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Electrochemical Study of Alkynyl Fe(II) Complexes

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Abstract

The behaviour of the neutral alkynyl complexes *trans*-$[FeBr(L)(depe)_2]$ (L = –C≡C–C(=CH_2)Ph **1*a***, –C≡C–CPh_2(H) **1*b***; depe = $Et_2PCH_2CH_2PEt_2$) is studied by cyclic voltammetry and the electrochemical P_L and E_L ligand parameters for the alkynyl ligands are estimated showing that they behave as very strong *net* electron-donors.

***Keywords**:* alkynyl, anodic behaviour, electrochemical ligand parameters, cyclic voltammetry.

Introduction

The tertiary propargylic alcohols, HC≡CC(OH)R_1R_2 (R_1, R_2 = alkyl or aryl), are very versatile species and by reaction with a metallic fragment they can be converted into vinylidene, allenylidene and alkynyl ligands. In particular the allenylidene complexes (*M*=C=C=C) present an extended unsaturated carbon chain and are expected to be highly reactive species (chemically [1-3] and

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electrochemically [4]) due to such a polyunsaturated system, and can lead to other unsaturated products, for example, alkynyl derivatives (*M*–C≡C–C). The synthesis and characterization of the latter species are being reasonably explored, but their electrochemical behaviour has been investigated only very scarcely.

This work concerns the cyclic voltammetric study of alkynyl complexes obtained from cationic allenylidene species of Fe(II), *i.e.*, the neutral alkynyl derivatives *trans*-[FeBr{–C≡C–C(=CH_2)Ph}$(depe)_2$] **1*a*** (depe = $Et_2PCH_2CH_2PEt_2$) and *trans*-[FeBr{–C≡C–CPh_2(H)}$(depe)_2$] **1*b***.

These compounds were obtained from the reaction of *trans*-[FeBr(=C=C=CR_1R_2)$(depe)_2$][BPh_4] (R_1 = Me, R_2 = Ph; R_1 = R_2 = Ph) [5] with an appropriate base or nucleophile [6]. The ligand parameters, P_L and E_L, of the alkynyl ligands are also estimated, allowing to identify the donor/acceptor electronic properties of such ligands, which are compared with those of the parent allenylidenes in their precursor complexes [7].

Results and discussion

The electrochemical behaviour of the neutral alkynyl complexes *trans*-[FeBr(L)$(depe)_2$] (L = –C≡C–C(=CH_2)Ph **1*a***, –C≡C–CPh_2(H) **1*b***) has been investigated by cyclic voltammetry (CV), in a 0.2M [NBu_4][BF_4]/CH_2Cl_2 solution, using a platinum-disc working electrode and an EG&G Model 273A potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A).

These complexes exhibit one reversible anodic wave (Table 1) at $E_{1/2}^{ox}$ = –0.06 V (**1*a***) and –0.13 V (**1*b***) *vs.* S.C.E., assigned to the metal oxidation (Fe(II)→Fe(III)), which is followed by a second one, at a more anodic potential (1.14 V – 1.19 V) (Fig. 1).

Attempts to study these complexes by controlled potential electrolysis were unsuccessful due to the poisoning of the electrode surface by species formed in the anodic processes.

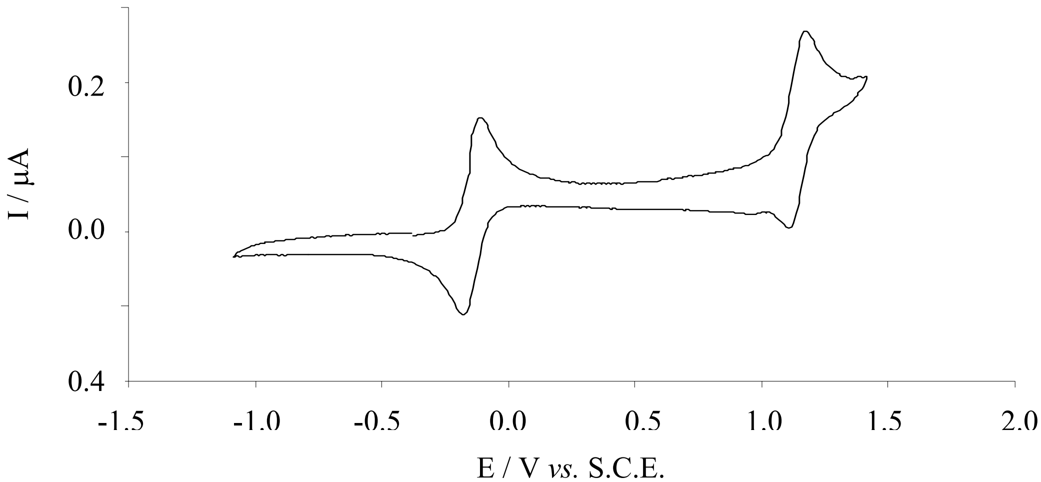

Figure 1. Anodic cyclic voltammogram, at 0.2 $V.s^{-1}$, for *trans*-[FeBr{−C≡C−$CPh_2(H)$}$(depe)_2$] **1*b*** in a 0.2 M $[Bu_4N][BF_4]/CH_2Cl_2$ solution, at a Pt disc working electrode.

Table 1. Anodic cyclic voltammetric data (first anodic wave) for the neutral alkynyl complexes *trans*-$[FeBr(L)(depe)_2]$.[a]

L	$E_{½}^{ox}$
−C≡C−C(=CH_2)Ph **1*a***	-0.06
−C≡C−CPh_2(H) **1*b***	-0.13

[a] Potential values in Volt ± 0.02 *vs.* S.C.E. (scan rate = 0.2 $V.s^{-1}$). The internal standard used was the redox couple $[Fe(\eta^5\text{-}C_6H_5)_2]^{0/+}$ ($E_{½}^{ox}$ = 0.525 V *vs.* S.C.E.).

Estimate of the ligand electrochemical parameters, P_L and E_L

The measured first oxidation potentials ($E_{½}^{ox}$) of the alkynyl complexes, viewed as closed shell octahedral-type complexes $[M_SL]$, with the alkynyl ligand (L) ligating the 16-electron $\{M_S\}$ = *trans*-$\{FeBr(depe)_2\}^+$ site, allow one to estimate (Table 2) the electrochemical P_L ligand parameter (a measure of the net electron π-acceptor minus σ-donor character of a ligand), by applying to these complexes the linear expression (1) proposed by Pickett *et al.* [8] and considering the known [9] values of E_S = 1.32 V and β = 1.10 for that iron(II) binding site.

$$E_{½}^{ox} [M_sL] = E_s + \beta \cdot P_L \quad (1)$$

where E_s is the electron-richness of the metal site $\{M_s\}$ and β is the polarisability of the metal site $\{M_s\}$.

Another redox potential parameterization approach for octahedral complexes was developed by Lever [10], who proposed an empirical relationship expressed by eq. (2) in which the redox potential (in volts *vs.* NHE) of a complex is related to electrochemical parameters determined by the ligands and the metal centre.

$$E_{½}^{ox} = I_M + S_M \cdot (\Sigma E_L) \quad (2)$$

where: ΣE_L - sum of the values of the ligand E_L parameter for all the ligands (additive effects); S_M and I_M - slope and intercept (dependent upon the metal, redox couple, spin state and stereochemistry).

The P_L and E_L ligand parameters are related by the empirical eq. (3), also proposed by Lever [10].

$$P_L\ (V) = 1.17 \cdot E_L - 0.86 \quad (3)$$

The values for the Lever E_L ligand parameter (Table 2) were estimated from eq. (2), the known [10] values of E_L for the other ligands, and I_M and S_M for the iron(II) centre. Identical values were obtained from eq. (3).

Table 2. Estimated P_L and E_L parameters for the alkynyl ligands.

Ligand	P_L / V	E_L / V *vs.* NHE
$-C{\equiv}C{-}C(=CH_2)Ph$ **1*a***	-1.25	-0.33
$-C{\equiv}C{-}CPh_2(H)$ **1*b***	-1.31	-0.38

The values of Table 2 indicate that $-C{\equiv}C{-}C(=CH_2)Ph$ behaves as a stronger *net* π-electron acceptor minus σ-donor ligand than $-C{\equiv}C{-}CPh_2(H)$.

In addition, the estimated P_L values are much lower than those of allenylidenes at the same metal centre (–0.32 to –0.38 V [7]), showing that the alkynyls behave as much stronger *net* electron donor ligands than the latter.

Final comments

These results show that the alkynyl ligands present E_L and P_L values much lower than those of the corresponding allenylidenes, indicating that the former ligands are much better net electron donors than the latter. They are even slightly better donors than the aromatic alkynyl ligand −C≡C−Ph (P_L = −1.22 V) [11].

In contrast, carbyne ligands are very effective π-electron acceptors [11, 12] and therefore the *net* electron donor character of these types of ligands decreases with the increase of the metal-carbon bond order, as follows:

alkynyl (*M*−C≡C−) (this work) > allenylidene (*M*=C=C=C<) > carbyne (*M*≡C−) [7] > carbyne (*M*≡C−) [11, 12]

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