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FULL PAPER

Reactions of a cyanosilane with an iron(II) centre. Synthesis and crystal structure of the isocyanotriphenylborate complex *trans*-[FeH(CNBPh$_3$)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] and anodic deprotonation of the hydrogen isocyanide (CNH) analogue

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Treatment of a thf solution of *trans*-[FeH(Cl)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with N≡CSiMe$_3$, in the presence of Na[BPh$_4$], formed *trans*-[FeH(CNBPh$_3$)(dppe)$_2$] **1** whose crystal structure was determined, whereas the use of Tl[BF$_4$] in an acidic medium, instead of Na[BPh$_4$], yielded *trans*-[FeH(CNH)(dppe)$_2$][BF$_4$] **2**. Complex **1** is also formed by BPh$_3$ addition to *trans*-[FeH(CN)(dppe)$_2$] **3** which can be obtained by reaction of *trans*-[FeH(Cl)(dppe)$_2$] with [NBu$_4$]CN in the presence of Tl[BF$_4$]. Complexes **1** and **3** undergo single-electron reversible oxidations upon cyclic voltammetry in an aprotic medium, and the electrochemical P_L ligand parameter was estimated (−0.51 V) for the CNBPh$_3^-$ ligand. Complex **2** undergoes anodically induced deprotonation to form the cyano-complex **3**$^+$ following a mechanism that has been established by digital simulation of cyclic voltammetry and allowed an estimate of the rate and acid/base equilibrium constants for the CNH/CN$^-$ interconversion in the **2**/**3** and **2**$^+$/**3**$^+$ pairs, showing that the oxidation of **2** leads to enhancements of its acidity constant and of the rate of proton loss by factors of *ca*. 1.5 × 10^7 and 500, respectively.

Introduction

The cyanosilane N≡CSiMe$_3$ was shown[1] to be a convenient source of the simplest isocyanide and aminocarbyne ligands, CNH$_x$ (x = 1 or 2, respectively), in reactions with the N$_2$-binding electron-rich rhenium(I) centre *trans*-{ReCl(dppe)$_2$} (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) to form *trans*-[ReCl(CNH)(dppe)$_2$] (in methanol) or *trans*-[ReCl(CNH$_2$)(dppe)$_2$][BF$_4$] (in the presence of HBF$_4$). In view of the rarity of well defined complexes with such ligands and of the current interest[2] in the development of their organometallic chemistry, of particular significance in the field of nitrogen fixation,[3,4] we have attempted to explore further the above type of reactivity of N≡CSiMe$_3$ towards a phosphinic iron(II) centre which is also able to bind dinitrogen, and we now report the results we have obtained. They show that the cyanosilane behaves as a source not only of the cyano group in the formation of the isocyanide CNH (upon H$^+$ addition) but also, unexpectedly, of isocyanotriphenylborate CNBPh$_3^-$ (upon addition of BPh$_3$ generated from BPh$_4^-$) which binds as the isocyanide isomer to the iron(II) centre. The complexes *trans*-[FeH(CNBPh$_3$)(dppe)$_2$] **1** (whose crystal structure is also reported now) and *trans*-[Fe(CNH)(dppe)$_2$][BF$_4$] **2** have thus been obtained from *trans*-[FeH(Cl)(dppe)$_2$]. Complex **2** has been reported by others,[4] by using a different route, the protonation of the corresponding cyano-complex.

Moreover, the mode of co-ordination of cyanoborates, in particular of cyanotriphenylborate, has been a matter of interest.[2] Either N-[5,6] or C-ligation[7] modes (cyano- or isocyano-isomers, respectively) have been recognised, and linkage isomerisation observed[5] in some cases, but the favourable conditions for promotion of those co-ordination modes have not yet been ascertained. Our report also includes a novel example of a situation in which BPh$_4^-$ does not behave as a simple spectator, but displays an active role in the reaction, in our case as an unexpected source of BPh$_3$ towards a cyanosilane. Examples of BPh$_4^-$ behaviour as a phenylating agent have been reported.[8]

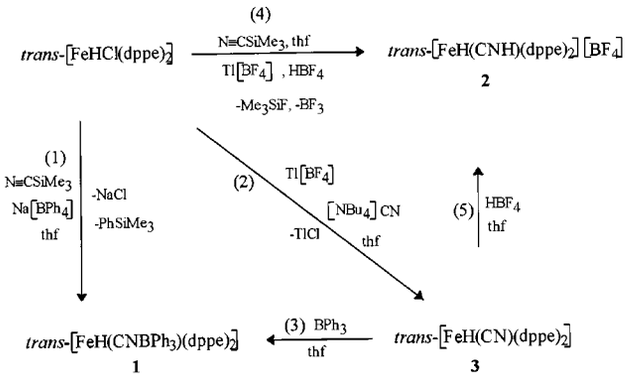
In addition, the investigation of the interconversion of the CNH and CN ligands at an iron centre and of its dependence on the metal oxidation state would be a matter of biological interest in view of the conceivable involvement[3] of such processes in the reduction of aqueous cyanide by nitrogenase. We have applied electrochemical methods to this study which allowed a full kinetic and thermodynamic description of those processes at both the oxidation state levels Fe^{II} and Fe^{III}. The dramatic promotion (in both thermodynamic and kinetic terms) of H$^+$ loss from CNH upon single-electron oxidation of complex **2** could then be evaluated.

Results and discussion

Syntheses and X-ray crystallography

Treatment of a thf solution of *trans*-[FeH(Cl)(dppe)$_2$] with N≡CSiMe$_3$ (in a threefold molar ratio), in the presence of Na[BPh$_4$] (in a stoichiometric amount), leads to the formation of the isocyanotriphenylborate complex *trans*-[FeH(CNBPh$_3$)(dppe)$_2$] **1** which was isolated as a yellow crystalline solid (*ca*. 45% yield) (reaction 1, Scheme 1) fully characterised by IR and multinuclear magnetic resonance spectroscopies, elemental analysis and X-ray diffraction (see below).

The synthesis of complex **1** conceivably involves the formation of the isocyanide intermediate [FeH(CNSiMe$_3$)(dppe)$_2$]$^+$



Scheme 1

(the free cyanosilane is known[9] to be in equilibrium with a small percentage, *ca*. 5%, of the isocyanide isomer), in preference to the isomeric nitrile $NCSiMe_3$ complex, as observed[1b] for the rhenium complex *trans*-[ReCl($CNSiMe_3$)(dppe)$_2$]. Desilylation of the $CNSiMe_3$ ligand by reaction with BPh_4^- would generate the cyano ligand and BPh_3 which, behaving as a Lewis acid, would add to ligated CN^- to form *in situ* the isocyanide ligand $CNBPh_3^-$ in complex **1**. To our knowledge, this is a novel overall route for the synthesis of a cyanoborate complex. The common procedure[7] to synthesize a C-bonded cyanoorganoborate ligand (*i.e.* the isocyanide isomer $CNBR_3$) involves Lewis acid addition of BR_3 to a cyano-complex precursor, and, in fact, this route can also be applied to the preparation of **1**, by adding BPh_3 to the known[10] complex *trans*-[FeH(CN)(dppe)$_2$] **3** (reaction 3, Scheme 1). However, the above route (1) to **1**, from $NCSiMe_3$, is a more direct one since it does not require the separate preparation of the cyano-complex **3**. We have obtained this complex by treatment of a thf solution of *trans*-[FeH(Cl)(dppe)$_2$] with [NBu_4]CN, in the presence of Tl[BF_4] as the chloride ligand abstractor (reaction 2, Scheme 1), following a similar route to that we have applied[11] to the synthesis of the isocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$]$^+$ by reaction of *trans*-[FeH(Cl)(dppe)$_2$] with CNR in the presence of the thallium salt.

An alternative rationalisation for the synthesis of complex **1** *via* **3** (reaction 3) would account for the conceivable generation of acid (NCH) upon hydrolysis of $NCSiMe_3$ (water and formamide have been detected in the crystals of **1** by X-ray diffraction analysis, see below). Further reaction of the acid thus generated with BPh_4^- and **3** would form **1**. Such a type of acid conversion of the cyano into the $CNBPh_3^-$ ligand has been reported[12] at *trans*-[Fe(CN)$_2$(TIM)] (TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) to give *trans*-[Fe($CNBPh_3$)$_2$(TIM)].

For complex **1**, ν(C≡N) in the IR spectrum appears as a strong band at 2090 cm^{-1} (KBr pellet) which falls within the 2140–2010 cm^{-1} range observed[11] for the isocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$]$^+$ and these wavenumbers, as expected, are lower than those known[13] for related organonitrile complexes (2250–2205 cm^{-1}). Moreover, ν(C≡N) in **1** is higher than in the cyano-complex **3** (2030 cm^{-1}), in agreement with its expected[5b] increase on formation of the adduct as a result of an effective depopulation of the C–N antibonding orbitals due to the bonding of the N to the boron atom.

In the ^{13}C NMR spectrum (CD_2Cl_2) of complex **1** (see Experimental section), the *C*$NBPh_3$ resonance occurs as a broad unresolved multiplet at δ 164.08, whereas the multiplet centred at δ 155.34 is assigned to the *ipso*-C nuclei of the phenyl rings in BPh_3. For the cyano-complex *trans*-[FeH(CN)(dppe)$_2$] **3** the *C*N resonance is a grossly resolved quintet ($^2J_{CP} \approx 15$ Hz) at δ 162.29. In the ^{1}H NMR (CD_2Cl_2) spectra of **1** and **3** the hydride resonance is the expected quintet at δ −14.61 ($^2J_{HP} = 49.1$ Hz) or −14.85 ($^2J_{HP} = 46.2$ Hz), respectively.

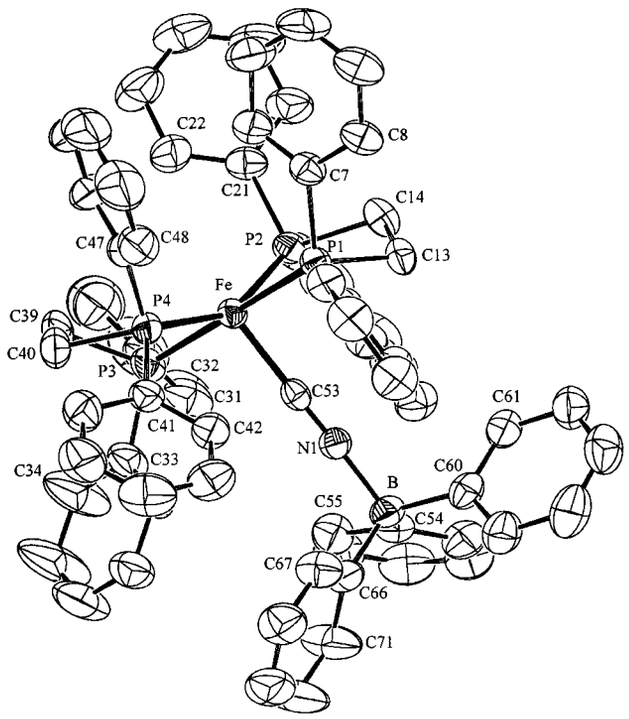


Fig. 1 Molecular structure of *trans*-[FeH($CNBPh_3$)(dppe)$_2$] **1** with atom labelling scheme. Displacement ellipsoids are drawn at the 50% probability level; atom H(1) is shown as a small circle of arbitrary radius.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Fe–C(53)	1.914(3)	N(1)–C(53)	1.163(4)
Fe–P(4)	2.2156(10)	N(1)–B	1.604(4)
Fe–P(3)	2.2355(11)	C(54)–B	1.629(5)
Fe–P(2)	2.2421(10)	C(60)–B	1.629(5)
Fe–P(1)	2.2451(10)	C(66)–B	1.633(5)
Fe–H(1)	1.37(3)		
N(1)–C(53)–Fe	177.4(3)	C(53)–Fe–P(2)	97.56(9)
C(53)–N(1)–B	178.4(3)	C(53)–Fe–P(1)	88.03(9)
N(1)–B–C(60)	106.3(3)	P(4)–Fe–P(3)	83.77(4)
N(1)–B–C(66)	106.4(3)	P(4)–Fe–P(2)	151.85(4)
N(1)–B–C(54)	107.0(3)	P(3)–Fe–P(2)	97.88(4)
H(1)–Fe–C(53)	177.4(3)	P(4)–Fe–P(1)	95.07(4)
H(1)–Fe–P(1)	95(1)	P(3)–Fe–P(1)	178.83(4)
C(53)–Fe–P(4)	110.49(9)	P(2)–Fe–P(1)	83.17(4)
C(53)–Fe–P(3)	92.33(9)		

The molecular structure of complex **1** has been determined by single-crystal X-ray diffraction analysis (Fig. 1), and selected bond distances and angles are given in Table 1. It presents an octahedral-type geometry with the diphosphines in the equatorial sites, the hydride and the $CNBPh_3^-$ ligands being mutually *trans*. The Fe–C≡N–B moiety is essentially linear [Fe–C(53)–N(1) and C(53)–N(1)–B angles of 177.4(3) and 178.4(3)°, respectively], and the Fe–C(53) and the N(1)–B bond lengths, 1.914(3) and 1.604(4) Å, are similar to those reported for the iron(II) complexes [Fe(CH_3)($CNBPh_3$)(CO)$_2$(PMe_3)$_2$], 1.910(3) and 1.592(4) Å,[7b] [Fe(η^1-C_5H_5)($CNBPh_3$)(CO)$_2$], 1.89(1) and 1.59(1) Å,[7c] and [Fe($CNBPh_3$)$_2$(TIM)], 1.904(3) and 1.575(4) Å,[12] respectively. The C(53)–N(1) distance in **1**, 1.163(4) Å, is also comparable to those observed for the latter complexes, 1.146(4),[7b] 1.14(1)[7c] or 1.135(3)[12] Å, respectively. The Fe–P (average) distance in **1**, 2.2346(11) Å, is slightly shorter than that found in the cationic complex *trans*-[FeH(η^1-P≡CBu^t)(dppe)$_2$][BPh_4], 2.276(2) Å,[14] conceivably as a result of a stronger π-electron releasing ability of the metal centre to the dppe ligands in the former.

The Fe–H(1) distance, 1.37(3) Å, is comparable with that of *trans*-[FeH(N_2)($Me_2PCH_2CH_2PMe_2$)$_2$][BPh_4], 1.32(2) Å,[15] but shorter than that of [FeH(N_2)P_4]Br (P_4 = $Ph_2PC_2H_4PPhC_2H_4$-$PPhC_2H_4PPh_2$), 1.53(9) Å,[16] and the expected value, 1.53 Å, based on the sum of the iron and hydrogen covalent radii.

Interestingly, the X-ray analysis also reveals the presence, in the lattice, of one disordered molecule of formamide plus one molecule of water, connected by a hydrogen bond, per molecule of complex **1**. We believe the water comes from traces of moisture in the solvent(s) and the formamide is formed from hydrolysis of $NCSiMe_3$ or of derived NCH.

If the reaction of *trans*-[FeH(Cl)(dppe)$_2$] with $NCSiMe_3$ in thf is carried out in the presence of Tl[BF_4] instead of Na[BPh_4], and in acidic medium (HBF_4), the isocyanide complex *trans*-[FeH(CNH)(dppe)$_2$][BF_4] **2** is the obtained product (reaction 4, Scheme 1). The cleavage of the N–Si bond of the cyanosilane is achieved by reaction with HBF_4 (formation of Me_3SiF) and the resulting cyano ligand is then protonated to form the ligating CNH. This reaction relates to the synthesis of the aminocarbyne complex *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] by treatment of *trans*-[ReCl($CNSiMe_3$)(dppe)$_2$] with HBF_4,[1b] which, however, at the more electron-rich rhenium centre, involves further protonation of the CNH ligand to CNH_2. At the less electron-rich iron site of the present study the ligating CNH is not susceptible to further protonation and the reaction does not proceed to the aminocarbyne level.

The conceivable involvement of the cyano complex *trans*-[FeH(CN)(dppe)$_2$] **3** as an intermediate in reaction (4) to give the isocyanide product **2** is corroborated by the alternative formation of the latter complex upon treatment of the former with HBF_4 (reaction 5, Scheme 1), a reaction already reported by others.[4] However, the single-pot route to **2** we have previously found[17] and now describe in detail (reaction 4) is a more direct one, and does not require the isolation of the cyano-complex **3**.

Electrochemistry

The electrochemical behaviour of the complexes of this study has been investigated by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) at a platinum disc electrode, in 0.2 mol dm^{-3} [NBu_4][BF_4]–thf.

Complexes *trans*-[FeH($CNBPh_3$)(dppe)$_2$] **1** and *trans*-[FeH(CN)(dppe)$_2$] **3** exhibit, by CV, a single-electron reversible anodic wave at $E_{\frac{1}{2}}^{ox}$ = 0.53 or 0.33 V *vs.* SCE, respectively, involving the expected $Fe^{II} \longrightarrow Fe^{III}$ oxidation. These values are higher than that observed (−0.11 V) for the oxidation of *trans*-[FeH(Cl)(dppe)$_2$] and lower than those (0.87–1.03 V) quoted[18] for the isocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$]$^+$ (R = alkyl or aryl), following the expected order of the net electron donor/acceptor ability of the variable ligand: $Cl^- > CN^- > CNBPh_3^- > CNR$. The isocyanotriphenylborate ligand thus behaves as a weaker net electron releaser, to the metal centre, than cyanide due to the electron acceptance of the triphenylboron group.

A quantitative comparison of the net electron donor/acceptor abilities of these ligands can be made by using a proposed[19] scale of electrochemical P_L ligand constants in terms of the linear relationship (1) between $E_{\frac{1}{2}}^{ox}$ (for closed shell

$$E_{\frac{1}{2}}^{ox}[M_sL] = E_s + \beta P_L \quad (1)$$

octahedral complexes [M_sL]) and P_L (for ligand L), applied to the {FeH(dppe)$_2$}$^+$ metal site {M_s}, in which E_s and β are the electron richness and the polarisability of this site (E_s = 1.04 V, β = 1.0[19]).

From the measured $E_{\frac{1}{2}}^{ox}$ value for complex **1** and the knowledge of E_s and β for its iron(II) site, the value of P_L = −0.51 V can be estimated for the first time for the $CNBPh_3^-$ ligand. On the basis of this P_L value, $CNBPh_3^-$ is in fact a much weaker net electron donor than Cl^- or CN^- (P_L = −1.19 or −1.0 V, respectively[19]), but only slightly weaker than NCMe (P_L = −0.58 V[19]) and marginally stronger than CNMe (P_L = −0.43 V[19]).

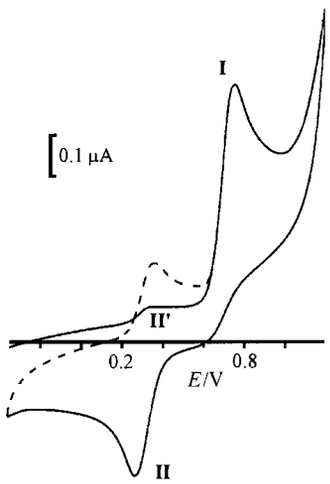


Fig. 2 Cyclic voltammogram of *trans*-[FeH(CNH)(dppe)$_2$] (0.81 mmol dm^{-3} in thf with 0.2 mol dm^{-3} [NBu_4][BF_4]) at 0 °C and at a platinum disc (d = 0.5 mm) working electrode. Potentials are given in V *vs.* SCE. Scan rate: 0.2 V s^{-1}.

A more complex electrochemical behaviour is displayed by the isocyanide complex *trans*-[FeH(CNH)(dppe)$_2$][BF_4] **2**. It exhibits, by CV, an irreversible anodic wave (I, Fig. 2, at 0 °C), at E_p^{ox} = 0.66 V *vs.* SCE. The anodic process at this wave generates, by proton loss (reaction 2), the oxidised form of the cyano-complex **3**, *trans*-[FeH(CN)(dppe)$_2$]$^+$ **3**$^+$, which is detected, upon scan reversal, by its cathodic wave (II) at a potential ($E_{\frac{1}{2}}^{red}$ = 0.33 V) that is identical to that observed (see above) for the redox pair *trans*-[FeH(CN)(dppe)$_2$]$^{0/+}$ of a genuine sample of **3**.

However, in contrast with the reversible character of the redox wave for the couple *trans*-[FeH(CN)(dppe)$_2$]$^{0/+}$, the cathodic wave II is only partially reversible. The irreversibility results from the presence of free H^+ [liberated according to eqn. (2) and by dissociation from **2** in solution as shown below]

$$\underset{\mathbf{2}}{trans\text{-}[FeH(CNH)(dppe)_2]^+} \overset{-e}{\rightleftharpoons} \underset{\mathbf{2}^+}{trans\text{-}[FeH(CNH)(dppe)_2]^{2+}} \longrightarrow \underset{\mathbf{3}^+}{trans\text{-}[FeH(CN)(dppe)_2]^+} + H^+ \quad (2)$$

which consumes *trans*-[FeH(CN)(dppe)$_2$] formed at wave II. The proton evolution at the anodic wave I is consistent with the detection, by CV and upon subsequent cathodic scan, of an irreversible and broad cathodic wave at E_p^{red} *ca.* −0.75 V assigned to H^+ reduction. Accordingly, by replacing the Pt by a vitreous carbon electrode, although *trans*-[FeH(CN)(dppe)$_2$]$^+$ is also generated at wave I, no cathodic wave for H^+ reduction is then observed due to its expected shift to a much lower potential beyond the solvent/electrolyte discharge. The presence of H^+ in solution also results, in part, from the slight acid dissociation, in thf, of *trans*-[FeH(CNH)(dppe)$_2$]$^+$ as accounted for by the detection, during the anodic sweep, of the oxidation wave (II′) (Fig. 2) of its conjugate base, *trans*-[FeH(CN)(dppe)$_2$] **3**.

The proton loss at the anodic wave of *trans*-[FeH(CNH)(dppe)$_2$]$^+$ **2** is consistent with the expected enhancement of the acidic character of CNH as a result of oxidation of the complex and parallels the anodically induced deprotonation reported[1c] for the aminocarbyne complex *trans*-[ReCl(CNH_2)(dppe)$_2$]$^+$.

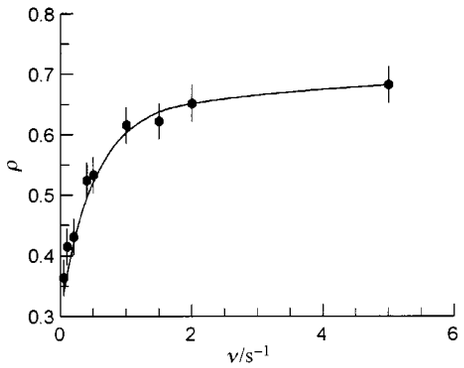
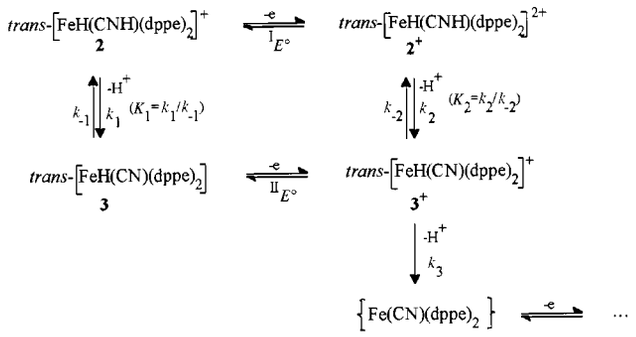


Fig. 3 Experimental (symbols) and theoretical (line) variation of $\rho = i_p^{II}/i_p^{I}$ (see text) as a function of scan rate. The solid line corresponds to the working curve for the mechanism described in Scheme 2 where $k_1 = 0.105 \pm 0.002$ s^{-1}, $k_{-1} = 30 \pm 1$ dm^3 mmol^{-1} s^{-1}, $k_2 = 50 \pm 1$ s^{-1}, $k_{-2} \approx 0$ and $k_3 = 0.25 \pm 0.02$ s^{-1}.

The cyclic voltammetric behaviour of the isocyanide complex **2** is dependent on the scan rate. The detected amount of *trans*-[FeH(CN)(dppe)$_2$]$^+$ relative to that of *trans*-[FeH(CNH)(dppe)$_2$]$^+$, as measured by the ratio, ρ, of the cathodic peak current of the former at wave II, following the oxidation of the latter at wave I, and the anodic peak current of the latter ($\rho = i_p^{II}/i_p^{I}$), increases with the increase of scan rate, although in a less pronounced way for higher scan rates (see Fig. 3, symbols); it would probably reach a maximum value followed by a decrease for sufficiently high scan rates which, however, were not possible to investigate accurately due to the strong interference of the solvent/electrolyte anodic discharge.

Moreover, the current function $i_p\, v^{-\frac{1}{2}}\, c^{-1}$ (v = scan rate, c = concentration) for the anodic peak current of wave I increases with the decrease of v (*e.g.*, by a factor of *ca.* 2 from 5 to 0.05 V s^{-1}) indicating the involvement of a higher number of electrons at lower scan rates. In agreement, the CPE at the anodic wave I led to the consumption of 2 F mol^{-1}. The cyclic voltammogram of the electrolysed solution revealed only the irreversible and broad cathodic wave assigned to H^+ reduction. Potentiometric titration of this solution indicated the loss of two protons during the CPE. One of these protons was derived from the CNH ligand (see above) whereas the other one was released from the metal at the derived cyano complex **3**$^+$, as confirmed by anodic CPE of a solution of **3** followed by potentiometric titration of the electrolysed solution. This is consistent with the observed behaviour[18] of the related hydrideisocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$]$^+$ (R = alkyl or aryl) which exhibit an anodic process with proton loss upon metal–hydride bond cleavage. Such a type of anodically induced proton loss, upon heterolytic M–H bond cleavage, has been well documented for a number of other hydride complexes,[20–22] and also occurs in our current system. However, the stronger acidic character of the CNH ligand, compared to its binding Fe–H centre, results in the dominant proton loss from that ligand, whereas the slower H^+ release from the metal can only occur at a later stage.

The described behaviour can be interpreted by considering the processes depicted in Scheme 2. Thus, the high-scan-rate limiting behaviour should correspond to the reversible single-electron oxidation of *trans*-[FeH(CNH)(dppe)$_2$]$^+$ **2**, since there would be no time for appreciable deprotonation (indeed, the cyclic voltammogram at 5 V s^{-1} already reveals a slight reversibility of wave I). However, upon decreasing the scan rate, there occurs an increasing conversion of the isocyanide complex **2**$^+$ into the derived cyanide product **3**$^+$ which, moreover, for sufficiently low scan rates undergoes an extensive degradation process. No significant variation of the above behaviour was detected upon changing the concentration of the complex, thus indicating the involvement of a first-order chemical step.



Scheme 2

The mechanism of Scheme 2 was investigated in detail by digital simulation (program CVSim[23]) of the cyclic voltammograms in the available range of scan rates. A good fit was obtained (Fig. 3) by considering the homogeneous rate constant values of $k_1 = 0.105 \pm 0.002$ s^{-1}, $k_{-1} = 30 \pm 1$ dm^3 mmol^{-1} s^{-1}, $k_2 = 50 \pm 1$ s^{-1}, $k_{-2} \ll k_2$ and $k_3 = 0.25 \pm 0.02$ s^{-1}. The low value of k_{-2} could also be estimated (9×10^{-4} dm^3 mmol^{-1} s^{-1}) by considering expression (3) derived from the known condition

$$\ln \frac{K_1}{K_2} = -\frac{F}{RT}({}^{I}E^{\circ} - {}^{II}E^{\circ}) \qquad (3)$$

$\Delta G^{\circ} = 0$ along the thermochemical cycle of Scheme 2, which relates the chemical equilibrium constants (acid dissociation constants) $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$ with the formal redox potentials for waves I and II.

Such acid dissociation constants were also estimated as $K_1 = 3.5 \times 10^{-3}$ mmol dm^{-3} and $K_2 = 5.5 \times 10^{4}$ mmol dm^{-3}, showing that a single-electron oxidation of the isocyanide complex **2** promotes the acidic character of the CNH ligand by a factor of *ca.* 1.5×10^7, *i.e.* a pK decrease of *ca.* 7. A related behaviour was observed[1c] for the aminocarbyne complex *trans*-[ReCl(CNH$_2$)(dppe)$_2$]$^+$ whose acid dissociation constant in NCMe increases from 6.3×10^{-6} to 2.5×10^{4} mmol dm^{-3} (pK decrease of *ca.* 9.6) upon single-electron oxidation. Although quite remarkable, these anodically induced pK decreases at the CNH$_x$ (x = 1 or 2) ligands are not so drastic as those reported, *ca.* 20–30,[20c,21] for some hydride complexes which undergo anodic M–H bond cleavage, in accord with the fact that, in our systems, the proton to be released is not so close to the metal redox centre (three bond distances separate them) as in the latter hydride complexes in which these atoms are directly connected.

At our iron system the isocyanide ligand is a stronger acid than the aminocarbyne at the above rhenium centre. Moreover, the rate of proton loss from the CNH ligand is enhanced by a factor of *ca.* 500 upon single-electron oxidation ($k_2/k_1 \approx 500$), and the proton eliminates faster from this ligand than from the iron centre ($k_2/k_3 \approx 200$).

Experimental

General

All the reactions were carried out under argon and using standard inert gas flow and vacuum techniques. Solvents were purified by standard procedures, *trans*-[FeH(Cl)(dppe)$_2$] was prepared by a published[10] method and N≡CSiMe$_3$ and HBF$_4$·Et$_2$O (Aldrich) were commercially available. Infrared measurements were carried out on a Perkin-Elmer 683 spectrophotometer, ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer.

The electrochemical experiments were performed on an EG&G PAR 173 potentiostat and an EG&G PARC 175 universal programmer. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell, at a platinum-wire or

disc working electrode, probed by a Luggin capillary connected to a silver wire pseudo-reference electrode; a platinum auxiliary electrode was employed. 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 potentials were measured in 0.2 mol dm^{-3} $[NBu_4][BF_4]$–thf by using $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ ($E_{\frac{1}{2}}^{ox} = 0.55$ V *vs.* SCE) or *trans*-$[FeH(Cl)(dppe)_2]^{0/+}$ ($E_{\frac{1}{2}}^{ox} = -0.11$ V *vs.* SCE) as internal reference. The mechanism of the redox induced deprotonation was investigated by simulation (program CVSim)[23] of the voltammograms at different scan rates (in the 0.05–10 V s^{-1} range) and various concentrations of the complex. The determination of the current ratios for both experimental and theoretical voltammograms was performed as described previously,[24] with $k_{het} = 0.01$ cm s^{-1}.

The acid base titrations of the electrochemically oxidised solutions were carried out by using a solution of KOH in MeOH which was standardised by titration against benzoic acid in CH_2Cl_2 or in thf. The results presented have been corrected for background effects by performing also, in each case, the titration of a blank solution of 0.2 mol dm^{-3} $[NBu_4][BF_4]$ which had been electrolysed under identical conditions to those used for the corresponding complex solution.

Syntheses

***trans*-[FeH(CNBPh$_3$)(dppe)$_2$] 1.** *A From trans-[FeH(Cl)(dppe)$_2$].* A thf solution (12 cm^3) of *trans*-$[FeH(Cl)(dppe)_2]$ (0.136 g, 0.153 mmol) and $NCSiMe_3$ (61.2 μl, 0.459 mmol), in the presence of $Na[BPh_4]$ (0.0571 g, 0.168 mmol), was stirred overnight and then taken to dryness *in vacuo*. Extraction with CH_2Cl_2 (4 cm^3), filtration and addition of diethyl ether resulted in the precipitation of **1** as a yellow crystalline solid which was filtered off, washed with diethyl ether and dried *in vacuo* (*ca.* 45% yield). One of the crystals was analysed by X-ray diffraction.

B From trans-[FeH(CN)(dppe)$_2$] 3. A thf solution (20 cm^3) of *trans*-$[FeH(CN)(dppe)_2]$ **3** (0.098 g, 0.110 mmol) was treated with BPh_3 (0.50 cm^3 of a 0.25 mol dm^{-3} thf solution, 0.125 mmol). After stirring for *ca.* 30 min, the final yellow solution was concentrated *in vacuo* and diethyl ether added. Further concentration followed by cooling at *ca.* −18 °C led to the precipitation of complex **1** as an orange solid which was filtered off, washed with diethyl ether and dried *in vacuo* (*ca.* 50% yield) (Found: C, 71.6; H, 5.6; N, 1.4. Calc. for $C_{71}H_{64}BFeNP_4\cdot CH_2Cl_2$: C, 71.6; H, 5.5; N, 1.2%. IR (KBr pellet): ν(C≡N) 2090s cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.25–6.69 [m, 55H, phenyl (dppe + $CNBPh_3$)], 2.15 [s, br, 8H, CH_2 (dppe)] and −14.61 (q, $^2J_{HP} = 49.1$ Hz, 1H, Fe*H*). ^{31}P-{^{1}H} NMR (CD_2Cl_2): δ −55.36(s) relative to $P(OMe)_3$. ^{13}C NMR (CD_2Cl_2): δ 164.08 (m, br, *C*$NBPh_3$), 155.34 (m, br, *ipso*-C of BPh_3), 137.51–123.11 [m, phenyl (BPh_3 + dppe)] and 32.91 [t, br, $J_{CH} = 131.9$ Hz, CH_2 (dppe)].

***trans*-[FeH(CNH)(dppe)$_2$][BF$_4$] 2.** *A From trans-[FeH(Cl)(dppe)$_2$].* A thf solution (40 cm^3) of *trans*-$[FeH(Cl)(dppe)_2]$ (0.447 g, 0.504 mmol), in the presence of $Tl[BF_4]$ (0.230 g, 0.789 mmol), was treated, with stirring, with $NCSiMe_3$ (0.60 cm^3, 4.5 mmol) and $[Et_2OH][BF_4]$ (dropwise addition of 10.0 cm^3 of a 1:51 Et_2O diluted solution of commercial 54%, 1.43 mmol of acid). After stirring overnight the solution was concentrated *in vacuo* and complex **2** precipitated upon addition of diethyl ether as a yellow solid which was filtered off, washed with diethyl ether and dried *in vacuo*. Further crops could be obtained from the mother-liquor upon concentration and addition of diethyl ether (*ca.* 70% yield).

B From trans-[FeH(CN)(dppe)$_2$] 3. A thf solution (30 cm^3) of *trans*-$[FeH(CN)(dppe)_2]$ **3** (0.150 g, 0.171 mmol) was treated, with stirring, with $[Et_2OH][BF_4]$ (dropwise addition of 3.6 cm^3 of a 1:100 Et_2O diluted solution of commercial 54%, 0.256 mmol). After *ca.* 1.5 h it was concentrated *in vacuo* and complex **2** precipitated as a yellow solid upon addition of *n*-pentane. Further crops could be obtained from the mother-liquor upon concentration and addition of diethyl ether (*ca.* 70% yield) (Found: C, 64.9; H, 5.0; N, 1.4. Calc. for $C_{53}H_{50}BF_4FeNP_4\cdot \frac{1}{4}CH_2Cl_2$: C, 64.7; H, 5.1; N, 1.4%). IR (KBr pellet): ν(C≡N) 2090s cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.4–7.0 [m, 40H, phenyl (dppe)], 2.38 [m, br, 4H, CH_2 (dppe)], 1.96 [m, br, 4H, CH_2(dppe)] and −12.17 (q, $^2J_{HP} = 45.9$ Hz, 1H, FeH]. ^{31}P-{^{1}H} NMR (CD_2Cl_2): δ −53.24(s) relative to $P(OMe)_3$. ^{13}C NMR (CD_2Cl_2): δ 170.75 (d, br, $^2J_{CH} \approx 65$ Hz, CNH), 137.56 [q, virtual $J_{CP} = 18.3$, *ipso*-C (phenyl, dppe)], 136.89 [q, virtual $J_{CP} = 18.3$, *ipso*-C (phenyl, dppe)], 134.8–127.0 [m, phenyl (dppe)] and 33.95 [t, br, $J_{CH} = 133.6$, CH_2 (dppe)] (q, virtual $J_{CP} = 12.4$ Hz, in the ^{1}H-coupled spectrum).

***trans*-[FeH(CN)(dppe)$_2$] 3.** A thf solution (40 cm^3) of *trans*-$[FeH(Cl)(dppe)_2]$ (0.337 g, 0.379 mmol) was treated with $[NBu_4]CN$ (0.305 g, 1.14 mmol) and $Tl[BF_4]$ (0.143 g, 0.492 mmol), and the resulting suspension was stirred overnight. The solution was then filtered and taken to dryness. Extraction with CH_2Cl_2 (10 cm^3), concentration and addition of diethyl ether led to the precipitation of complex **3** as a yellow solid which was filtered off, washed with diethyl ether and dried *in vacuo* (*ca.* 59% yield) (Found: C, 70.5; H, 5.6; N, 1.6. Calc. for $C_{53}H_{49}FeNP_4\cdot\frac{2}{5}CH_2Cl_2$: C, 70.2; H, 5.4; N, 1.5%). IR (KBr pellet): ν(C≡N) 2030 w, m cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.4–7.0 [m, 40H, phenyl (dppe)], 2.48 [m, br, 4H, CH_2 (dppe)], 2.02 [m, br, 4H, CH_2 (dppe)] and −14.85 (q, $^2J_{HP} = 46.2$ Hz, 1H, FeH). ^{31}P-{^{1}H} NMR (CD_2Cl_2): δ −49.09(s) relative to $P(OMe)_3$. ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ 162.29 (q, br, $^2J_{CP} \approx 15$, CN), 139.31 [q, virtual $J_{CP} = 8.8$, *ipso*-C (phenyl, dppe)], 138.72 [q, virtual $J_{CP} = 7.1$, *ipso*-C (phenyl, dppe)], 134.40–127.39 [m, phenyl (dppe)] and 34.14 (q, virtual $J_{CP} = 12.4$ Hz, CH_2 (dppe)].

X-Ray crystallography

Crystal data for *trans*-[FeH(CNBPh$_3$)(dppe)$_2$]·HCONH$_2$·H$_2$O. $C_{72}H_{69}BFeN_2O_2P_4$, $M = 1184.97$, triclinic, space group $P\bar{1}$, $a = 13.685(3)$, $b = 13.746(3)$ and $c = 19.616(4)$ Å, $\alpha = 109.10(2)$, $\beta = 102.78(2)$ and $\gamma = 63.49(2)°$, $U = 3107.9(12)$ Å^3, $T = 293(2)$ K, $Z = 2$, μ(Mo-Kα) = 0.392 mm^{-1}.

Cell dimensions were obtained from 7012 reflections measured and no equivalent data were collected. Final $wR(F^2) = 0.1111$, $R1 = 0.0397$. Intensity data were collected using a Syntex P-1 diffractometer in the range $2.08 < \theta < 25.05°$ with index ranges $-15 \le h \le 15$, $-16 \le k \le 15$, $0 \le l \le 23$.

Experimental data were processed using the PROFIT procedure.[25] An absorption correction was not applied due to the small value of μ. The structure was solved by direct methods and refined by full-matrix anisotropic least squares. Hydrogen atom positions were found from difference synthesis; their coordinates and isotropic thermal parameters were also refined. Structure solution and refinement were performed using the SHELXTL 81[26] and SHELXL 93[27] packages respectively.

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See http://www.rsc.org/suppdata/dt/1999/467/ for crystallographic files in .cif format.

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