

organocyanamide ligands, and the occurrence of the cathodic process in complexes with organocyanamide ligands which, when uncoordinated, do not display any cathodic wave) suggest that the cathodic process involves the metal reduction. In agreement, complexes (1) display E_{p}^{red} at values (- 1.8 to - 2.0 V) which are very similar to that observed (- 1.97 V) [3] for the reduction of the related *trans*-[PtCl₂(PPh₃)₂] complex which is believed to be centred at the metal [Pt(II) → Pt(0)].

The non detection of any cathodic wave in complexes (3), whereas it is observed in (2), suggests that, in these cationic species, the chloride ligand presents, relative to CF₃, a destabilizing effect on the LUMO.

References

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STRUCTURE-POTENTIAL RELATIONSHIPS FOR THE NITRILE COMPLEXES *trans*-[FeBr(NCR)(Et₂PCH₂CH₂PEt₂)₂][BF₄]

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SUMMARY

The electrochemical behaviour, in aprotic medium, of the 18-electron octahedral-type nitrile complexes *trans*-[FeBr(NCR)(depe)₂][BF₄] (R = alkyl or aryl, depe = Et₂PCH₂CH₂PEt₂) was studied by cyclic voltammetry and controlled potential electrolysis. They undergo two successive single-electron reversible oxidations and electrochemical ligand and metal site parameters [which measure the electronic properties of the nitrile ligands and their binding iron(II) or iron(III) centre] were estimated from the measured half-wave oxidation potential values.

RESULTS AND DISCUSSION

The electrochemical behaviour of the complexes *trans*-[FeBr(NCR)(depe)₂][BF₄] (R = alkyl or aryl, depe = Et₂PCH₂CH₂PEt₂) was studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), in 0.2 M [NBu₄][BF₄]/CH₂Cl₂, at a Pt-wire or -gauze electrode, respectively, at low temperature (-10 to -65 °C) in view of their rapid decomposition in solution at higher temperatures.

These complexes exhibit, by CV, two successive single-electron reversible oxidations at $E_{1/2}^{ox}$ ca. 0.63 to 0.91 V and $E_{1/2}^{ox}$ ca. 1.35 V vs. S.C.E., respectively (Fig. 1). The first anodic wave is assigned to the Fe(II) to Fe(III) oxidation and the second one to the Fe(III/IV) redox couple. A single-electron irreversible cathodic wave

is also observed at E_p^{red} in the range -1.30 to -1.91 V vs. S.C.E. (wave III). The species generated at this wave undergoes a reversible oxidation (wave IV), but this process has not yet been investigated in detail.

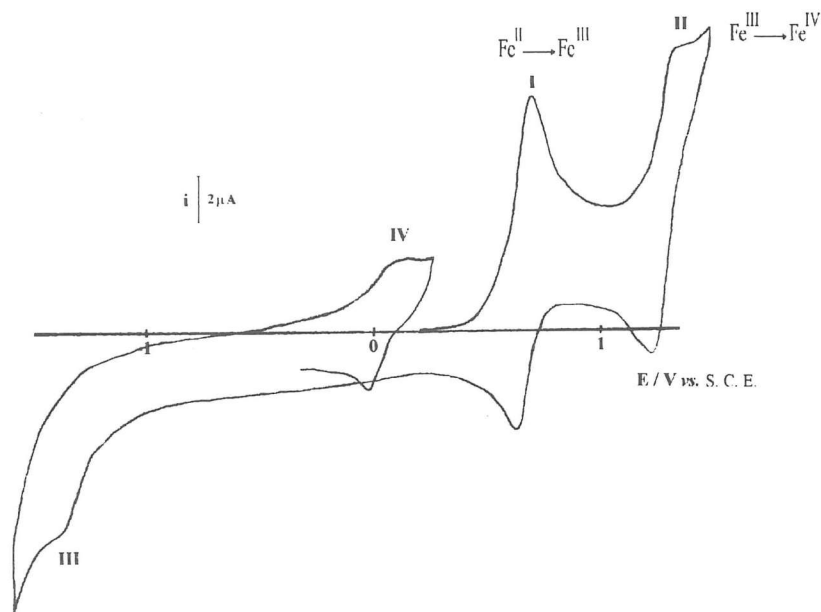


Fig. 1 - Cyclic voltammogram of $trans\text{-}[\text{FeBr}(\text{NCCH}_2\text{C}_6\text{H}_4\text{OMe-4})(\text{depe})_2][\text{BF}_4]$ at -10°C in $0.2\text{ M } [\text{NBu}_4][\text{BF}_4]/\text{CH}_2\text{Cl}_2$, at a Pt disc electrode (scan rate = 100 mV s^{-1}). Potential in Volt vs. S.C.E..

The plot of $E_{1/2}^{ox}$ for the complexes $trans\text{-}[\text{FeBr}(\text{L})(\text{depe})_2]^+$ ($\text{L} = \text{CO}, \text{NPh}, \text{NCMe}$ or Br^-) versus the P_L ligand parameter [1] (for ligand L) was shown to be linear and expressed by the following relationship:

$$E_{1/2}^{ox} [\text{FeBr}(\text{L})(\text{depe})_2]^+ = (1.26 \pm 0.07) + (1.1 \pm 0.1) P_L(\text{L}) \quad (1)$$

which allowed to estimate the values of the E_s (electron-richness) and β (polarisability) parameters for the $trans\text{-}\{\text{FeBr}(\text{depe})_2\}^+$ metal centre: $E_s = 1.26\text{ V}$, $\beta = 1.1$. The polarisability is comparable with that known [1] for the related $trans\text{-}\{\text{FeH}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\}^+$ site ($\beta = 1.0$), but the former centre presents a somewhat lower electron-richness ($E_s = 1.26\text{ V}$) than the later one (with a lower E_s value, 1.04 V [1]), indicating, a weaker net electron donor ability of the bromide compared with the hydride ligand.

From the above expression, it was also possible to estimate the P_L values of the other nitrile ligands of this study (Table 1). Cyanamides appear as the strongest net electron donors (with the lowest P_L values) whereas the aromatic organonitriles with electron accepting substituents behave as the weakest ones.

Table 1 - P_L values for nitrile ligands.

L	$P_L(\text{L}) / \text{V}$
$\text{NCN}(\text{CH}_3)_2$	-0.60
$\text{NCN}(\text{C}_2\text{H}_5)_2$	-0.59
NCNH_2	-0.57
NCCH_3	-0.55
NCCH_2CH_3	-0.55
$\text{NCCH}_2\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$	-0.55
$\text{NCC}_6\text{H}_4\text{OCH}_3\text{-4}$	-0.54
$\text{NCC}_6\text{H}_4\text{CH}_3\text{-4}$	-0.52
NCC_6H_5	-0.50
$\text{NCC}_6\text{H}_4\text{F-4}$	-0.46
$\text{NCC}_6\text{H}_4\text{NO}_2\text{-4}$	-0.44

In addition, the corresponding values for the Lever E_L ligand parameter [2] were estimated (Table 2) from the following known empirical correlation between E_L and P_L : $P_L = 1.17 E_L - 0.86$ (in which E_L is expressed in V vs. N.H.E.).

Table 2 - E_L values for nitrile ligands.

L	E_L (L) / V vs. N. H. E.	
	$trans\text{-}\{\text{FeBr}(\text{depe})_2\}^+$ ^a	Lever ^b
NCN(CH ₃) ₂	0.22	—
NCN(C ₂ H ₅) ₂	0.23	—
NCNH ₂	0.25	—
NCCH ₃	0.26	0.34
NCCH ₂ CH ₃	0.26	0.33
NCCH ₂ C ₆ H ₄ OCH ₃ -4	0.26	—
NCC ₆ H ₄ OCH ₃ -4	0.27	0.38
NCC ₆ H ₄ CH ₃ -4	0.29	0.37
NCC ₆ H ₅	0.31	0.37
NCC ₆ H ₄ F-4	0.34	—
NCC ₆ H ₄ NO ₂ -4	0.36	—

^a Obtained in this work for this metal centre. ^b Quoted by A. B. P. Lever [2].

Linear relationships were also observed between $E_{1/2}^{\text{ox}}$ [for the Fe(II/III) and Fe(III/IV) redox couples] and ΣE_L (for all the ligands of the complexes), being expressed by eqs. 2 and 3, respectively (in which $E_{1/2}^{\text{ox}}$ is in V vs. N.H.E.).

$$E_{1/2}^{\text{ox}} = (1.39 \pm 0.02) \Sigma E_L(L) - (0.66 \pm 0.02) \quad (2)$$

$$E_{1/2}^{\text{ox}} = (1.8 \pm 0.3) \Sigma E_L(L) - (0.7 \pm 0.4) \quad (3)$$

These expressions were analysed in terms of a general relationship proposed by Lever [2], $E_{1/2}^{\text{ox}} = S_M(\Sigma E_L) + I_M$, allowing to estimate the S_M and I_M parameters for these redox couples [Fe(II/III): $S_M = 1.39$, $I_M = 0.66$ V vs. N.H.E.; Fe(III/IV): $S_M = 1.8$, $I_M = 0.7$ V vs. N.H.E.]. The S_M and I_M values for the Fe(II/III) redox couple are somewhat different from those previously proposed by Lever [2] ($S_M = 1.10$, $I_M = 0.43$ V vs. N.H.E) by taking into consideration a variety of iron(III/II) centres.

However, our values characterize more accurately the particular metal centre of this study which also provides, for the first time, the S_M and I_M values for an Fe(III/IV) system.

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