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Synthesis and electrochemical behaviour of the cyanamide-isocyanide complexes of rhenium, *trans*-$[ReL(CNR)(Ph_2PCH_2CH_2PPh_2)_2]^+$ ($L = NCNH_2$ or $NCNH^-$)

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Abstract

Reaction of *trans*-$[ReCl(CNR)(dppe)_2]$ (R = Me (Ia) or ^{t}Bu (Ib); dppe = $Ph_2PCH_2CH_2PPh_2$) in CH_2Cl_2 with cyanamide in the presence of $TlBF_4$ forms the new cyanamide-isocyanide complexes *trans*-$[Re(CNR)(NCNH_2)(dppe)_2][BF_4]$ (R = Me (IIa) or ^{t}Bu (IIb)), which upon treatment by ^{t}BuOK or Et_3N give *trans*-$[Re(NCNH)(CNR)(dppe)_2]$ (R = Me (IIIa) or ^{t}Bu (IIIb)). The electrochemical behaviour of these species was studied by cyclic voltammetry and controlled potential electrolysis at a Pt electrode in an aprotic solvent, and cathodic reduction of II results in the formation of III.

Introduction

Cyanamide ($NCNH_2$) has recently been recognized as a substrate of nitrogenase [1], but its coordination chemistry is almost unknown, in spite of its interest in various fields of science (e.g., it has been identified in interstellar space [2], and is thought to be an amino acid precursor and a prebiotic molecule [3]), and it has been used as a fertilizer [4], as a mild condensing agent, as a starting material for heterocyclic synthesis [5], and in the treatment of alcoholism [6].

The complex $[W(CO)_5(NCNH_2)]$ [7] was the only organometallic compound containing a cyanamide ligand found in a Chemical Abstracts search covering the last fifteen years in spite of several reports of reactions involving use of cyanamide as a starting material. The cyanoimido complex *trans*-$[Mo(NCN)_2(dppe)_2]$, whose structure was confirmed by an X-ray diffraction study, was recently obtained [8] from the reaction of cyanamide with *trans*-$[Mo(N_2)_2(dppe)_2]$. Both $Et_2TlNHCN$ and $(Et_2Tl)_2NCN$ were reported to be formed from reaction of Et_3Tl with $NCNH_2$ in 1 : 1 and 2 : 1 ratio [9], respectively.

Our interest in the study of the activation of nitrogenase substrates by transition metal sites led us to synthesize a variety of neutral complexes with electron-rich metal centres, such as $[ReCl(N_2)(CNR)\{P(OMe)_3\}_3]$ (R = aryl or alkyl) [10] in which activation of the isocyanide to electrophilic attack occurs with resulting

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reductive cleavage of the C≡N bond to give the corresponding amine and hydrocarbons. In the case of *trans*-[ReClL(dppe)$_2$] (L = CNR or NCR), containing a more stable metal centre, electrophilic attack by acid or Lewis acid at the coordinated isocyanide or nitrile affords the carbyne-like ligands CNZR (Z = H [11] or Lewis acid [12]) or the methyleneamido species, NCHR [13], respectively, without complete reduction of the ligand.

Related cationic species have also been prepared, particularly by chloride-abstraction from *trans*-[ReCl(CNR)(dppe)$_2$] (I), in the presence of L = isocyanide, acetonitrile, carbonyl [14] or phenylacetylene [15], to give the corresponding complexes *trans*-[ReL(CNR)(dppe)$_2$]$^+$ which do not react with the electrophiles. In the present work, we have extended this approach to the synthesis of the first cyanamide complexes of rhenium, *trans*-[Re(NCNH$_2$)(CNR)(dppe)$_2$]$^+$ (R = Me (IIa) or ^{t}Bu (IIb)), have studied their reactions with base, and have investigated their electrochemical behaviour.

Results and discussion

Preparation and characterization of the cyanamide complexes

Chloride-abstraction from *trans*-[ReCl(CNR)(dppe)$_2$] (I; R = Me or ^{t}Bu) in CH$_2$Cl$_2$ by TlBF$_4$ in the presence of a slight excess of cyanamide (NCNH$_2$) affords *trans*-[Re(CNR)(NCNH$_2$)(dppe)$_2$][BF$_4$] (R = Me (IIa) or ^{t}Bu (IIb)) (reaction 1).

$$\begin{aligned}&trans\text{-}[\mathrm{ReCl(CNR)(dppe)_2}] + \mathrm{NCNH_2} + \mathrm{TlBF_4} \xrightarrow{\mathrm{CH_2Cl_2}} \\ &\qquad trans\text{-}[\mathrm{Re(CNR)(NCNH_2)(dppe)_2}][\mathrm{BF_4}] + \mathrm{TlCl} \qquad (1)\end{aligned}$$

These complexes are yellow and their IR spectra (Table 1) exhibit strong or medium intensity bands at ca 2250 cm^{-1} (with a shoulder at 2290 cm^{-1}) which are assigned to ν(N≡C) of the cyanamide ligand, and are comparable in position with

Table 1

Analytical [a] and physical data for complexes *trans*-[Re(CNR)(NCNH$_2$)(dppe)$_2$][BF$_4$] (R = Me (IIa) or ^{t}Bu (IIb)) and *trans*-[Re(NCNH)(CNR)(dppe)$_2$] (R = Me (IIIa) or ^{t}Bu (IIIb))

Complex	X	Colour	Analyses (Found (calc.) (%))			IR		Yield (%)
			C	N	H	ν(NH)	ν(C≡N)	
IIa	BF$_4$	Pale-yellow	57.0 (57.3)	3.7 (3.7)	4.9 (4.6)	3240 br	2290sh 2240m 2020sh 1950s,br	80
IIb [b]	BF$_4$	Yellow	56.3 (56.8)	3.7 (3.4)	5.2 (4.9)	3260 br	2290w 2250m 1980s	80
IIIa [c]		Yellow	58.5 (58.5)	3.5 (3.7)	4.8 (4.7)		2135s 1820s,br	60
IIIb [d]		Greenish-yellow	61.0 (61.2)	4.2 (2.7)	5.6 (5.1)		2160s 1985s,br	50

[a] Required values in parentheses. [b] 1/2 CH$_2$Cl$_2$ of crystallization. [c] CH$_2$Cl$_2$ of crystallization. [d] 1/4 KBF$_4$ of contamination.

Table 2

^{1}H and ^{31}P NMR data [a] for complexes *trans*-[Re(CNR)(NCNH$_2$)(dppe)$_2$][BF$_4$] (R = Me (IIa) or ^{t}Bu (IIb)) and *trans*-[Re(NCNH)(CNR)(dppe)$_2$] (R = Me (IIIa) or ^{t}Bu (IIIb))

Complex	X	δ (ppm) [b]		^{1}H			^{31}P
				Integration		Assignment	δ(ppm) [c]
IIa	BF$_4$	7.3–6.7	m	40	(40)	C$_6$*H*$_5$ (dppe)	−106.8 s
		4.35 [d]	br	1.6	(2)	N*H*$_2$ (NCNH$_2$)	
		3.02	s	3	(3)	C*H*$_3$ (CNMe)	
		2.49	m	4	(8)	C*H*$_2$ (dppe)	
		2.20	m	4			
IIb	BF$_4$	7.7–6.5	m	40	(40)	C$_6$*H*$_5$ (dppe)	−104.7 s
		3.95 [d]	br	2	(2)	N*H*$_2$ (NCNH$_2$)	
		2.57	s	4	(8)	C*H*$_2$ (dppe)	
		2.15	s	4			
		1.16	s	9	(9)	C*H*$_3$ (^{t}BuNC)	
IIIa		7.2–7.0	m	40	(40)	C$_6$*H*$_5$ (dppe)	−108.8 s
		2.65	s	3	(3)	C*H*$_3$ (CNMe)	
		2.38	t [e]	8	(8)	C*H*$_2$ (dppe)	
		0.14	br	1	(1)	N*H* (NCNH)	
IIIb		7.6–6.6	m	40	(40)	C$_6$*H*$_5$ (dppe)	−105.8 s,br
		2.5	s,br	4	(8)	C*H*$_2$ (dppe)	
		2.3	s,br	4			
		1.3	s,br	9	(9)	C*H*$_3$ (^{t}BuNC)	
		1.1	br	ca 0.6 [f]	(1)	N*H* (NCNH)	

[a] In CH$_2$Cl$_2$, unless stated otherwise; required values in parentheses. [b] Relative to internal SiMe$_4$. [c] Relative to P(OMe)$_3$, assigned to 4*P* (dppe). [d] Disappears upon addition of D$_2$O. [e] $1/2|^2J(\text{PH})+{}^3J(\text{PH})| = 7.4$ Hz (virtual coupling). [f] Lower than expected possibly due to proton exchange with traces of moisture.

those quoted [7] for the ligating cyanamide in [W(CO)$_5$(NCNH$_2$)] (2315 sh and 2270 cm^{-1}).

These ν(NC) values for the cyanamide ligand are considerably higher (by ca 100 cm^{-1}) than those observed for the free species (2190 and 2150 cm^{-1}), in agreement with their η^1-coordination through the cyano group, acting mainly as a σ-donor.

The IR spectra of the complexes II also show other strong or medium intensity bands at lower wavenumbers, in the 1980–1950 cm^{-1} range, which are assigned to ν(C≡N) of the isocyanide ligand, as observed [14] in the related complex *trans*-[Re(CNMe)(NCMe)(dppe)$_2$]Cl (2065 and 2140 cm^{-1} for the methylisocyanide or the acetonitrile ligand, respectively). The lower ν(CN) frequencies for CNMe in complexes II compared with that for this isocyanide-acetonitrile compound are in accord with the expected (see below) stronger electron donor character of cyanamide than of acetonitrile, which favours π-acceptance by the isocyanide and reduces its σ-donation.

The same complexes display two medium or strong intensity IR bands (1585m, 1570m cm^{-1} (IIa); 1585m, 1565m cm^{-1} (IIb)) which are assigned to δ(NH) for the cyanamide ligand. Upon coordination, the stretching frequencies for the amino group of cyanamide drop from 3425 cm^{-1} and 3335 cm^{-1} for the free ligand to ca 3250 cm^{-1} (Table 1).

In the proton NMR spectra of complexes II (Table 2), the signal from the amino protons resonance in the coordinated cyanamide is observed at δ ca 4 ppm (a value somewhat lower than that for the free ligand) and, as expected, disappears upon addition of D_2O.

The proposed *trans* geometry is confirmed by the ^{31}P NMR spectra in which the expected singlets are observed, at δ −106.8 (IIa) and −104.7 ppm (IIb) relative to $P(OMe)_3$, for the four equivalent phosphorus nuclei of the two dppe ligands (Table 2).

Elemental microanalyses are also consistent with the proposed formulations (Table 1).

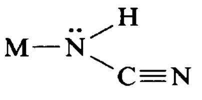
The observed behaviour of cyanamide towards the cationic rhenium centre contrasts with that [16] towards *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo or W), which involves dehydrogenation of the substrate by the electron-rich reducing Group VI metal centre to give the cyanoimido complexes *trans*-$[M(NCN)_2(dppe)_2]$. This type of reaction has not been observed at the former metal centre, in accord with its lower electron-rich character and weaker reducing ability [17,18].

Deprotonation of the coordinated cyanamide in complexes II occurs in the presence of a base, such as ^tBuOK or Et_3N, to afford *trans*-$[Re(NCNH)(CNR)(dppe)_2]$ (R = Me (IIIa) or ^tBu (IIIb)), containing ligating hydrogen cyanamide, which were isolated as yellow and greenish-yellow solids, respectively; addition of acid, namely $[Et_2OH][BF_4]$, regenerates the amino group of cyanamide (reaction 2). These results are consistent with those from the electrochemical studies described below.

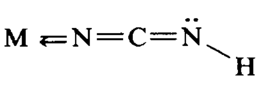
$$trans\text{-}[Re(CNR)(NCNH_2)(dppe)_2]^+ \underset{H^+}{\overset{Base}{\rightleftharpoons}} trans\text{-}[Re(NCNH)(CNR)(dppe)_2] \tag{2}$$

The IR spectra of complexes III exhibit two strong bands (Table 1) at 2135s and 1820s,br cm^{-1} (IIIa), or 2160s and 1985s,br cm^{-1} (IIIb). In both complexes the latter band is broad and is assigned to $\nu(C{\equiv}N)$ of the isocyanide ligand, in agreement with IR data [22] for the related complexes *trans*-$[ReCl(CNMe)(dppe)_2]$ and *trans*-$[ReCl(CN^tBu)(dppe)_2]$ for which $\nu(C{\equiv}N)$ appears as a broad band at 1830 cm^{-1} and 1920 cm^{-1} respectively. For complexes IIIa and IIIb the former band appears at a wavenumber (2135 cm^{-1} or 2160 cm^{-1}, respectively) comparable with that observed (at 2080 cm^{-1}) for $\nu(N{\equiv}C)$ in $[NCNH][Bu_4N]$ prepared by monodeprotonation of cyanamide involving treatment of a solution of this species in methanol/dichloromethane with a stoichiometric amount of $[Bu_4N]OH$. Therefore, it is ascribed to $\nu(N{\equiv}C)$ of ligating $NCNH^-$.

In principle, two η^1-coordination modes should be possible for this ligand:



or



The observation in the IR spectrum of the strong band assigned to $\nu(N{\equiv}C)$, discussed above, favours the coordination through the amido nitrogen atom.

In the ^1H NMR spectrum of IIIa, a broad signal which is observed at δ ca 0.14 ppm, and partly disappears upon addition of D_2O, is assigned to NCN*H*. The CN*Me* resonance gives rise to the expected singlet at δ 2.65 ppm, whereas the dppe-methylene proton resonance is observed as a triplet (at δ 2.38 ppm) due to virtual coupling to the P nuclei, $1/2\ |^2J(PH)+{}^3J(PH)| = 7.4$ Hz.

In the case of IIIb the broad resonance observed at δ 1.1 ppm is assigned to NCN*H*. The resonance of the ^{t}Bu of the isocyanide ligand appears as a broad singlet at δ 1.3 ppm, and the two resonances centered at 2.5 and 2.3 ppm are assigned to the dppe-methylene protons.

The *trans* geometry of these complexes is confirmed by the singlet (δ −108.8 (IIIa) and −105.8 ppm (IIIb) relative to $P(OMe)_3$) observed in their ^{31}P NMR spectra.

Electrochemical studies

Anodic behaviour and estimate of the P_L *ligand parameter*

Complexes II display two anodic waves (Table 3) upon cyclic voltammetry at a Pt electrode in tetrahydrofuran (THF) or CH_2Cl_2/0.2 *M* $[NBu_4][BF_4]$; moreover, in the latter solvent, a third and less well defined anodic wave is observed at a higher potential.

The first anodic wave corresponds to a quasi-reversible single electron process, and is assigned to the $Re^{I} \rightarrow Re^{II}$ oxidation, as reported [19] for related complexes, whereas the second is irreversible.

The first anodic wave occurs at a potential $[{}^{I}E^{ox}_{1/2} = 0.38$ or 0.42 V vs SCE, for IIa or IIb, respectively], which is considerably lower than that observed for *trans*-$[Re(CNR)(CNR_1)(dppe)_2]^+$ (R,R_1 = alkyl or aryl) (0.79–1.05 V) [14,19] or for *trans*-$[Re(CNMe)(NCMe)(dppe)_2]^+$ (0.63 V) [14], in agreement with the expected stronger net electron σ-donor/π-acceptor ability of $NCNH_2$ than of isocyanides or NCMe.

In cyclic voltammetry the neutral complexes *trans*-$[Re(NCNH)(CNR)(dppe)_2]$ (III) show two single-electron reversible anodic waves, at ${}^{I}E^{ox}_{1/2} = -0.06$ (R = Me) or −0.09 V (R = ^{t}Bu) and at ${}^{II}E^{ox}_{1/2} = 0.52$ (R = Me) or 0.48 V (R = ^{t}Bu) vs SCE. As expected, these oxidation potentials are considerably lower than the corresponding ones for the parent cationic complexes II; moreover, the oxidation potentials of the first anodic waves lie below those for the related compounds *trans*-[ReCl(CNR)-$(dppe)_2]$ ($E^{ox}_{1/2} = 0.08$ or 0.06 V for R = Me or ^{t}Bu, respectively) [18], indicating that the hydrogen cyanamide ligand, $NCNH^-$, behaves as a stronger net electron donor than Cl^- (see below).

Table 3

Electrochemical data [a] for complexes *trans*-$[Re(CNR)(NCNH_2)(dppe)_2][BF_4]$ (R = Me (IIa) or ^{t}Bu (IIb)) and *trans*-$[Re(NCNH)(CNR)(dppe)_2]$ (R = Me (IIIa) or ^{t}Bu (IIIb))

Complex	${}^{I}E^{ox}_{1/2}$	${}^{II}E^{ox}_{1/2}({}^{II}E^{ox}_{p})$ [b]	${}^{III}E^{ox}_{1/2}$ [c]	E^{red}_{p}
IIa	0.38	(1.05)	1.34	−0.76
IIb	0.42	(1.21)	1.40	−0.85
IIIa	−0.06	0.52		−1.11 [c]
IIIb	−0.09	0.48		−1.26

[a] Values in Volt ±20 mV SCE, measured by cyclic voltammetry (at 100 mV s^{-1}), at a Pt electrode, in THF (unless stated otherwise)/0.2 *M* $[Bu_4N][BF_4]$, using as internal standard *trans*-[ReCl(CNMe)-$(dppe)_2]^{0/+}$ ($E^{ox}_{1/2} = 0.08$ V) or $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ ($E^{ox}_{1/2} = 0.545$ V). [b] Values in parentheses for irreversible waves. [c] In CH_2Cl_2.

However, the electronic properties of the cyanamide ligands used in this study can better be compared by estimating the corresponding values of the electrochemical P_L ligand parameter [20], a proposed measure of the net electron π-acceptor minus σ-donor character of a ligand (L) binding an octahedral-type 16-electron metal site $\{M_s\}$ (the lower is P_L, the stronger is the net electron donor character of the ligand). This can be done in making use of equation 3 [20], which relates the half-wave oxidation potential of octahedral-type 18-electron complexes $[M_sL]$ with the P_L ligand parameter and the electron-richness (E_s) and polarisability (β) of the metal site.

$$E^{ox}_{1/2}[M_sL] = E_s\{M_s\} + \beta\{M_s\} \cdot P_L \qquad (3)$$

Through the application of this equation to complexes *trans*-$[Re(CNR)L(dppe)_2]^+$ (L = cyanamide (II) or $NCNH^-$ (III)) and by using the values of $E^{ox}_{1/2}$ measured in this study, as well as the known values of E_s and β for their metal centres $\{Re(CNR)(dppe)_2\}^+$ ($E_s = 1.15$ V for R = Me or ${}^tBu$; $\beta = 0.90$ or 0.92 for R = Me or ${}^tBu$, respectively) [18], the following P_L values have been estimated for those L ligands: -0.85 ($NCNH_2$) and -1.34 V ($NCNH^-$).

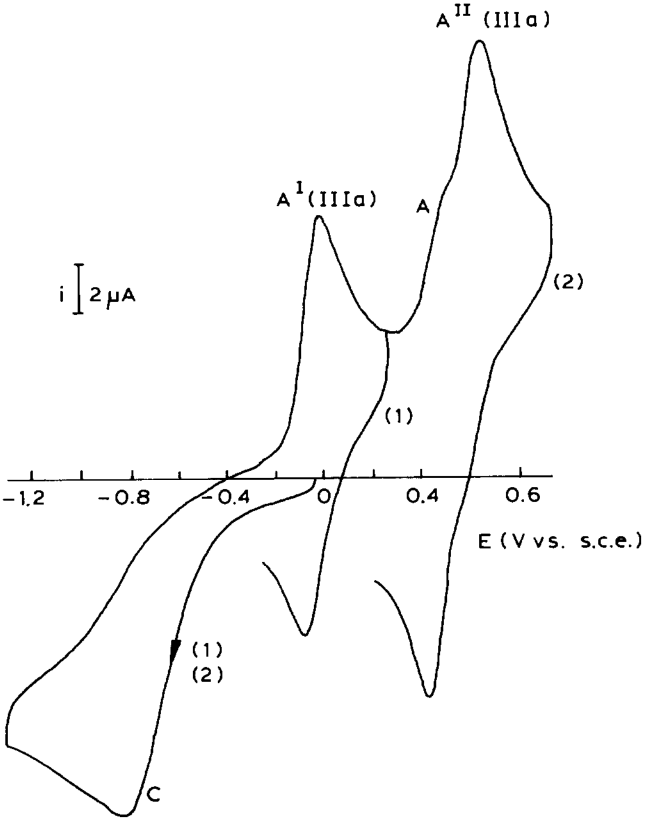


Fig. 1. Cyclic voltammograms ((1) and (2) independently recorded, both initiated by the cathodic sweep), at a Pt electrode, of a solution of IIa in THF/0.2 *M* $[Bu_4N][BF_4]$ (ν = 400 mV/s). C,A—Cathodic and first anodic wave, respectively, of (IIa). A^I(IIIa), A^{II}(IIIa)—First and second anodic waves, respectively, of IIIa generated upon cyclic voltammetric reduction of IIa at wave C.

These results indicate that $NCNH_2$ behaves as a stronger net electron donor than, e.g., acetonitrile or ammonia ($P_L = -0.57$ or -0.77 V, respectively) [20]; the anionic ligand $NCNH^-$ shows, as expected, a much better net electron donor ability ($P_L = -1.34$ V), appearing to be a stronger net electron donor than even chloride or azide ($P_L = -1.19$ or -1.26 V, respectively) [20].

Moreover, the sequence of P_L values for the *N*-bonded ligands (L) of this study agrees with that observed for $\nu(C\equiv N)$ of the methylisocyanide ligand in the *trans* position (2065, 1980–1950 and 1820 cm^{-1}, for L = NCMe, cyanamide and $NCNH^-$, respectively): an increase in the net electron donor ability of the former ligands (decrease of P_L) enhances the π-acceptance by the isocyanide (and possibly reduces its σ-donor ability) and therefore causes a decrease in $\nu(C\equiv N)$.

Cathodic behaviour

Upon cyclic voltammetry, at a Pt electrode in THF or CH_2Cl_2, the freshly-prepared cationic cyanamide complexes II undergo a single-electron irreversible cathodic reduction (Table 3) at E_p^{red} ca -0.8 (IIa) or -0.9 V (IIb) vs SCE. The involvement of a single-electron cathodic process was also demonstrated by controlled potential electrolysis (CPE).

Cathodically-induced dehydrogenation occurs to give the deprotonated species *trans*-[Re(NCNH)(CNR)$(dppe)_2$] (III) (reaction 4), which were identified by their characteristic redox waves detected upon electrochemical reduction of II (by cyclic voltammetry (Fig. 1) or by CPE). Complexes III were the only detected products from the cathodic reduction of II and a quantitative conversion of the latter into the former by CPE was then observed. Moreover, ammonia was not detected (by spectrophotometry) in the final electrolyzed solution. Therefore, no further reaction of the hydrogen cyanamide ligand was observed at the cathodic potential of II.

$$trans\text{-}[Re(CNR)(NCNH_2)(dppe)_2]^+ \xrightarrow{+e(-H)} trans\text{-}[Re(NCNH)(CNR)(dppe)_2] \quad (4)$$

As shown above, complexes III are also formed by reaction of II with a base such as ^tBuOK or Et_3N (reaction 2) whereas addition of HBF_4 to complexes III regenerate complexes II; such a reversible deprotonation/protonation process has also been confirmed by addition of base or acid to the electrolyte solution of II or III followed by detection *in situ*, by cyclic voltammetry, of the corresponding products.

In contrast to the above-mentioned cathodic reduction of II, their attempted chemical reduction by magnesium is not a suitable method of deprotonation; although a chemical reaction appears to occur, upon work-up of the reaction solution only the starting complex II is recovered, possibly regenerated by traces of moisture in the solvents.

The cathodic behavior of the cyanamide complexes II is similar to that observed for other cationic protonated compounds of Re, such as the carbyne or the η^2-vinyl species *trans*-[ReCl(≡C–CH_2R)$(dppe)_2$]$^+$ or *trans*-[ReCl{=C(CH_2Ph)CH_2}-$(dppe)_2$]$^+$ which, upon cathodic reduction, also undergo dehydrogenation to afford their parent vinylidene or allene complexes, *trans*-[ReCl(=C=CHR)$(dppe)_2$] or *trans*-[ReCl(η^2-CH_2–C=CHPh)$(dppe)_2$], respectively [21].

Concluding remarks

A variety of organonitrogenated species appears to be formed as a result of activation of cyanamide by a transition metal centre. This substrate is dehydrogenated by the electron-rich and readily oxidizable centres $\{M(dppe)_2\}$ (M = Mo or W) to give the cyanoimido(2-) species NCN [16]; this type of reaction does not occur at the less electron-rich sites $\{Re(CNR)(dppe)_2\}^+$ (R = Me or ${}^tBu$), complexes containing ligating cyanamide being obtained. The latter ligands can undergo deprotonation by base or upon cathodic reduction to yield the hydrogen cyanamide anion, $NCNH^-$. The conditions required for the formation of these ligands have not yet been fully clarified, but the properties of the activating metal centre (namely its electron-rich character and redox behaviour) are believed to play a fundamental role.

Electrochemical techniques appear to provide useful ways of studying the relative net electron donor/acceptor ability of those ligands and for investigation of their interconversion.

Experimental

All manipulations and reactions were performed under dinitrogen by standard inert-gas flow and vacuum techniques. Solvents were purified before use by standard procedures. Cyanamide and $[Et_2OH][BF_4]$ were used as purchased from Fluka. Et_3N was dried over sodium wire. *trans*-$[ReCl(CNR)(dppe)_2]$ (R = Me, ${}^tBu$) complexes were prepared by published methods [22].

Infrared measurements were carried out on a Perkin–Elmer 683 spectrophotometer. ${}^1H$ and ${}^{31}P$ NMR spectra were recorded on a Bruker CPX 300, JEOL PTF 100 or JEOL JNM-PS-100 Fourier transform spectrometer. The electrochemical experiments were performed on a EG&G PARC 173 potentiostat/galvanostat and a EG&G PARC 175 universal programmer. The redox potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–tetrahydrofuran or dichloromethane at a platinum electrode. The values of the oxidation or reduction potentials are quoted relative to SCE, and were measured using as internal reference the redox couples *trans*-$[ReCl(CNMe)(dppe)_2]^{0/+}$ ($E_{1/2}^{ox} = 0.08$ V) or $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ ($E_{1/2}^{ox} = 0.545$ V vs SCE).

Synthesis of complexes

trans-*[Re(CNR)(NCNH$_2$)(dppe)$_2$]BF$_4$ (R = Me (IIa) or ${}^tBu$ (IIb)).* These complexes were prepared in the same way. In a typical preparation, that of IIa, *trans*-$[ReCl(CNMe)(dppe)_2]$ (0.30 g, 0.28 mmol) was added to $NCNH_2$ (0.015 g, 0.36 mmol) and $TlBF_4$ (0.10 g, 0.33 mmol) in CH_2Cl_2 (20 cm^3) and the suspension stirred for 2 h. The white solid (TlCl) was filtered off and the solution was concentrated *in vacuo* to about half of the volume. Addition of Et_2O (10 cm^3) induced formation of bright yellow crystals of *trans*-$[Re(CNMe)(NCNH_2)(dppe)_2][BF_4]$ (IIa) which were filtered off, washed with Et_2O, and dried *in vacuo* (0.25 g, ca 80% yield).

trans-*[Re(NCNH)(CNR)(dppe)$_2$] (R = Me (IIIa) or ${}^tBu$ (IIIb)).* A suspension of *trans*-$[Re(CNR)(NCNH_2)][BF_4]$ (R = Me (IIa) or ${}^tBu$ (IIb)) (0.115 g, 0.099 mmol (R = Me) or 0.120 g, 0.109 mmol (R = ${}^tBu$)) and ${}^tBuOK$ (0.050 g, 0.45 mmol) in

THF (15 cm^3) was stirred for 0.5 h. The solution was filtered and the volume of the solvent reduced. Upon addition of Et_2O (7 cm^3), the product was obtained as a yellow (IIIa) or greenish-yellow (IIIb) solid (0.060 g, ca 60% yield).

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