ELECTROCHEMICAL BEHAVIOUR OF *trans*-[FeH(CN)(dppe)$_2$] ADDUCTS

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Dedicated to Professor Sergio Roffia in recognition of his achievements.

Electrochemical behaviour of various metallo cyano adducts of *trans*-[FeH(CN)(dppe)$_2$], *viz.* the dinuclear complexes [FeH(dppe)$_2$(μ-CN)PdCl$_2$(PPh$_3$)], [FeH(dppe)$_2$(μ-CN)NiCl$_2$(PCy$_3$)], and trinuclear [{FeH(dppe)$_2$(μ-CN)}$_2$(ReOCl$_3$)], [{FeH(dppe)$_2$(μ-CN)}$_2$PtCl(Ph)] and [{FeX-(dppe)$_2$(μ-CN)}$_2$WCl$_3$(OH)] (X = Cl or OH, dppe = 1,2-diphenylphosphinoethane, PCy$_3$ = P(C$_6$H$_{11}$)$_3$), as well as the benzoylisocyanide mononuclear adduct *trans*-[FeH(CNCOPh)-(dppe)$_2$], is reported. All of them exhibit Fe^{II}/Fe^{III}-based oxidations (which are reversible, except for *trans*-[FeH(CNCOPh)(dppe)$_2$]). The metallocyanide bridges C≡N–Re–N≡C and C≡N–W–N≡C in [{FeH(dppe)$_2$(μ-CN)}$_2$(ReOCl$_3$)] and [{FeX(dppe)$_2$(μ-CN)}$_2$WCl$_3$(OH)], respectively, allow electronic communication between the iron centres, with possible generation of mixed-valence Fe^{II}/Fe^{III} complexes whose comproportionation constant could be estimated in the former case. From the values of the measured oxidation potentials, the electrochemical P_L and E_L ligand parameters have been estimated for the metallocyanide ligands that were shown to behave as stronger net electron donors than organoisocyanides, although weaker than cyanide itself. Ligand-centred reduction processes were also observed to lead, in the cases of complexes *trans*-[FeH(CNCOPh)(dppe)$_2$] (CNCOPh-based reduction) and [FeH(dppe)$_2$(μ-CN)PdCl$_2$(PPh$_3$)] (Pd^{II}-based reduction in the CNPdCl$_2$(PPh$_3$)$^-$ metallocyanide ligand), to the dissociation of the adduct, with regeneration of the parent cyano complex *trans*-[FeH(CN)(dppe)$_2$], thus reflecting the reductive decrease of the electrophilic (or Lewis acidic) character of the benzoyl and {PdCl$_2$(PPh$_3$)} groups.
Keywords: Bridging cyanide; Heteronuclear complexes; Comproportionation constant; Electrochemistry; Cyclic voltammetry; Redox-potential parameterisation; Iron; Transition metals; Multinuclear complexes.

The investigation of the coordination chemistry of cyanide has long been a matter of great interest in view of the synthetic versatility of this ligand in inorganic, material and medicinal fields[1], and its significance in biology[2].

We have also been paying attention to this interesting unsaturated small molecule and have already reported[3–11] some studies on its activation towards electrophiles, in particular by coordination to low-valent Re^I or Fe^{II} phosphinic centres. For example, the hydridoisocyanide complex *trans*-$[FeH(CNH)(dppe)_2]^+$ could be obtained by protonation (with HBF_4) of the cyano complex *trans*-$[FeH(CN)(dppe)_2]$ that can also add BPh_3 to give the isocyanotriphenylborate product *trans*-$[FeH(CNBPh_3)(dppe)_2]$ (ref.[2]). We have recently reported[11] the extension of the chemical study of this cyano complex to other electrophilic agents and found that the ligated cyanide can readily undergo aroylation, alkylation and addition of various transition- metal Lewis acids, producing, in the former cases, isocyanide complexes and, in the latter ones, di- or trinuclear adducts with bridging cyanide (Scheme 1). The metallocyanide bridge, in principle, may promote interaction between the metal centres. The possibility of such a metal–metal interaction *via* the cyanide bridge in these heteronuclear compounds would be of interest in view of its significance in a diversity of fields[12]. We have addressed this point by having performed an electrochemical study reported herein.
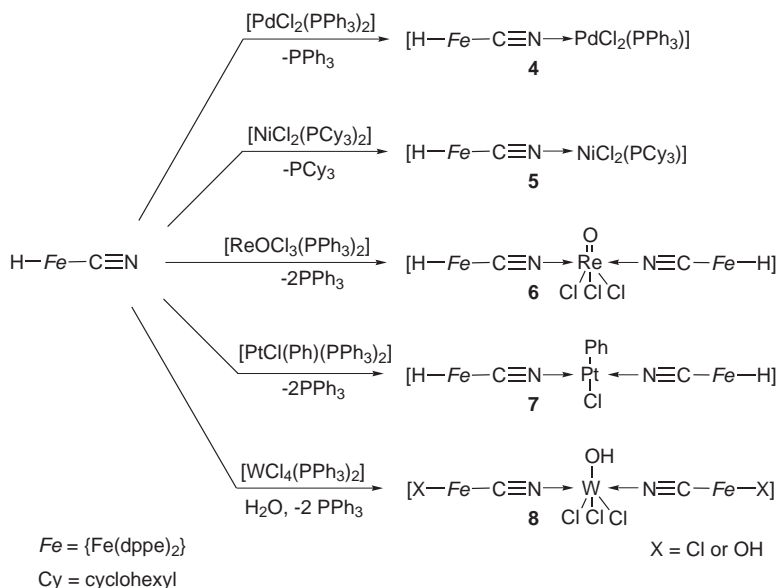
SCHEME 1

The current investigation also includes the new dinuclear Fe^{II}/Ni^{II} complex [FeH(dppe)$_2$(μ-CN)NiCl$_2$(PCy$_3$)] (**5**), generated *in situ* by mixing stoichiometric amounts of *trans*-[FeH(CN)(dppe)$_2$] and [NiCl$_2$(PCy$_3$)$_2$] in the electrolytic medium.

In addition, this study has also allowed to estimate the electrochemical P_L and E_L ligand parameters (see below), which measure the net electron-donor/acceptor character of all the cyano-derived ligands. This has been achieved for the first time for metallo-cyano-type ligands.

The comproportionation constant of a mixed-valence cyano-bridged complex has also been evaluated. In some cases, the electron-transfer induced dissociation of the ligated cyano adduct has been detected.

RESULTS AND DISCUSSION

The isocyanide complexes *trans*-[FeH(CNR)(dppe)$_2$]X (R = PhCO, X=Cl (**1**); R = Me, X = I (**2**); R = Et, X = BF$_4$ (**3**)) were prepared as previously reported[11] from the reaction of *trans*-[FeH(CN)(dppe)$_2$] with appropriate aroylating or alkylating agents. The di- and trinuclear complexes with one or two bridging cyanides [FeH(dppe)$_2$(μ-CN)PdCl$_2$(PPh$_3$)] (**4**), [FeH(dppe)$_2$(μ-CN)-NiCl$_2$(PCy$_3$)] (**5**), [{FeH(dppe)$_2$(μ-CN)}$_2$(ReOCl$_3$)] (**6**), [{FeH(dppe)$_2$(μ-CN)}$_2$-PtCl(Ph)] (**7**) and [{FeX(dppe)$_2$(μ-CN)}$_2$WCl$_3$(OH)] (**8**) were formed when using [PdCl$_2$(PPh$_3$)$_2$], [NiCl$_2$(PCy$_3$)$_2$], [ReOCl$_3$(PPh$_3$)$_2$], [PtCl(Ph)(PPh$_3$)$_2$] or [WCl$_4$(PPh$_3$)$_2$], respectively, as the transition-metal Lewis acid source[11].

The electrochemical behaviour of the complexes was studied in 2×10^{-1} M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ or THF by cyclic voltammetry (CV) and controlled-potential electrolysis (CPE), at Pt disc and Pt gauze electrodes, respectively. Relevant data are given in Table I.

Mononuclear Complexes

The benzoylisocyanide complex **1** exhibits, in the cyclic voltammogram (scan rate of 0.2 V s^{-1}) an irreversible oxidation wave (Fig. 1) at $E_{p/2}^{ox}$ = 1.24 V *vs* SCE. This potential is more positive than those for the analogous alkylisocyanide complexes **2** and **3** ($E_{1/2}^{ox}$ = 0.87 and 0.90 V, respectively[13]) or even for the related arylisocyanide compounds *trans*-[FeH(CNC$_6$H$_4$X-4)-(dppe)$_2$]$^+$ (X = OMe, Me, NO$_2$) (*ca* 0.9–1.0 V)[14]. This difference indicates the strongest electron-withdrawing ability of the benzoyl group in comparison with all the other R groups of the CNR ligands. These oxidation potential values follow the expected order of the π-acceptor character of the isocya-

Table I
Cyclic voltammetric data^a for the mono-, di- and trinuclear adducts of *trans*-[FeH(CN)(dppe)$_2$], and of the Lewis acid precursors

Complex	$E_{1/2}^{ox}$ ($E_{p/2}^{ox}$)	E_p^{red}
trans-[FeH(CNCOPh)(dppe)$_2$]$^+$ (**1**)	$(1.24)^b$	-1.44^c
trans-[FeH(CNMe)(dppe)$_2$]$^+$ (**2**)^d	0.87	–
trans-[FeH(CNEt)(dppe)$_2$]$^+$ (**3**)^e	0.90	–
trans-[FeH(CN)(dppe)$_2$]^f	0.30	–
[HFe(dppe)$_2$(μ-CN)PdCl$_2$(PPh$_3$)] (**4**)	0.43	$-1.04, -1.38^g$
[HFe(dppe)$_2$(μ-CN)NiCl$_2$(PCy$_3$)] (**5**)^h	0.79 (0.97)	-0.78
[{HFe(dppe)$_2$(μ-CN)}$_2$(ReOCl$_3$)] (**6**)^i	0.49, 0.70	-1.46
Lewis acid		
[PdCl$_2$(PPh$_3$)$_2$]	–	-1.10^j
[NiCl$_2$(PCy$_3$)$_2$]	(1.16)	-0.96^k
[ReOCl$_3$(PPh$_3$)$_2$]^l	1.39	$-0.52, -1.44$
[PtCl(Ph)(PPh$_3$)$_2$]^{l,m}	(1.44)	-0.95

^{a} Electrode potentials (half-wave potential $E_{1/2}$ for the reversible processes or (half)-peak potential $E_{p/2}$ and E_p for the irreversible ones) in volt ±0.02 *vs* SCE measured in 2×10^{-1} M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ (unless stated otherwise) at a scan rate of 0.2 V s^{-1}, using a Pt disc (d = 0.5 mm) electrode. ^{b} A second anodic wave was observed at E_p^{ox} = 1.55 V, conceivably due to oxidation of the chloride counter-ion and/or of the product formed in the first oxidation. ^{c} In the subsequent reverse anodic scan, the redox process of *trans*-[FeH(CN)-(dppe)$_2$] ($E_{1/2}^{ox}$ = 0.31 V) was observed. ^{d} From ref.[13] for the analogous compound with BF$_4^-$ as the counter-ion, in CH$_2$Cl$_2$; from ref.[14] $E_{1/2}$ = 0.83 V in THF solution for the analogous compound with BF$_4^-$ as the counter-ion. ^{e} From ref.[14] for the analogous compound with BF$_4^-$ as the counter-ion. ^{f} From ref.[14]; included for comparative purposes. ^{g} In the subsequent reverse anodic scan, other anodic waves were detected at $E_p^{ox} \approx 0$ V and $E_{1/2}^{ox} \approx 0.28$ V, the latter due to the *trans*-[FeH(CN)(dppe)$_2$]$^{0/+}$ redox process. ^{h} Generated *in situ*; after the initial anodic scan, a new reduction process was detected at -1.05 V. ^{i} In THF at -40 °C. ^{j} On the subsequent reverse anodic scan, an oxidation wave is detected at E_p^{ox} = 0.03 V. ^{k} On the subsequent reverse anodic scan, an oxidation wave is detected at E_p^{ox} = 0.50 V. ^{l} At -40 °C. ^{m} Upon anodic scan reversal, a reduction wave is detected at 0.65 V.

nide ligand and of the stabilisation of the highest occupied molecular orbital (HOMO) of the complex.

Such oxidations, which involve the Fe^{II} $\Rightarrow$ Fe^{III} conversion, exhibit potential values that are much higher than that of the neutral cyano complex *trans*-[FeH(CN)(dppe)$_2$] ($E_{1/2}^{ox}$ = 0.33 V). This is in accordance with the stronger net σ-donor ability of the cyanide ligand in the latter complex compared to those of the isocyanides, as indicated by the corresponding values of the electrochemical P_L ligand parameter[15], a measure of the net π-acceptor minus σ-donor character of a ligand. The P_L values estimated[13] for these ligands at the *trans*-{FeH(dppe)$_2$}$^+$ site are as follows: –0.74 (CN$^-$), –0.17 (CNMe), –0.14 (CNEt), 0.20 V (CNCOPh).

A second anodic wave of complex **1** was observed at E_p^{ox} = 1.55 V. It is conceivably due to the oxidation of the chloride counter-ion and/or of the product formed in the first oxidation; it was not investigated further.

Complex **1** also exhibits an irreversible reduction wave at E_p^{red} = –1.44 V (Fig. 1). Interestingly, upon scan reversal beyond this wave, the redox wave of *trans*-[FeH(CN)(dppe)$_2$] (which was initially not present in the solution) is detected (Table I). This has been confirmed by exhaustive controlled-potential electrolysis at the reduction wave of **1**, which consumes 1 F mol^{-1} and generates the cyano complex. Hence, the reduction of **1** leads to the formation of the corresponding cyano complex, indicating the conceivable cathodically induced N–C(acyl) bond cleavage according to Scheme 2.
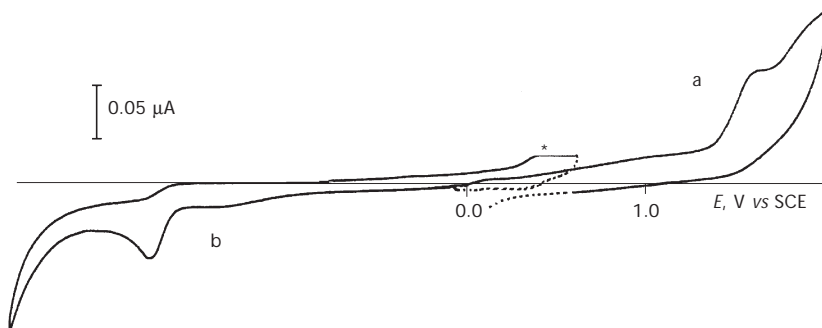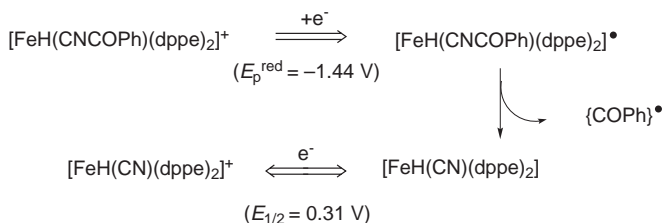

F$_{IG}$. 1
Cyclic voltammogram of 3.6 × 10^{-4} M *trans*-[FeH(CNCOPh)(dppe)$_2$]Cl (**1**) in CH$_2$Cl$_2$ containing 2 × 10^{-1} M Bu$_4$NBF$_4$ at a Pt disc (d = 0.5 mm) working electrode: a anodic scan; b cathodic scan. Asterisk indicates *trans*-[FeH(CN)(dppe)$_2$] generated upon the cathodic scan. Scan rate: 0.2 V s^{-1}

$$[FeH(CNCOPh)(dppe)_2]^+ \xrightarrow{\quad +e^- \quad} [FeH(CNCOPh)(dppe)_2]^\bullet$$

$$(E_p^{red} = -1.44 \text{ V})$$

$$\{COPh\}^\bullet$$

$$[FeH(CN)(dppe)_2]^+ \xleftrightarrow{\quad e^- \quad} [FeH(CN)(dppe)_2]$$

$$(E_{1/2} = 0.31 \text{ V})$$

SCHEME 2

Di- and Trinuclear Complexes

The dinuclear complexes **4** and **5** (the latter generated *in situ* in this study) exhibit in the cyclic voltammogram (scan rate of 0.2 V s⁻¹) one reversible anodic wave (wave I). For compound **5**, a second, irreversible anodic wave (wave II) is observed at a higher potential (Fig. 2). The assignment of the redox waves is based on the electrochemical behaviour of the above Fe^{II} complexes and of the precursor transition-metal Lewis acid components (Table I).

Hence, the oxidation potential values of the first wave ($^I E_{1/2}^{ox}$) which involves the Fe$^{II} \Rightarrow$ Fe^{III} oxidation (0.43 for **4** and 0.79 V for **5**, respectively) are more positive than that of the parent cyano complex (0.30 V). The same applies for the above organoisocyanide complexes **1**–**3**. This positive potential shift reflects the conversion of the cyanide from the terminal to the bridging coordination mode.
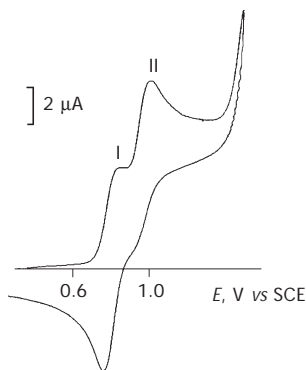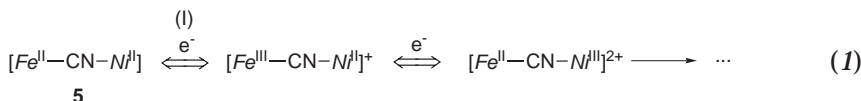

FIG. 2
Cyclic voltammogram of 3.6×10^{-4} M [FeH(dppe)$_2$(μ-CN)NiCl$_2$(PCy$_3$)] (**5**), generated *in situ* in CH$_2$Cl$_2$ containing 2×10^{-1} M Bu$_4$NBF$_4$ at a Pt disc (d = 0.5 mm) working electrode. Scan rate: 0.2 V s⁻¹

The second oxidation wave of the Fe/Ni complex **5** ($^{II}E_{p/2}^{ox}$ = 0.97 V) is assigned to the Ni^{II} ⇒ Ni^{III} oxidation, on the basis of the following arguments: (i) no second oxidation wave is observed for the Fe/Pd complex **4**, in accordance with the absence of any oxidation wave in the cyclic voltammogram of [PdCl$_2$(PPh$_3$)$_2$], up to the solvent-electrolyte discharge potential; (ii) in complex **5**, the $^{II}E_{p/2}^{ox}$ value (0.97 V) is lower than that of the Ni^{II} ⇒ Ni^{III} oxidation potential of [NiCl$_2$(PCy$_3$)$_2$] ($E_{1/2}^{ox}$ = 1.22 V), as expected in view of the replacement, in the latter complex, of one phosphine (PCy$_3$) by one nitrile-type ligand. The ligating {FeH(CN)(dppe)$_2$} group in **5** and nitriles are commonly stronger net electron donors than phosphines (*e.g.*, NCPh and PPh$_3$ have P_L values of –0.40 and –0.35 V, respectively[15]).

Hence, the anodic behaviour of complex **5** can be summarised by Eq. (*1*).

$$[Fe^{II}\!\!-\!\!CN\!\!-\!\!Ni^{II}] \underset{\text{(I)}}{\overset{e^-}{\rightleftharpoons}} [Fe^{III}\!\!-\!\!CN\!\!-\!\!Ni^{II}]^+ \overset{e^-}{\rightleftharpoons} [Fe^{II}\!\!-\!\!CN\!\!-\!\!Ni^{III}]^{2+} \longrightarrow \cdots \qquad (\textbf{1})$$

5

For the trinuclear Fe/Re/Fe complex **6**, two reversible single-electron oxidation waves are detected at $^{I}E_{1/2}^{ox}$ = 0.49 and $^{II}E_{1/2}^{ox}$ = 0.70 V (Fig. 3). These values fall well within the range of Fe^{II}/Fe^{III} oxidation potentials for the above isocyanide complexes, being much lower than that (1.39 V) for the [ReOCl$_3$(PPh$_3$)$_2$] Lewis acid precursor. Hence, such oxidation waves of **6** are ascribed to the two sequential Fe^{II} ⇒ Fe^{III} oxidations, reflecting an interaction between the two iron centres propagated throughout the bridging cyanide groups and the Re atom. In fact, if no Fe–Fe interaction occurred,
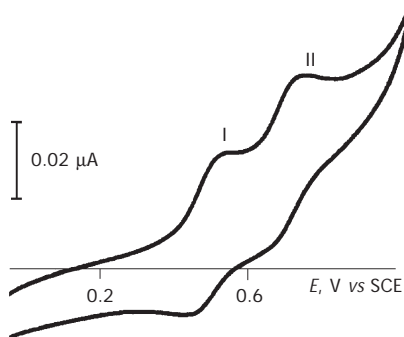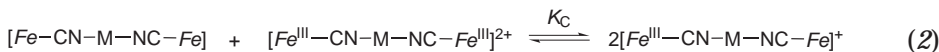

Fig. 3
Cyclic voltammogram of 2.6 × 10^{-4} M [{FeH(dppe)$_2$(μ-CN)}$_2$ReOCl$_3$] (**6**) in CH$_2$Cl$_2$ containing 2 × 10^{-1} M Bu$_4$NBF$_4$ at a Pt disc (d = 0.5 mm) working electrode. Scan rate: 0.2 V s^{-1}

the oxidation of any of the iron(II) centres would not affect the other iron(II) site and merely a single oxidation wave (due to an overall two-electron process) would be observed.

By using the experimental $E_{1/2}^{ox}$, the comproportionation constant $K_C = \exp |n_I {}^I E_{1/2}^{ox} - n_{II} {}^{II} E_{1/2}^{ox}|/25.69$ (at 298 K, with $E_{1/2}$ in mV)[16], *i.e.*, the equilibrium constant for reaction (*2*) ($n_I = n_{II} = 1$; $|{}^I E_{1/2}^{ox} - {}^{II} E_{1/2}^{ox}| = 210$ mV), was calculated in order to evaluate the stabilisation of the mixed-valence Fe^{II}–Fe^{III} state in **6**. The obtained value, $K_C = 3.5 \times 10^3$, suggests[17] a class II mixed-valence system, with delocalisation taking place and the two types of site being distinguishable: a situation usually occurring when at least one group (organic or metal-centre based) forms a bridge between the two ions of different valencies. The K_C value thus estimated is comparable with those for $[\{M(\mu\text{-NC})\}_2\{RuCp(PPh_3)_2\}]^+$ (Cp = η^5-C_5H_5): $K_C = 1.1 \times 10^3$ for M = Fe(CO)Cp and $K_C = 1.2 \times 10^4$ for M = Fe(bpy)$_2$ [18]; for $[Au\{(\mu\text{-NC})Mn(CO)_2[P(OR)_3](dppm)\}_2]^+$ with bridging cyanides: $K_C = 5.7 \times 10^4$ for R = Me and 8.5×10^4 for R = Et [19], and for $[\{FeH(dppe)_2\}_2(\mu\text{-NCCH=CHCN})]^{3+}$ with a bridging fumaronitrile: $K_C = 1.6 \times 10^3$ (ref.[20]). It is lower than that for $[\{FeCp(dppe)\}\{FeCp(L)\}(\mu\text{-NC})]$ ($K_C = 1.6 \times 10^{11}$ for L = dppe and 3.0×10^{10} for L = dppm; dppm = diphenylphosphinomethane)[21]. However, it is higher than those for several weakly coupled class II dipyridyl-bridged bis(pentaammineruthenium) dinuclear complexes (K_C ranging between 4 and 890)[22].
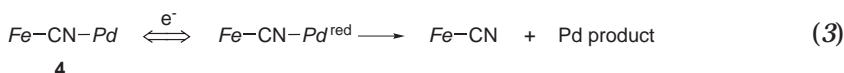
$$[Fe\text{--}CN\text{--}M\text{--}NC\text{--}Fe] \quad + \quad [Fe^{III}\text{--}CN\text{--}M\text{--}NC\text{--}Fe^{III}]^{2+} \; \underset{}{\overset{K_C}{\rightleftharpoons}} \; 2[Fe^{III}\text{--}CN\text{--}M\text{--}NC\text{--}Fe]^+ \qquad (2)$$

6

$Fe = \{Fe(dppe)_2\}$

Complexes **7** and **8** with the trinuclear Fe–CN–Pt–NC–Fe and Fe–CN–W–NC–Fe moieties, respectively, are highly unstable in the electrolyte solution, even at –40 °C. However, in the initial anodic scan of **7**, a reduction oxidation wave is observed at $E_{1/2}^{ox} = 0.31$ V, ascribed to the *trans*-$[FeH(CN)(dppe)_2]^{0/+}$ redox process, indicating dissociation of the adduct. An irreversible anodic process is detected at a higher potential ($E_p^{ox} = 0.70$ V) which, upon scan reversal, forms a reduction wave at $E_p^{red} = 0.65$ V. The second oxidation wave, which gradually fades in the course of the CV experiments with a concomitant increase of the former (due to the liberated cyano complex) is tentatively assigned to the iron(II) oxidation of a dinuclear Fe(CN)Pt complex. The Pt centre is expected to be oxidised at a much higher potential, since the parent complex $[PtCl(Ph)(PPh_3)_2]$ shows its oxidation at $E_{p/2}^{ox} = 1.51$ V (Table I).

For complex **8**, the two consecutive reversible oxidation waves at $E_{1/2}^{ox} \approx$ 0.50 and 0.66 V, which were detected only during the initial anodic scan, are tentatively attributed to the two sequential $Fe^{II} \Rightarrow Fe^{III}$ oxidations, indicating an iron–iron interaction through the cyanide bridges and the W atom. This interaction appears to be weaker than that observed for complex **6** (with Re in the bridge), where the separation of the two oxidation waves is more pronounced.

The heteronuclear complexes **4**–**6** also exhibit reduction processes (in the E_p^{red} range of –0.8 to –1.5 V) which are assumed to reside at the Lewis acid metal sites whose precursor complexes also undergo cathodic processes between –0.5 and –1.4 V (Table I). Interestingly, in the case of the Fe/Pd complex **4**, a cathodically induced dissociation occurs, as indicated by the liberation of the cyano complex *trans*-[FeH(CN)(dppe)$_2$]. The reversible oxidation wave of the latter complex is detected during the subsequent reverse anodic scan, together with another oxidation wave at $E_p = 0.0$ V, a value identical to that of the oxidation wave generated upon reduction of [PdCl$_2$(PPh$_3$)$_2$]. These observations indicate that the reduction of complex **4** is centred at the Pd^{II} site and leads to a decrease of its Lewis acidic character to such an extent that liberation of its {FeH(CN)(dppe)$_2$} ligand takes place (Eq. (*3*)).
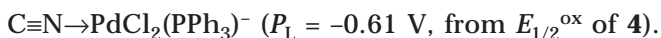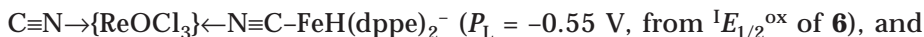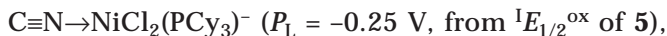
$$Fe\text{–}CN\text{–}Pd \quad \overset{e^-}{\Longleftrightarrow} \quad Fe\text{–}CN\text{–}Pd^{red} \longrightarrow \quad Fe\text{–}CN \quad + \quad Pd \text{ product} \qquad (3)$$

4

Electrochemical P_L and E_L Ligand Parameters

It is still noteworthy to mention that from the value of the Fe^{II}/Fe^{III} oxidation potential of the di- and trinuclear complexes, it is possible to estimate, for the first time, the P_L ligand parameter for the corresponding cyanide adducts as ligands. By applying Eq. (*4*)[15], the oxidation potential of members of a series of closed-shell octahedral-type complexes [M$_S$L] (with a variable L ligand) is related to the electron-richness (E_S) and polarisability (β) of the metal site {M$_S$}, and with the P_L ligand parameter (Table II).

$$E^{ox}[M_S L] = E_S + \beta P_L \qquad (4)$$

Using the known values[15] of E_S (1.04 V) and β (1.0) for the {FeH(dppe)$_2$}$^+$ site, the values of the P_L parameter (Table II) have thus been estimated for

the following ligated metallocyanide adducts, ordered according to their increasing net electron-donor character:

$C{\equiv}N{\rightarrow}NiCl_2(PCy_3)^-$ (P_L = –0.25 V, from $^1E_{1/2}{}^{ox}$ of **5**),

$C{\equiv}N{\rightarrow}\{ReOCl_3\}{\leftarrow}N{\equiv}C{-}FeH(dppe)_2{}^-$ (P_L = –0.55 V, from $^1E_{1/2}{}^{ox}$ of **6**), and

$C{\equiv}N{\rightarrow}PdCl_2(PPh_3)^-$ (P_L = –0.61 V, from $E_{1/2}{}^{ox}$ of **4**).

They are all better net electron donors than organoisocyanides $C{\equiv}NR$ (*e.g.*, CNMe, CNEt and CNCOPh display P_L values of –0.17, –0.14 and 0.20 V, respectively, estimated in the same way)[13], but weaker than cyanide itself (–0.74 V)[15]. Hence, the electron-donor ability of the cyano ligand decreases as a result of its *N*-ligation to a transition-metal Lewis acid, as expected, but not so much as upon its alkylation or aroylation. The effect of $\{NiCl_2(PCy_3)\}$ is similar to that of BF_3, as shown by the similarity of the P_L values for the $C{\equiv}NNiCl_2(PCy_3)^-$ (–0.25 V) and $C{\equiv}NBF_3{}^-$ (–0.24 V)[13] ligands. On the other hand, the effect of $\{ReOCl_3(NC)FeH(dppe)_2\}$ approaches that of BPh_3, since the P_L values for the corresponding cyanide adducts (see **6** above and $C{\equiv}NBPh_3{}^-$) are –0.55 V and –0.51 V (ref.[13]), respectively.

The electrochemical parameterisation approach developed by Lever[23] has also been applied (Table II). It is expressed by Eq. (5) in which the redox potential (*E*) of a metal complex (expressed in V *vs* NHE) is related to electrochemical parameters determined by ligand and metal centre properties (I_M

TABLE II
Estimated values of the ligand electrochemical P_L and E_L parameters for the cyano-derived ligands (L)

Complex	L	$P_L{}^a$	$E_L{}^b$
4	$(CN)PdCl_2(PPh_3)^-$	–0.61	–0.14
5	$(CN)NiCl_2(PCy_3)^-$	–0.25	0.19
6	$(CN)(ReOCl_3)(\mu\text{-}CN)FeH(dppe)_2{}^-$	–0.55	–0.09
Fe ^{c}	CN^- ^{d}	–0.74^e	–0.26
1	$CNCOC_6H_5{}^d$	0.20^f	0.60^f
2	$CNMe^d$	–0.17^f	0.26^f
3	$CNEt^d$	–0.14^f	0.29^f

^{a} In volt. ^{b} From Eq. (5), in V *vs* NHE. ^{c} *Fe* = *trans*-[FeH(CN)(dppe)$_2$]. ^{d} Included for comparative purposes. ^{e} From ref.[15]. ^{f} From ref.[13].

and S_M) and to the sum of the values of the electrochemical E_L parameter for all the ligands (ΣE_L).

$$E = I_M + S_M(\Sigma E_L) \tag{5}$$

From the redox potentials E (V *vs* NHE) of the complexes and the S_M and I_M values[23] for the low-spin Fe^{II} centre in this study (1.10 and –0.43 V, respectively), and taking into account the known[23] E_L values for the chelating dppe (0.36 V) and hydride (–0.30 V) ligands, it was possible to estimate the unknown E_L values for the metallocyanide ligands in this study. Ligand comparisons analogous to those mentioned above, but now based on E_L instead of P_L, can also be withdrawn from the estimated E_L values.

Alternatively, the E_L values could be calculated from the empirical linear expression (*6*) roughly relating the electrochemical ligand parameters E_L and P_L (ref.[23]). However, they would differ considerably from the E_L values estimated above on the basis of Eq. (*5*), thereby reflecting the limitations of Eq. (*6*).

$$P_L = 1.17E_L - 0.86 \tag{6}$$

Concluding Remarks

The presence of a redox-active Fe^{II}/Fe^{III} centre in the various cyano adducts of *trans*-[FeH(CN)(dppe)₂] studied in this work provides a convenient probe for the application of electrochemical methods as useful tools for the investigation (i) of the metal–metal interaction *via* a cyano or a cyano-containing bridge, namely in electrochemically generated mixed-valence complexes, and (ii) of the net electron-donor/acceptor properties of the novel metallo-cyano-derived ligands.

The latter goal, which involves the estimate of the ligand electrochemical parameters P_L and E_L, has been applied to metallo cyano ligands for the first time in this study and allows their comparison, *e.g.*, with organyl isocyanides, showing that the former behave as considerably stronger net electron donors. Such behaviour accounts for the observed reversibility of the iron(II) centred oxidation waves of the di- and trinuclear adducts with such ligating metallocyanides, in contrast with the known[14,24] anodically-induced Fe–H bond cleavage (H⁺ loss) in the organyl isocyanide complexes *trans*-[FeH(CNR)(dppe)₂], in which the acidity of the hydride ligand is pro-

moted by the π-electron-withdrawing character of CNR. However, such a reaction can also occur for the benzoyl isocyanide complex **1**, caused by the strong electron-acceptor ability of the CNCOPh ligand. In fact, the oxidation wave of **1** presents an irreversible character.

Hence, the extension of the redox potential parameterisation and quantification of ligand- and metal-centre effects, already established for octahedral mononuclear complexes, to di- and trinuclear adducts, can provide useful information for the understanding of their behaviour and deserves further investigation.

EXPERIMENTAL

Complexes **1**–**4** and **6** were synthesised according to a general procedure described previously[11]. Complex **5** was generated *in situ* by adding a stoichiometric amount of [NiCl$_2$-(PCy$_3$)$_2$] to the electrolyte solution of *trans*-[FeH(CN)(dppe)$_2$].

The electrochemical experiments were performed under a N$_2$ atmosphere, on an EG&G PAR 173 potentiostat and an EG&G PARC 175 universal programmer, or on an EG&G PARC 273 potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A). For the cyclic voltammetric (CV) studies, a two-compartment three-electrode cell was employed, equipped with a platinum-wire working electrode, probed by a Luggin capillary connected to a silver-wire pseudoreference electrode and a platinum auxiliary electrode. For the controlled potential electrolyses (CPE), a three-electrode H-type cell was used. The two compartments were separated by a glass frit and equipped with platinum gauze working and auxiliary electrodes. A Luggin capillary connected to a silver-wire pseudoreference electrode was used to control the working electrode potential. The CPE experiments were monitored regularly by CV, thus assuring that no significant potential drift occurred during the electrolyses. The potentials were measured by CV in CH$_2$Cl$_2$ (or THF) containing 2×10^{-1} M Bu$_4$NBF$_4$; the values are quoted relative to the saturated calomel electrode (SCE) by using the *trans*-[FeHCl(dppe)$_2$]$^{0/+}$ ($E° = -0.143$ and -0.110 V *vs* SCE in CH$_2$Cl$_2$ and THF, respectively) or [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ redox couples ($E_{1/2}^{ox} = 0.525$ and 0.545 V *vs* SCE in CH$_2$Cl$_2$ and THF, respectively) as the internal standards. Potential values measured relatively to the SCE were converted to the NHE scale by adding $+0.24$ V[25].

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