

The cleavage of a N—H bond of the cyanamide ligand at our Mo complex, by base attack, is also corroborated by IR and NMR spectroscopies and therefore the above product from the cathodic reduction of our complex is tentatively formulated as *trans*-[MoH₂(NCNH)(NCNH₂)(dppe)₂][BF₄].

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REDOX BEHAVIOUR OF ALKYNOL-DERIVED ALLENYLIDENE COMPLEXES OF IRON(II)

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Abstract

The cyclic voltammetric behaviour of the allenylidene complexes *trans*-[FeBr(L)(depe)₂][BF₄] (L = CCC(Me)Ph **1a**, CCCPh₂ **1b**, CCCEt₂ **1c**) is reported and the electrochemical *P_L* and *E_L* ligand parameters for the allenylidene ligands are estimated showing that they behave as slightly weaker *net* electron-donors than organonitriles.

Key Words: Allenylidene, redox properties, iron complexes, electrochemical ligand parameters.

Introduction

Correlating the redox-potential with molecular properties of coordination compounds has been a matter of interest since long and in particular the investigation of its dependence on the electronic properties of the ligands and the metal centres has been the object of growing attention [1]. The latter aspect suggests that it should be possible to define electrochemical parameters, as determined by the oxidation potential, that could constitute a measure of such properties.

An approach was presented by C. J. Pickett *et al.* [2] who proposed a scale of ligand constants, *P_L*, which is defined according to equation (1) and is a measure of the *net* electron π -electron acceptor minus σ -donor ability of the ligand:

$$P_L = E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_5\text{L}] - E_{1/2}^{\text{ox}}[\text{Cr}(\text{CO})_6] \quad (1)$$

This scale is used to analyse the *E_{1/2}^{ox}* of various closed-shell octahedral complexes [M_sL], in terms of the linear approximation given by equation (2) in which *E_s* and β are the electron-richness and polarisability, respectively, of the metal site {M_s}.

$$E_{1/2}^{ox} [M_6L] = E_0 + \beta \cdot P_L \quad (2)$$

Another parameterisation approach for octahedral complexes was developed by Lever [3] who proposed a general redox-potential structure relationship expressed by equation (3) in which the redox potential (in volts vs. NHE) of a complex is related with electrochemical parameters determined by ligand and metal centre properties.

$$E_{1/2}^{ox} = I_M + S_M \cdot (\Sigma E_L) \quad (3)$$

In this expression, ΣE_L is the sum of the E_L values for all the ligands (additive effects), S_M and I_M are the slope and intercept (dependent upon the metal, redox couple, spin state and stereochemistry).

Lever also suggests an empirical equation (eq. 4) that correlates the P_L parameter previously introduced by Pickett and the E_L parameter.

$$P_L (V) = 1.17 \cdot E_L - 0.86 \quad (4)$$

In this work it is illustrated the cyclic voltammetry study of the phosphinic iron(II) complexes *trans*-[FeBr(L)(depe)₂][BF₄] (L = CCC(Me)Ph, CCCPh₂, CCCEt₂) with small unsaturated carbon (allenylidene) ligands.

Results and discussion

The electrochemical behaviour of the allenylidene complexes *trans*-[FeBr(L)(depe)₂][BF₄] **1** (L = CCC(Me)Ph **1a**, CCCPh₂ **1b**, CCCEt₂ **1c**), derived from the reaction of the appropriate alkynol with a parent iron complex, has been investigated by cyclic voltammetry (CV), in 0.2M [NBu₄][BF₄]/CH₂Cl₂, at a Pt-wire, using an EG&G Model 273A potentiostat.

The cyclic voltammograms exhibit two oxidation waves at ca. 0.90-1.20 V vs. S.C.E. and at ca. 1.70 V vs. S.C.E.. They are assigned to the Fe(II) → Fe(III) and Fe(III) → Fe(IV) oxidations (Figure 1, Table 1).

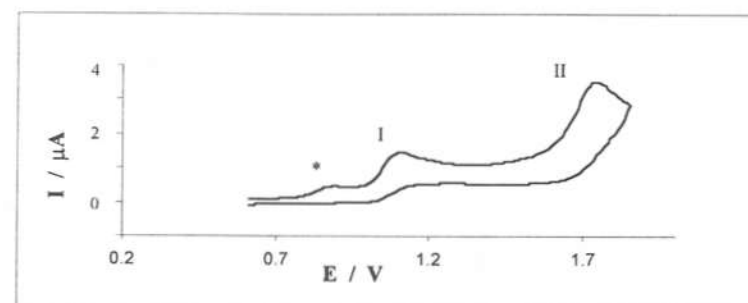


Fig. 1 - Cyclic voltammogram, at 0.2 V.s⁻¹, for *trans*-[FeBr(CCCPh₂)(depe)₂][BF₄] **1b** in 0.2 M [Bu₄N][BF₄]/CH₂Cl₂ solution, at a Pt disc working electrode.* Impurity (Br⁻).

Table 1 - Anodic cyclic voltammetric data for the allenylidene complexes *trans*-[FeBr(L)(depe)₂][BF₄] **1**.^a

L	^I E _p ^{ox} (^I E _{1/2} ^{ox})	^{II} E _p ^{ox}
C=C=C(Me)Ph 1a	(0.93)	1.69
C=C=CPh ₂ 1b	(0.97)	1.71
C=C=CEt ₂ 1c	0.99	1.71

^a Potential values in Volt vs. S.C.E. (scan rate = 0.2 V.s⁻¹). The internal standard used was the couple [Fe(η⁵-C₆H₅)₂]^{0/+} (E_{1/2}^{ox} = 0.525 V vs. S.C.E.).

From the values of the first oxidation potential measured for these complexes and the knowledge of the electron-richness (E_s) and polarizability (β) [4] for the *trans*-{FeBr(dppe)₂}⁺ metal centre ($E_s = 1.32$ V vs. S.C.E. and $\beta = 1.10$), and by using equation (2), it was estimated for the first time the P_L parameter for the allenylidene ligands.

Table 2 - Estimated P_L and E_L parameters for the allenylidene ligands.

Ligand	P_L / V	E_L / V vs. NHE
C=C=C(Me)Ph	-0.35	0.43
C=C=CPh ₂	-0.32	0.46
C=C=CEt ₂	-0.38	0.41

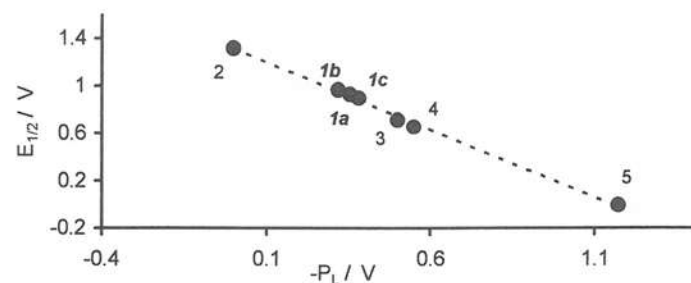
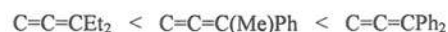


Fig. 2 - Plot of $E_{1/2}^{ox}$ for complexes $trans$ -[FeBr(L)(depe)₂][BF₄] (L = CCC(Me)Ph (1a), CCCPh₂ (1b), CCCEt₂ (1c), CO (2), NCPH (3), NCMe (4) and $trans$ -[FeBr₂(depe)₂] 5, versus the P_L ligand constant.

The $E_{1/2}^{ox}$ values for the complexes $trans$ -[FeBr(L)(depe)₂][BF₄] (L = CCC(Me)Ph, CCCPh₂, CCCEt₂) versus the P_L values for the allenylidene ligands follow the same linear plot as that observed for the related compounds, $trans$ -[FeBr(L)(depe)₂][BF₄] (L = CO 2, NCPH 3, NCMe 4) and $trans$ -[FeBr₂(depe)₂] 5 [4] (Fig. 2). Moreover the estimated values are in agreement with the expected increasing order of the *net* π -electron acceptor minus σ -donor ability of the ligands, as follows:



In addition, such estimated P_L values are slightly higher than those of organonitriles at the same metal centre (-0.44 to -0.55 V [4]), suggesting that the allenylidenes behave as weaker *net* electron donor ligands than the latter.

Furthermore, the corresponding values for the Lever E_L ligand parameter were estimated from the observed relationship that correlates $E_{1/2}^{ox}$ and ΣE_L (for the ligands of the complexes) (eq. 3) (Table 2). Identical values (within ± 0.01 V) were obtained from the known empirical correlation between E_L and P_L (eq. 4). As observed for the P_L parameter, the E_L values are higher than those of the organonitriles (0.26 – 0.36 V vs. NHE) [4] at the same metal site, corroborating the above conclusion on their relative *net* electron donor characters.

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