutral or cationic species.

Related anionic cyanide and other pseudohalide complexes [NBu$_4$][MX(N$_2$)(dppe)$_2$] (M = Mo or W; X = CN, SCN or N$_3$) have been prepared [14] by reaction of *trans*-[M(N$_2$)$_2$(dppe)$_2$] with [NBu$_4$]X. In contrast with these complexes, which contain the strong net electron acceptor N_2 [14], our anionic **1** and **2** do not contain such a stabilizing ligand, which accounts for their low stability in solution (see below).

Complexes **1** and **2** show strong IR bands at 1945 and 1995 cm^{-1} respectively, assigned to ν(CN) (Tables 1 and 2). The higher frequency observed for **2** is consistent with competion of both cyanides for metal π-electron density, whereas in **1** the π-electron donation from chloride to metal promotes π-electron acceptance by the *trans* cyanide.

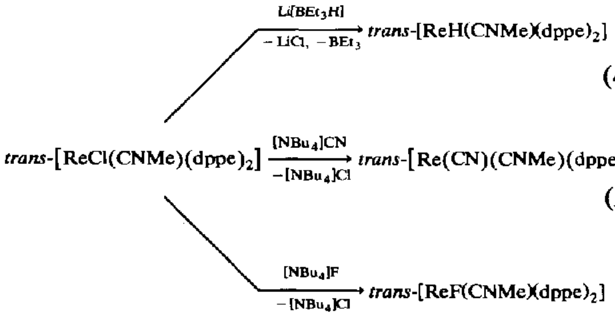
The single ν(CN) band for **2** suggests the *trans* geometry, which is confirmed by the singlet resonance in its ^{31}P NMR spectrum ($\delta = -107.0$ ppm relative to P(OMe)$_3$). Complex **1** either is not appreciably soluble in the usual solvents or undergoes decomposition, and thus no reliable NMR data could be collected. Nevertheless, for both complexes the [NBu$_4$]$^+$ counter-ion gives characteristic ^{1}H NMR patterns assigned by spin-decoupling experiments (Table 2).

Complex **2** is unstable in solution (see above), particularly in CH_2Cl_2 where ready oxidation occurs to give the red paramagnetic species *trans*-[Re(CN)$_2$(dppe)$_2$] (**3**), which exhibits ν(CN) as a single strong band at 2020 cm^{-1}, higher than ν(CN) in **1** and **2**, and in accord with the higher metal oxidation state of **3**.

The cyanide in **1** undergoes alkylation and the complex *trans*-[ReH(CNMe)(dppe)$_2$] (**4**) was obtained upon treatment of **1** in dichloromethane, with trimethylsilyl triflate, $CF_3SO_3SiMe_3$ (reaction (3)). Moisture would account for the protonation of the metal and the cleavage of the N–Si bond at a trimethylsilyl isocyanide intermediate *trans*-[ReCl(CNSiMe$_3$)(dppe)$_2$] [15], with formation of dimethylsilanediol (Me$_2$Si(OH)$_2$) and thence polysiloxanes, although no such products were sought or found.

$$[\mathrm{NBu_4}][\mathrm{ReCl(CN)(dppe)_2}] \xrightarrow{\mathrm{CF_3SO_3SiMe_3}} trans\text{-}[\mathrm{ReH(CNMe)(dppe)_2}] \qquad (3)$$

The hydride complex **4** can also be prepared, with a higher yield, by reaction of *trans*-[ReCl(CNMe)(dppe)$_2$] (**5**) with superhydride Li[BEt$_3$H] in CH_2Cl_2 (eqn. (4)). The chloride in **5** can also be displaced by other nucleophiles. The cyano or the fluoro complexes *trans*-[Re(CN)(CNMe)(dppe)$_2$] (**6**) or *trans*-[ReF(CNMe)(dppe)$_2$] (**7**) are obtained from the reactions of **5** in toluene or CH_2Cl_2 with [NBu$_4$]CN (eqn. (5)) or [NBu$_4$]F (eqn. (6)), respectively:



$$trans\text{-}[\mathrm{ReCl(CNMe)(dppe)_2}] \xrightarrow[-\mathrm{LiCl},\ -\mathrm{BEt_3}]{\mathrm{Li[BEt_3H]}} trans\text{-}[\mathrm{ReH(CNMe)(dppe)_2}] \qquad (4)$$

$$trans\text{-}[\mathrm{ReCl(CNMe)(dppe)_2}] \xrightarrow[-[\mathrm{NBu_4}]\mathrm{Cl}]{[\mathrm{NBu_4}]\mathrm{CN}} trans\text{-}[\mathrm{Re(CN)(CNMe)(dppe)_2}] \qquad (5)$$

$$trans\text{-}[\mathrm{ReCl(CNMe)(dppe)_2}] \xrightarrow[-[\mathrm{NBu_4}]\mathrm{Cl}]{[\mathrm{NBu_4}]\mathrm{F}} trans\text{-}[\mathrm{ReF(CNMe)(dppe)_2}] \qquad (6)$$

The methyl isocyanide complexes are yellow solids and the *trans* geometry is indicated by their ^{31}P NMR spectra (δ -91.9 s (**3**), -108.4 s (**5**) or -104.7 ppm (d, ^2J(PF) = 23.4 Hz) in CD_2Cl_2) (Table 2). Consistent with this geometry, the hydride resonance of **4** in the ^{1}H NMR spectrum is a quintet, ^2J(HP) = 21.2 Hz, at $\delta = -7.67$ ppm (in CD_2Cl_2).

Their IR spectra exhibit strong bands assigned to ν(CN) in the range 2010–1800 cm^{-1}, (Table 1).

For the isocyanides, ν(CN) reflects the electronic properties of the *trans* ligand, decreasing with the increase in the ligand net electron donor ability: 1950 cm^{-1} (**6**, with cyanide, a σ-electron donor and π-electron acceptor) > 1915 cm^{-1} (**4**, with hydride, a σ-electron donor) > 1800 cm^{-1} (**7**, with fluoride, a σ- and π-electron donor). These frequencies, and in particular that of the fluoro complex **7**, are well below the value of approximately 2150 cm^{-1} for free methyl isocyanide, as a result of the strong π-electron release from the metal.

2.2. *Molecular structures of trans-[ReX(CNMe)(dppe)$_2$] (X = H (4) or Cl (5))*

Crystals suitable for X-ray diffraction analysis were isolated for *trans*-[ReX(CNMe)(dppe)$_2$] (X = H (**4**) or

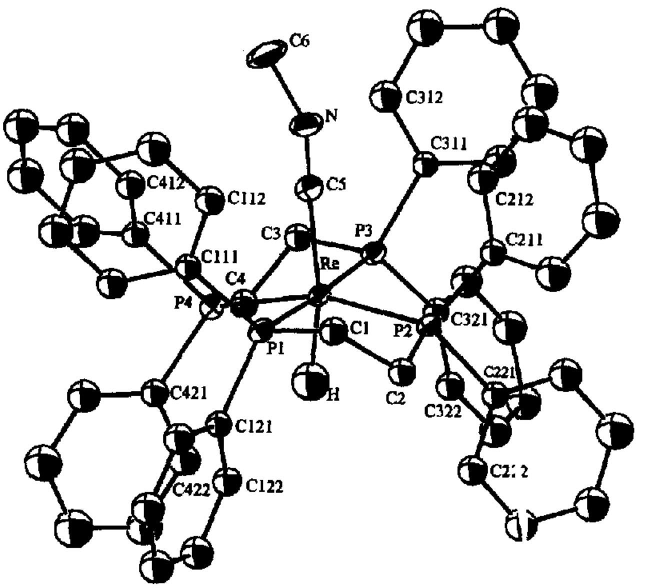


Fig. 1. Molecular structure of *trans*-[ReH(CNMe)(dppe)$_2$] (4) with ellipsoids drawn at 70% probability level.

Cl (5)), the former obtained by reaction (3) and the latter from N_2 replacement by CNMe at *trans*-[ReCl(N_2)(dppe)$_2$] according to a published [6,9] procedure. Their molecular structures are depicted in Figs. 1 and 2, and selected bond lengths and angles are indicated in Table 3.

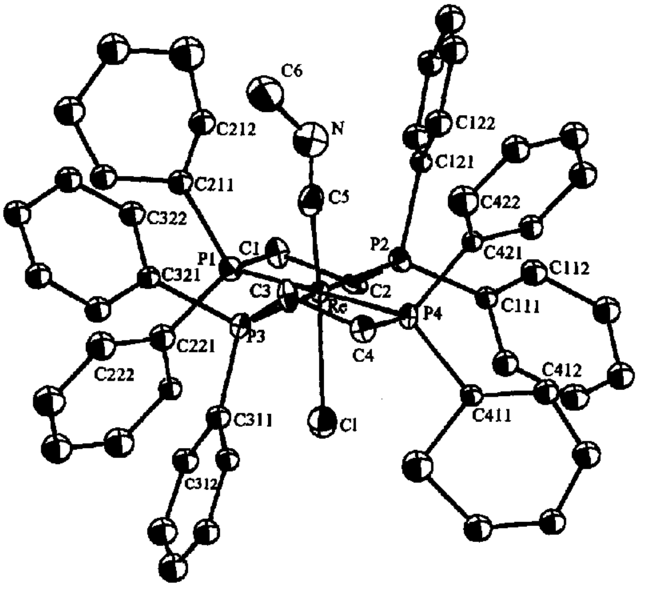


Fig. 2. Molecular structure of *trans*-[ReCl(CNMe)(dppe)$_2$] (5) with ellipsoids drawn at 70% probability level.

TABLE 3. Selected bond lengths (Å) and angles (°) for *trans*-[ReH(CNMe)(dppe)$_2$] (4) and *trans*-[ReCl(CNMe)(dppe)$_2$] (5)

Complex	4	5
Re–Cl	–	2.607(5)
Re–H	1.54(7)	–
Re–P(av)	2.36	2.40
Re–C(5)	1.947(8)	1.861(12)
C(5)–N	1.207(9)	1.210(15)
N–C(6)	1.416(9)	1.417(17)
P–C(av)	1.85	1.86
P–Ph(av)	1.84	1.84
C–C(av)	1.52	1.53
Cl–Re–C(5)	–	175.8(3)
H–Re–C(5)	164 (2)	–
P(1)–Re–P(2)	82.1(2)	81.8(2)
P(3)–Re–P(4)	82.0(2)	79.2(2)
Re–C(5)–N	177.6(6)	174.0(9)
C(5)–N–C(6)	147.7(7)	139.4(10)

In both the Re atom exhibits octahedral coordination with four P atoms in the equatorial positions, whereas the terminal C atom of the isocyanide and the hydride or chloride occupy the apical positions.

The coordinated H atom was located in **4**, and the Re–H bond length, 1.54(7) Å, is comparable with the average Re–H distances reported for other hydride complexes, such as [ReH_5L_3] [L = PPh_3, 1.54(5) Å; L = $PMePh_2$, 1.688(5) Å] [16a], [$Re_2H_5(Me_2PCH_2PMe_2)$] [PF_6], (1.7(1) Å) [16b], and *trans*- or *cis*-[$ReH_2(mhp)_2(PPh_3)_2$] [PF_6] (mhp = anion from 2-hydroxy-6-methylpyridine) (1.61(7) Å) [16c]. The differences are not significant in view of the common low accuracy in the determination of these metal–hydrogen distances [16a,b].

The isocyanide in each complex is markedly bent, with angles at the N atom of 147.7(7)° (**4**) or 139.4(10)° (**5**), this is believed to be electronic in origin, an extreme form being represented by the following valence band formulation:

$$Re{=}C{=}\ddot{N}\diagdown_{Me}$$

Consistent with this, a short rhenium–carbon bond length and an elongated unsaturated C–N bond in the isocyanide are observed.

In fact, the bound isocyanide has considerable carbene character, and the Re–C bond length, 1.947(6) Å (**4**) or 1.861(12) Å (**5**), is even shorter than that reported, 2.046(8) Å [10], for the vinylidene complex *trans*-[ReCl(=C=CHPh)(dppe)$_2$] and than that estimated [17a] for an Re=C double bond, 1.91 Å, from the sum of the double bonded radii of Re (1.24 Å) and C sp^2 (0.67 Å). Moreover, the unsaturated C–N bond length, 1.207(8) Å (**4**) or 1.210(15) Å (**5**), is much longer than the average value, 1.14 Å, quoted [17b] for a C≡N triple bond. This suggests double-bond character consistent with the low ν(CN) values (see above).

Short metal–carbon (isocyanide) distances and extended C≡N bond lengths have also been reported for other isocyanide complexes with related electron-rich binding sites, in particular *trans*-$[ReCl(CN^tBu)(dppe)_2]$ (1.926(9) Å and 1.154(10) Å, respectively) [8], *mer*-$[Re(\eta^1\text{-}S_2PPh_2)(N_2)(CNMe)(PMe_2Ph)_3]$ (1.93(1) Å and 1.20(2) Å, respectively) [18], *mer*-$[ReCl(N_2)(CNMe)\{P(OMe)_3\}_3]$ (2.07(2) Å and 1.12(2) Å, respectively) [19] or *trans*-$[Mo(CNMe)_2(dppe)_2]$ (2.101(7) Å and 1.10(1) Å respectively) [20]. However, none of these complexes has such a bent isocyanide. Only the molybdenum diisocyanide complex exhibits a clearly bent geometry, with an angle of 156(1)° [20], whereas the tert-butyl isocyanide in the above-mentioned rhenium complex is essentially linear ($\measuredangle$CαNC, 174.0(9)°) [8], conceivably as a result of steric effects.

Rare examples of bent isocyanides at much less electron-rich metal centres are provided by $[Mo(\eta^5\text{-}C_5H_5)_2(CN^tBu)]$ [21] or *cis*-$[Fe(CN)_2(CNMe)_4] \cdot 4CHCl_3$ [22], with bending angles of 139.5(4)° or 156(7)° respectively, but such bendings conceivably are steric in origin, resulting from intermolecular packing forces.

In our complexes, this bending (which is more pronounced with **5** with a π-electron donor chloride than with **4** with a non-π-donor hydride) results from extensive π-electron release from the electron-rich metal to a C≡N π^* orbital, leading to a weakening of this bond, a strengthening of the metal–carbon bond and a localization of electronic charge at the nitrogen atom. It can also be rationalized by extended Hückel calculations [23] and by simplified π-MO schemes [24] derived from Walsh-type diagrams where the HOMO has M–C bonding and C–N antibonding character.

The isocyanide is activated towards electrophilic attack at its N atom and, for example, the aminocarbyne complexes *trans*-$[ReCl(CNHR)(dppe)_2][BF_4]$ (**8**) (R = H [15], alkyl or aryl [6]) or *trans*-$[M(CNHMe)(CNMe)(dppe)_2][BF_4]$ (M = Mo or W) [25] were obtained by reaction of HBF_4 with *trans*-$[ReCl(CNR)(dppe)_2]$ or *trans*-$[M(CNMe)_2(dppe)_2]$ respectively. Since the molecular structures of **8** (R = H [15] or Me [6]) have previously been determined, we can for the first time directly observe the molecular structural rearrangements resulting from the conversion of a bound isocyanide (CNMe) into the corresponding aminocarbyne (CNHMe).

As a consequence of the protonation of the isocyanide in **5**, the expected shortening of the rhenium–carbon bond is evident, from 1.861(12) Å in **5** to 1.798(30) Å [6] in the aminocarbyne complex **8** (R = Me). Moreover, the unsaturated C–N bond lengthens from 1.210(15) Å in **5** to 1.347(32) Å [6] in **8** (R = Me). This is in accord with some simplified π- MO schemes [24], as well as with theoretical calculations [23] which indicate that a β-electrophilic attack at the isocyanide leads to an increase in both the σ- and the π-overlap populations of the Re–C bond and to a decrease in such populations for the C–N bond. Nevertheless, protonation at N appears to be charge controlled rather than frontier orbital controlled, since the nitrogen (in contrast with the Re and the isocyanide carbon) carries an appreciable negative net atomic charge whereas the HOMO is mainly localized at the Re and Cl atoms [23]. The decrease in the Re–Cl distance, from 2.607(5) Å in **5** to 2.484(6) Å [6] in **8** (R = Me), with the concomitant lengthening of the Re–P average distance, from 2.399(5) Å in **5** to 2.457(7) Å [6] in **8** (R = Me) are also noteworthy. This suggests stronger π-electron acceptance of the aminocarbyne compared with the isocyanide ligand, as revealed [26] by the much higher oxidation potential of the aminocarbyne complexes relative to the parent isocyanide complexes.

2.3. Electrochemical studies

The electrochemical behaviour of the complexes has been investigated by cyclic voltammetry. Two single-electron reversible or *quasi*-reversible waves are observed for each complex, and they have been assigned as in Table 4. No reliable cyclic voltammetry data could be obtained for **1**, because of its decomposition in solution (see above).

The neutral dicyano complex of rhenium(II) *trans*-$[Re(CN)_2(dppe)_2]$ (**3**) has the expected $Re^{II/I}$ cathodic wave at $E_{1/2}^{red} = -0.49$ V, which is identical with that observed for $E_{1/2}^{ox}$ of the first anodic process, $Re^{I/II}$, for the corresponding anionic species *trans*-$[Re(CN)_2(dppe)_2]^-$ (**2**).

The neutral isocyanide complexes *trans*-$[ReX(CNMe)(dppe)_2]$ (X = CN (**6**), F (**7**) or H (**4**)) are oxidized at much more anodic potentials, those of the

TABLE 4. Cyclic voltammetric data in CH_2Cl_2 [a] for the cyanide and isocyanide complexes of rhenium

Complex	$E_{1/2}^{ox}$ (V)	
	$Re^{I/II}$	$Re^{II/III}$
$[NBu_4][$*trans*-$Re(CN)_2(dppe)_2]$ (**2**)	−0.49	0.75
trans-$[Re(CN)_2(dppe)_2]$ (**3**)	−0.49 [b]	0.75
trans-$[Re(CN)(CNMe)(dppe)_2]$ (**6**)	0.29	1.19 [c]
trans-$[ReH(CNMe)(dppe)_2]$ (**4**)	−0.07	0.95 [c]
trans-$[ReF(CNMe)(dppe)_2]$ (**7**) [d]	−0.06	0.92

[a] Values of half-wave oxidation potential (±20 mV *vs.* (SCE)), measured by cyclic voltammetry (at 200 mV s^{-1}).

[b] Cathodic wave ($E_{1/2}^{red}$).

[c] Irreversible wave ($E_{p/2}^{ox}$).

[d] In THF.

TABLE 5. Fractional atomic co-ordinates ($\times 10^4$) for [Re(H)(CNMe)(dppe)$_2$]·CH$_2$Cl$_2$

	x	*y*	*z*
Re	2268.0(2)	4330.9(2)	2355.9(1)
P(1)	1271 (1)	3917 (1)	1424 (1)
C(1)	330 (6)	5263 (6)	941 (3)
P(2)	776 (1)	6148 (1)	2152 (1)
C(2)	−367 (6)	6050 (6)	1554 (3)
P(3)	3368 (1)	4714 (1)	3248 (1)
C(3)	4490 (6)	3367 (6)	3605 (4)
P(4)	3245 (1)	2467 (1)	2836 (1)
C(4)	3823 (6)	2531 (6)	3734 (4)
C(5)	3581 (5)	4452 (5)	1604 (3)
N	4387 (5)	4567 (5)	1147 (3)
C(6)	5596 (7)	4081 (8)	791 (5)
H	1518 (57)	3944 (56)	3025 (40)
C(111)	2254 (6)	3122 (5)	646 (3)
C(112)	2817 (6)	3654 (6)	81 (4)
C(113)	3660 (8)	3008 (7)	−470 (5)
C(114)	3890 (8)	1897 (7)	−460 (5)
C(115)	3354 (7)	1358 (7)	77 (4)
C(116)	2518 (7)	1976 (6)	635 (4)
C(121)	79 (6)	3256 (5)	1614 (3)
C(122)	−381 (6)	3083 (6)	2344 (4)
C(123)	−1302 (7)	2614 (7)	2495 (4)
C(124)	−1759 (8)	2299 (7)	1916 (4)
C(125)	−1292 (7)	2461 (7)	1193 (4)
C(126)	−385 (6)	2932 (6)	1039 (4)
C(211)	1138 (6)	7336 (5)	1634 (3)
C(212)	2345 (7)	7232 (6)	1381 (4)
C(213)	2601 (8)	8116 (8)	957 (5)
C(214)	1658 (8)	9089 (8)	775 (5)
C(215)	457 (9)	9220 (8)	1038 (5)
C(216)	205 (8)	8345 (7)	1463 (5)
C(221)	−276 (6)	6852 (5)	2938 (3)
C(222)	−1169 (6)	6419 (6)	3280 (4)
C(223)	−1983 (7)	6917 (7)	3890 (4)
C(224)	−1881 (8)	7834 (7)	4165 (5)
C(225)	−986 (8)	8253 (8)	3860 (5)
C(226)	−178 (7)	7763 (7)	3239 (4)
C(311)	4361 (6)	5560 (5)	2959 (3)
C(312)	5581 (7)	5063 (7)	2671 (4)
C(313)	6310 (9)	5718 (8)	2420 (5)
C(314)	5824 (8)	6863 (8)	2464 (5)
C(315)	4619 (8)	7364 (8)	2737 (5)
C(316)	3875 (7)	6725 (7)	2968 (4)
C(321)	2677 (5)	5288 (5)	4156 (3)
C(322)	1430 (6)	5474 (6)	4379 (4)
C(323)	913 (7)	5856 (6)	5074 (4)
C(324)	1629 (7)	6046 (7)	5558 (4)
C(325)	2846 (7)	5873 (7)	5354 (4)
C(326)	3378 (7)	5501 (6)	4653 (4)
C(411)	4653 (6)	1484 (5)	2357 (3)
C(412)	4966 (6)	1694 (6)	1603 (4)
C(413)	5998 (7)	974 (7)	1223 (4)
C(414)	6750 (8)	18 (7)	1584 (5)
C(415)	6476 (8)	−222 (8)	2335 (5)
C(416)	5418 (7)	485 (7)	2724 (4)
C(421)	2350 (6)	1540 (6)	3104 (3)
C(422)	1493 (6)	1744 (6)	3733 (4)
C(423)	750 (8)	1087 (8)	3931 (5)
C(424)	833 (9)	263 (9)	3470 (5)
C(425)	1654 (8)	53 (8)	2847 (5)
C(426)	2410 (7)	696 (6)	2668 (4)
C(7)	3323 (15)	8587 (14)	4607 (9)
Cl(1)	2672 (4)	8861 (4)	5551 (3)
Cl(2)	4526 (9)	9166 (9)	4597 (5)
Cl(3)	4820 (7)	8302 (7)	4452 (4)

fluoride complex 7 and hydride complex 4 being comparable with that quoted (+0.08 V) [9], for the related chloride complex *trans*-[ReCl(CNMe)(dppe)$_2$]. These values reflect the order of the net π-electron acceptor minus σ-donor ability of the ligands: CNMe > CN$^-$ > Cl$^-$ $\gtrsim$ F$^-$ $\gtrsim$ H$^-$. This property can be measured by the electrochemical ligand parameter P_L [27] estimated to be −0.96 V for CN$^-$, −1.19 V for Cl$^-$, −1.34 V for F$^-$ and −1.36 V for H$^-$, by considering the known [12] values for the electron-richness ($E_s = 1.15$ V) and polarizability ($\beta = 0.90$) of *trans*-{Re(CNMe)(dppe)$_2$}$^+$.

The P_L values for CN$^-$, Cl$^-$ and H$^-$ are comparable with those reported [27] (−1.00 V, −1.19 V and −1.22 V, respectively) whereas that for F$^-$ (−1.3 V) is now reported for the first time.

3. Conclusions

In a recent study, we have shown [28] that azide and other pseudohalides (such as isocyanate and isothiocyanate) can stabilize a *trans* metal–N$_2$ bond, in particular in *trans*-[ReX(N$_2$)(dppe)$_2$] (X = N$_3$, NCO or NCS). We now report that cyanide, a stronger net electron π-acceptor than these pseudohalides, can replace N$_2$ itself at rhenium(I) to form very electron-rich anionic species which are readily oxidizable and whose synthetic potentialities have been explored by methylation of the cyanide ligand to form a methyl isocyanide complex. The methyl isocyanide ligand at such an electron-rich centre would be expected to be bent, and this has been clearly established by X-rays for the first time for rhenium. Previous to this study, electronically induced isocyanide bending has been reported only in *trans*-[Mo(CNMe)$_2$(dppe)$_2$] [20]. Our rhenium complexes exhibit much more pronounced bending because of the strong electron donor ability of the ligand in the *trans* position (chloride or hydride), compared with the molybdenum diisocyanide complex in which the *trans*-isocyanides compete for metal d electrons.

4. Experimental details

All manipulations and reactions were performed under dinitrogen by standard inert-gas flow and vacuum techniques. Solvents were purified before use by standard procedures. [NBu$_4$]CN and CF$_3$SO$_3$SiMe$_3$

were used as purchased from Fluka and Janssen respectively, and *trans*-[ReCl(N$_2$)(dppe)$_2$] [29] and *trans*-[ReCl(CNMe)(dppe)$_2$] [6,9] were prepared by published methods.

IR were carried out on a Perkin–Elmer 683 spectrophotometer. ^{1}H and ^{31}P NMR spectra were recorded on a Varian 300 spectrometer. The electrochemical experiments were performed on an EG&G PARC 173 potentiostat–galvanostat and an EG&G PARC 175 universal programmer. The redox potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]-CH$_2$Cl$_2$ (or THF) at a platinum electrode. The values of the oxidation or reduction potentials are quoted relative to SCE and were measured using the redox couple [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ ($E_{1/2}^{ox}$ = 0.57 V *vs.* SCE, in CH$_2$Cl$_2$) as internal reference.

4.1. Syntheses of complexes

4.1.1. [NBu$_4$][ReCl(CN)(dppe)$_2$] (1) and [NBu$_4$][trans-Re(CN)$_2$(dppe)$_2$] (2)

A solution of *trans*-[ReCl(N$_2$)(dppe)$_2$] (0.50 g, 0.48 mmol) in toluene (100 cm^3) was treated with [NBu$_4$]CN (0.30 g, 1.12 mmol) and the suspension was stirred in sunlight for 3 h. The yellow solid (mixture of **1** with **2**) was then filtered off and washed with CH$_2$Cl$_2$ (10 cm^3) to leave a residue of **1** which was dried *in vacuo* (yield, about 0.30 g (50%)).

Complex **2** was isolated from the filtered toluene solution upon concentration and addition of Et$_2$O (yield, about 0.15 g (25%)).

However, a better yield of **2** could be obtained as follows.

[NBu$_4$]CN (0.50 g, 1.86 mmol) was added to a solution of *trans*-[ReCl(N$_2$)(dppe)$_2$] (1.00 g, 0.96 mmol) in toluene (100 cm^3) and the suspension was stirred in sunlight for about 8 h. The solution was separated from the solid (A; mixture of **1** with **2**) by filtration, concentrated to about 20 cm^3 and, upon addition of Et$_2$O, **2** precipitated as a yellow solid which was filtered off, washed with Et$_2$O (2 × 5 cm^3) and dried *in vacuo*. A further amount of **2** was obtained by addition of CH$_2$Cl$_2$ (10 cm^3) to the solid A followed by filtration and addition of Et$_2$O (10 cm^3), leading to the precipitation of **2** (total yield, about 0.80 g (65%)).

4.1.2. trans-[Re(CN)$_2$(dppe)$_2$] (3)

A CH$_2$Cl$_2$ solution (20 cm^3) of [NBu$_4$][*trans*-Re(CN)$_2$(dppe)$_2$] (**2**) (0.20 g, 0.16 mmol) was stirred in air for about $\frac{1}{2}$ h. The addition of Et$_2$O (20 cm^3) led to the precipitation of **3**, which was filtered off and dried *in vacuo* (yield, about 0.15 g (90%)).

TABLE 6. Fractional atomic co-ordinates (× 10^4) for [Re(Cl)(CNMe)(dppe)$_2$]

	x	*y*	*z*
Re	0	0	0
Cl	−2828(3)	1767(3)	−82(2)
C(5)	2011(11)	−1168(10)	−46(7)
N	3322(13)	−2022(13)	17(9)
C(6)	4477(10)	−2267(17)	−668(10)
P(2)	−299(2)	−1856(2)	1469(1)
P(1)	−690(2)	−1073(2)	−1116(2)
C(1)	−1194(8)	−2410(8)	−212(6)
C(2)	−1692(7)	−2186(8)	909(6)
P(3)	303(2)	1935(2)	−1461(1)
P(4)	694(2)	1131(2)	1110(1)
C(3)	1756(8)	2108(9)	−855(5)
C(4)	1372(8)	2525(8)	208(6)
C(111)	−992(7)	−1683(8)	2750(5)
C(112)	−1042(8)	−2900(9)	3627(6)
C(113)	−1565(9)	−2460(10)	4644(7)
C(114)	−2315(9)	−965(9)	4669(7)
C(115)	−2366(9)	3(10)	3861(7)
C(116)	−1706(8)	−185(9)	2847(6)
C(121)	1317(7)	−3860(7)	1997(5)
C(122)	2606(9)	−4043(10)	2221(7)
C(123)	3793(10)	−5530(10)	2613(7)
C(124)	3621(10)	−6788(11)	2746(7)
C(125)	2216(8)	−6561(9)	2482(6)
C(126)	1016(9)	−5065(9)	2108(6)
C(211)	718(8)	−2482(9)	−1709(6)
C(212)	1877(8)	−3566(9)	−1288(6)
C(213)	3023(13)	−4779(14)	−1381(10)
C(214)	2853(11)	−4731(12)	−2447(8)
C(215)	1599(10)	−3570(11)	−3196(8)
C(216)	529(8)	−2439(9)	−2822(6)
C(221)	−2167(8)	234(9)	−2235(6)
C(222)	−1988(10)	1044(10)	−3245(7)
C(223)	−3150(11)	2120(12)	−4101(8)
C(224)	−4555(10)	2343(11)	−3956(8)
C(225)	−4822(10)	1544(11)	−2932(8)
C(226)	−3655(7)	491(8)	−2088(6)
C(311)	−1165(8)	3870(8)	−1993(6)
C(312)	−1247(7)	5255(8)	−2054(6)
C(313)	−2483(8)	6707(9)	−2514(6)
C(314)	−3738(10)	6872(10)	−2967(7)
C(315)	−3786(9)	5577(10)	−2929(7)
C(316)	−2599(8)	4127(9)	−2443(6)
C(321)	1135(7)	1571(8)	−2781(5)
C(322)	1898(8)	121(8)	−2841(6)
C(323)	2494(8)	−150(9)	−3747(6)
C(324)	2424(8)	1269(9)	−4691(6)
C(325)	1754(8)	2713(9)	−4567(6)
C(326)	966(8)	2798(9)	−3687(6)
C(411)	−544(7)	2354(8)	1928(5)
C(412)	−239(8)	2145(9)	3041(6)
C(413)	−1218(9)	3207(9)	3525(7)
C(414)	−2513(8)	4475(9)	2901(6)
C(415)	−2886(9)	4708(10)	1794(7)
C(416)	−1977(10)	3739(11)	996(8)
C(421)	2358(7)	−193(7)	2178(5)
C(422)	3692(10)	−229(11)	1993(8)
C(423)	4857(9)	−1187(10)	2848(7)
C(424)	4751(9)	−2109(10)	3840(7)
C(425)	3407(9)	−2107(9)	4029(7)
C(426)	2209(8)	−1172(8)	3189(6)

4.1.3. *trans-[ReH(CNMe)(dppe)$_2$] (4)*

A solution of [NBu_4][*trans*-ReCl(CN) (dppe)$_2$] (**1**) (0.25 g, 0.19 mmol) in CH_2Cl_2 (10 cm^3) was treated with $CF_3SO_3SiMe_3$ (0.080 cm^3, 0.41 mmol) and stirred for 1 h. Concentration *in vacuo* to about 5 cm^3 followed by the addition of Et_2O (5 cm^3) led to the precipitation of **4** as a yellow crystalline solid which was filtered off, washed with Et_2O and dried *in vacuo* (yield, about 0.10 g (50%)).

Complex **4** could also be obtained with a higher yield by treating a solution of *trans*-[ReCl(CNMe)-(dppe)$_2$] (0.15 g, 0.14 mmol) in CH_2Cl_2 (10 cm^3) with Li[BEt_3H] (0.50 cm^3 of a 1 M THF solution) and stirring for 24 h. The white solid formed was then removed by filtration, the solution concentrated to about 2 cm^3 and Et_2O (6 cm^3) added, leading to a yellow crystalline precipitate of **4**, which was filtered off and dried *in vacuo* (yield, about 0.10 g (70%)).

4.1.4. *trans-[Re(CN)(CNMe)(dppe)$_2$] (6)*

A toluene (200 cm^3) solution of *trans*-[ReCl-(CNMe)(dppe)$_2$] (0.21 g, 0.20 mmol) and [NBu_4]CN (0.070 g, 0.26 mmol) was stirred for 2 h with Tl[BF_4] (0.075 g, 0.26 mmol). The white powder was then removed by filtration, and the filtrate was treated with Et_2O (15 cm^3) and cooled to about 5 °C, leading to the precipitation of **6** as a yellow solid which was filtered off, dried *in vacuo* and recrystallized from CH_2Cl_2 (2 cm^3) V-pentane (2.5 cm^3) (yield, about 0.090 g (43%)).

4.1.5. *trans-[ReF(CNMe)(dppe)$_2$] (7)*

A solution of *trans*-[ReCl(CNMe)(dppe)$_2$] (**5**) (0.16 g, 0.15 mmol) in CH_2Cl_2 (10 cm^3) was treated with 1 cm^3 of a 1 M solution of [NBu_4]F (1 mmol) in THF and stirred for 20 h. Et_2O (20 cm^3) was then added, a white powder was filtered off and pentane (15 cm^3) added to the filtrate.

The final solution was concentrated *in vacuo* and, upon addition of Et_2O, a mixture of **7** with **5** precipitated as a yellow solid. Repeated recrystallization from CH_2Cl_2–Et_2O always produced **7** contaminated with **5**.

4.2. *X-ray diffraction analyses*

4.2.1. *Crystal data for trans-[ReH(CNMe)(dppe)$_2$]. CH_2Cl_2 (4)*

$M_r = 1109.1$; triclinic; space group, $P1$; $a = 11.612(2)$ Å, $b = 12.769(3)$ Å and $c = 18.010(3)$ Å; $\alpha = 83.74(2)°$, $\beta = 82.87(1)°$ and $\gamma = 68.94(2)°$; $V = 2466.5$ Å^3; $Z = 2$, $D_c = 1.49$ g cm^{-3}; μ(Mo-Kα) = 27.28 cm^{-1}.

All measurements were made with an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Cell dimensions and orientation matrices were obtained by least-squares refinement of setting angles for 25 automatically centred reflections with $15° \leqslant \theta \leqslant 25°$. The intensities of 8161 independent reflections in the range $1.5 \leqslant \theta \leqslant 27°$ were measured by the ω–2θ scan mode. The data were corrected for Lorentz and polarization effects and empirically for absorption.

A total of 7686 reflections satisfied the criterion $F \geqslant 3\sigma(F)$ and were used for the structure solution and refinement. The Re atom was located from a Patterson map, and the other non-hydrogen atoms were found from subsequent difference Fourier syntheses. The coordinated hydrogen atom, whose presence was proved by ^{1}H NMR spectroscopy, was located in the electron density map and refined, while those in the dppe and $CNCH_3$ were inserted in idealized positions, riding in the parent carbon atoms, with no constraints in the isotropic temperature factors. The CH_2Cl_2 molecule was refined using a disorder model with one of the Cl atoms disordered over two positions.

The weighting scheme $w = 2.512/[\sigma(F)^2 + 0.000586F^2]$ was found to give acceptable agreement analysis. Final refinement gave $R = 0.049$ and $R_w = 0.057$. The largest peak in the final difference Fourier syntheses was 1.5 electrons Å^{-3} and is 0.6 Å away from the disordered Cl atom of the solvent molecule.

4.2.2. *Crystal data for trans-[ReCl(CNMe)(dppe)$_2$] (5)*

$M_r = 1059.6$; triclinic; space group, $P1$; $a = 10.439(5)$ Å, $b = 10.502(4)$ Å and $c = 12.655(6)$ Å; $\alpha = 71.72(4)°$, $\beta = 87.12(3)°$ and $\gamma = 61.17(5)°$; $V = 1145.5$ Å^3; $Z = 1$; $D_c = 1.54$ g cm^{-3}; μ(Mo-Kα) = 28.8 cm^{-1}.

All measurements were made with an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Cell dimensions and orientation matrices were obtained by least-squares refinement of setting angles for 25 automatically centred reflections with $13 \leqslant \theta \leqslant 16.5°$. The intensities of 5801 independent reflections in the range $1.0 \leqslant \theta \leqslant 28$ were measured by the ω–2θ scan mode. The data were corrected for Lorentz and polarization effects and empirically for absorption.

A total of 5792 reflections satisfied the criterion $F \geqslant 3\sigma(F)$ and were used for the structure solution and refinement. The Re atom was located from a Patterson map, and the other non-hydrogen atoms were found from subsequent difference Fourier syntheses. The hydrogen atoms of the dppe and $CNCH_3$ were inserted in idealized positions, riding in the parent carbon atoms, with no constraints in the isotropic temperature factors. The reflections 0 0 1, −1 0 1, 2 0 1, 2 1 1 suspected of suffering from extinction were removed from the refinement.

Final refinement gave $R = 0.029$. The largest peak in the final difference Fourier syntheses was 2 electrons Å^{-3} and is 0.9 Å away from the Re atom.

All computations required to solve and refine the structure were made with SHELX76 [30]; drawings were made with ORTEP-II [31]. Atomic scattering factors were taken from ref. 32. Final fractional atomic positional parameters for the non-hydrogen atoms are presented in Tables 5 and 6. Anisotropic and isotropic thermal motion parameters, fractional atomic coordinates for the hydrogen atoms and complete tables of bond lengths and angles are available from the Cambridge Crystallographic Data Centre.

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