Scheme

For the scan rate of $0.2\ Vs^{-1}$, the simulated and experimental cyclic voltammograms are in good agreement (Fig 2., solid line and symbols, respectively). However, an acceptable fitting has not yet been achieved for the entire range of scan rates under study.

Preparative scale electrolysis has also been performed in the presence of a 4 molar excess of pyrogallol leading to the consumption of 5 Faradays/mol of the vanadium complex. Attempts to isolate the products from the electrolysed solution have not yet been successful.

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ESTIMATE of ELECTROCHEMICAL LIGAND PARAMETERS in IRON(II) ADDUCTS of [FeH(CN)(dppe)2]

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Abstract

The cyclic voltammetric study of the following isocyanide complexes derived from *trans*-[FeH(CN)(dppe)2] **1** (dppe = $Ph_2PCH_2CH_2PPh_2$) enabled the estimate of the values of the electrochemical Pickett P_L and Lever E_L ligand parameters for the corresponding cyano-derived ligands: *trans*-[FeH(CNR)(dppe)2]A **2** [R = H (**2a**) or Et (**2c**), $A^- = BF_4^-$; R = Me (**2b**), $A^- = I^-$; R = C(O)Ph (**2d**), $A^- = Cl^-$] or *trans*[FeH(CN$\rightarrow$X)(dppe)2] **3** [X = BPh_3 (**3a**), $VCl_3(thf)_2$ (**3b**) or BF_3 (**3c**)].

Keywords: Iron complexes; Cyclic voltammetry; Cyano-derived ligands; Isocyanides; Ligand parameters.

Results and discussion

All the cyano-derived iron complexes exhibit, at 200 mV s^{-1} (Table), a reversible (or irreversible, compounds **2a** and **2d**) anodic wave at $E_{1/2}^{ox}$ (or $E_{p/2}^{ox}$) in the 0.30 – 1.24 V *vs.* SCE range. As expected, the oxidation wave of the neutral complexes **1** and **3** are shown at lower potentials, in the 0.30 – 0.80 V *vs.* SCE range, in comparison with those of the cationic complexes **2**.

Within the neutral complexes, the iron compound **2a**, derived from protonation of the parent complex **1**, presents an anomalously low oxidation potential suggesting that CNH is involved in hydrogen bonding with the BF_4^- counter-ion, *i.e.*

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$Fe-CN-H\cdots FBF_3^-$ [with Fe representing the metal centre under study $\{FeH(dppe)_2\}^+$]. The relative tendency of the cyanide ligand to undergo protonation *versus* formation of a hydrogen bond has already been observed and discussed for some rhenium centres [1]. Lowering the π-electron releasing ability of the binding metal site would be expected to decrease the basic character of the cyanide ligand and thus to enhance its tendency for hydrogen bond formation rather than formation of a covalent CN–H bond in a stable Fe-CNH compound, with a resulting cathodic shift of the oxidation potential relatively to that expected for the corresponding genuine CNH complex [1].

The oxidation potential of the complexes reflects the relative electron donor/acceptor abilities of the ligands as measured by the electrochemical P_L ligand parameter proposed by Pickett [2] who, based on experimentally observed oxidation potentials of the members of a series of closed-shell octahedral-type complexes [M_SL] (with a variable L ligand binding the 16-electron M_S metal site) and those of the homologous [$Cr(CO)_5L$] complexes, proposed the expressions (1) and (2).

$$E^{ox}[M_SL] = E_S\{M_S\} + \beta\{M_S\}.P_L \qquad (1)$$

$$E_S = E^{ox}[M_S(CO)] \qquad (2)$$

The parameters E_S and β are associated to the binding metal centre M_S, and the former measures its electron-richness and is given (eq. 2) by the oxidation potential of its carbonyl complex [$M_S(CO)$] (the higher E_S the lower the electron-richness), whereas β is a measure of the polarisability of the metal site [2]. P_L is defined as the difference $E^{ox}[Cr(CO)_5L] - E^{ox}[Cr(CO)_6]$ and considered as a measure of the net electron σ-donor minus π-acceptor ability of the ligand L (the lower this character the higher P_L).

By applying the previously reported [2] E_S and β parameters for the iron site of this study $\{FeH(dppe)_2\}^+$ ($E_S = 1.04$, $\beta = 1.0$), it was possible to estimate the P_L parameter for CN⁻ as well as for the cyano-derived ligands (Table), ordered as follows according to their increasing net electron-donor character: CNC(O)Ph ($P_L = 0.20$ V), CNEt ($P_L = -0.14$ V), CNMe ($P_L = -0.17$ V), $CNBF_3^-$ ($P_L = -0.24$ V), $CNVCl_3(thf)_2^-$ ($P_L = -0.42$ V), CNH···FBF_3 ($P_L = -0.45$ V), $CNBPh_3^-$ ($P_L = -0.51$ V), CN⁻ ($P_L = -0.74$ V).

Table: Cyclic voltammetric data for the iron complexes **1**, **2** and **3** and values of the ligand electrochemical Pickett P_L and Lever E_L parameters for the cyano-derived ligands (L).

Compound	L	$E_{1/2}^{ox}(E_{p/2}^{ox})$ [a]	P_L (V)	E_L [b]	E_L [c]
1	CN⁻	0.30	-0.74	-0.26	0.10
2a	CNH···FBF_3	(0.59)	-0.45	0.01	0.35
2b	CNMe	0.87	-0.17	0.26	0.60
2c	CNEt	0.90	-0.14	0.29	0.62
2d	CNC(O)Ph	(1.24)	0.20	0.60	0.91
3a	$CNBPh_3^{\cdot-}$	0.53	-0.51	-0.05	0.30
3b	$CNVCl_3(thf)_2^-$	0.62	-0.42	0.03	0.38
3c	$CNBF_3^-$	0.80	-0.24	0.20	0.53

[a] In Volts *vs.* SCE. [b] From eq. 3, in Volts *vs.* NHE. [c] From eq. 4, in Volts *vs.* NHE.

The acylisocyanide CNC(O)Ph is the strongest net electron acceptor of this series, with a P_L value similar to that of η^2-vinyl (0.20 V) [3], being even higher than that of carbonyl (0 V) [2], while the P_L parameters for CNMe and CNEt are similar to those previously reported [3] for coordinated isocyanides presenting a bent geometry. The novel metallaisocyanide $CNVCl_3(thf)_2^-$, as well as CNH···FBF_3 and $CNBPh_3^-$, have P_L parameters in the range usually observed for linearly coordinated isocyanides, being stronger net electron donors than the organoisocyanides.

The P_L parameter for cyanide is considerably higher than that previously reported (-1.00 V [2]), a fact that may be indicative of the dependence of the net electron donor/acceptor ability of this ligand on the electronic properties of the binding metal site. In fact, the P_L parameter for this ligand has previously been estimated [2] at the metal centers $\{MoY(dppe)_2\}$ with a strong π-electron acceptor ligand (Y = CO or N_2) which would raise the electron donor ability of cyanide thus leading to a lower P_L value. Although in the case under study the iron centre has a lower electron-richness than those of the Mo sites, the hydride ligand in *trans* position to cyanide is a strong electron donor and therefore opposes the electron release from the latter ligand with a

resulting increase of its P_L value. A related behaviour was previously recognized for organoisocyanides [3] whose net electron donor/acceptor ability depends on the electron-richness of the binding metal site that even influences their coordination mode. Indeed, at electron-rich metal centers, e.g. {ReCl(dppe)$_2$} with $E_S = 0.68$ V, isocyanides behaved as strong net-electron acceptors generally presenting a bent geometry and P_L values ranging from -0.07 to -0.18 V. At much less electron-rich metal centers, e.g. {Cr(CO)$_5$} with $E_S = 1.5$ V, they coordinate linearly and the estimated P_L parameters were considerably lower, ranging from -0.33 to -0.44 V.

Another electrochemical parametrization approach was developed by Lever [4,5] who proposed a general redox potential-structure relationship expressed by eq. (3) in which the redox potential of a complex (expressed in volts vs. NHE) is related with electrochemical parameters determined by ligand and metal centre properties. Hence, ΣE_L is the sum of the values of the electrochemical E_L ligand parameter for all the ligands (additive effects), whereas S_M and I_M depend upon the metal and redox couple, the spin state and stereochemistry.

$$E = I_M + S_M \cdot (\Sigma E_L) \qquad \text{(V vs. NHE)} \qquad (3)$$

From the known S_M and I_M values [4] for the low-spin iron complexes under study (1.10 and –0.43, respectively), and taking into account the already known [4] E_L values for the chelating dppe (0.36 V) and for hydride (-0.30 V), it was possible to estimate the previously unknown E_L values for the isocyanides of this study (Table), ordered according to their net electron donor ability (similarly as above for the P_L values): CNC(O)Ph ($E_L = 0.60$ V) < CNEt ($E_L = 0.29$ V) < CNMe ($E_L = 0.26$ V) < CNBF$_3^-$ ($E_L = 0.20$ V) < CNVCl$_3$(thf)$_2^-$ ($E_L = 0.03$ V) < CNH···FBF$_3$ ($E_L = 0.01$ V) < CNBPh$_3^-$ ($E_L = -0.05$ V) < CN$^-$ ($E_L = -0.26$ V).

Alternatively, from the above P_L values of the isocyanide ligands, one could also try to estimate the Lever E_L values by taking into account the observed [4] overall linear relationship (except for carbon monoxide [4] and other strong π-electron acceptors such as carbynes [6]) between the two parameters [eq. (4), in which P_L is in V and E_L in V vs. NHE].

$$P_L = 1.17 \times E_L - 0.86 \qquad (4)$$

However, the thus obtained values (Table, last column) differ considerably (by ca. 0.3 V) from those estimated above by using eq. (3) applied to the iron centre, suggesting that equation (4) is also not valid for isocyanides which, as CO and carbynes, can also behave as effective π-electron acceptors. The failure of eq. (4) to be applied to isocyanides conceivably also accounts for the higher E_L value previously reported [4] for CNMe (0.37 V), relatively to our estimated value (0.26 V), since the former was then obtained by using that expression.

Experimental

The electrochemical experiments were performed on an EG & G PAR 273 potentiostat / galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A) or on an EG & G PAR 173 potentiostat / galvanostat and an EG & G PARC 175 Universal programmer. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell, at a platinum-disc working electrode (d = 0.5 mm), probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum auxiliary electrode was employed. Controlled potential electrolysis was carried out in a two-compartment three-electrode 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 experiments were performed in an inert atmosphere (N$_2$) at room temperature, the potentials were measured in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$ (or thf) in the presence of ferrocene as the internal standard, and the redox potential values are quoted relative to the saturated calomel electrode (SCE) by using the [Fe(η^5-C$_5$H$_5$)$_2$]$^{0/+}$ couple [$E_{1/2}^{ox} = 0.53$ or 0.55 V vs. SCE, in 0.2 mol dm^{-3} [NBu$_4$][BF$_4$] / CH$_2$Cl$_2$ or thf, respectively]. Potential values measured relatively to the SCE were converted to the normal hydrogen electrode (NHE) by adding +0.24 V [7].

The complexes **1**, **2** and **3** were synthesized by following a general procedure described previously [8].

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ELECTROCHEMICAL BEHAVIOUR OF BENZALDEHYDE AT PLATINUM

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Abstract

The reactions of 5 mM benzaldehyde at platinum in 0.1 M $HClO_4$ were studied by means of differential electrochemical mass spectrometry (DEMS) combined with cyclic voltammetry. It was observed that this compound oxidises completely to CO_2 at $E > 0.60$ V vs. RHE (reference hydrogen electrode), but also produces toluene, benzene and cyclohexane in the potential region for hydrogen adsorption and H_2 evolution. No partial or total hydrogenation of toluene was observed. These results are compared and discussed with those previously obtained for benzyl alcohol and benzoic acid.

Keywords: Benzaldehyde; Benzyl alcohol; Benzoic acid; Platinum; Electrochemical mass spectrometry (DEMS)

Introduction

The electrochemical behaviour of benzyl alcohol [1-3] and benzoic acid [4] has been previously studied at platinum electrodes in acid media. The aim of this research was to establish the influence of the substituent in the aromatic ring on the reactivity of the aromatic compound. Both these molecules adsorb irreversibly at the platinum surface and oxidise to carbon dioxide. Applying the method of displacement with CO [1,2], it was established that benzyl alcohol adsorbs dissociatively producing benzene, but also suffers hydrogenolysis when the adsorption takes place in the hydrogen adsorption/desorption region of platinum, forming adsorbed toluene. The dissociation reaction produces adsorbed CO from the alcoholic group in addition to benzene from the aromatic ring. Partial and total hydrogenation compounds from benzene and toluene were detected simultaneously with the production of molecular hydrogen [2,3].

On the other hand, CO cannot displace benzoic acid and no hydrocarbons were detected from its reduction [4]. However, partial desorption of the adlayer was observed during the cathodic

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