

# The Reactivity of an Iron(II)/Iron(III) System with Polyamine Ligands in Ethanol: An Electrochemical Study

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The pentadentate ligand picdien [ $L_A$ ; 1,9-bis(2'-pyridyl)-2,5,8-triazanonane]] and  $[Fe(DMSO)_6](NO_3)_3$  produce the hexacoordinate coordination compound  $[FeL'_B]^{2+}$  after reaction in ethanol. This compound shows a change in the oxidation state of  $Fe^{III}$  to  $Fe^{II}$  as well as an increase in the denticity of the starting ligand  $L_A$ . The new ligand  $L'_B$  {1,9-bis(2'-pyridyl)-5-[(ethoxy-2'-pyridyl)methyl]-2,5,8-triazanon-1-ene} has an imine carbon–nitrogen double bond. This study provides evidence for the nature of the intermediate species during the formation of  $[FeL'_B](BPh_4)_2$ . A systematic study was performed based on the evolution of the voltammograms observed after the addition of ligand ( $L_A$ ,  $L_B$ ) or base (LiOEt) to  $Fe^{III}$ ,  $Fe^{II}$  solutions or stoichiometric metal-ligand mixtures ( $L_B$  is  $L'_B$  without the imine group). The stability of  $FeL_A^{3+}$  and  $FeL_A^{2+}$  species in acidic media and under nitrogen atmosphere was confirmed. The reactivity of  $FeL_B^{3+}$  and  $FeL_A^{3+}$

systems was found to be very similar, and the reduction products were found to be  $Fe^{II}$  species with simultaneous ligand oxidation, which, in both cases, produces an imine double bond, giving rise to an intramolecular redox reaction. The following disproportionation equation describes the general form of this process:  $2 FeL^{3+} \rightleftharpoons FeL^{2+} + FeL'^{2+} + 2 H^+$ . The oxidation was verified by the double bond formation in  $L_A$  and  $L_B$  giving rise to  $L'_A$  and  $L'_B$  as can be seen in the general equation:  $R^1-CH_2-NH-R^2 \rightleftharpoons R^1-CH=N-R^2 + 2 H^+ + 2 e^-$ . The disproportionation reaction for  $FeL_A^{3+}$  and  $FeL_B^{3+}$  species depends on the acidity level of the media: this reaction cannot be verified in acidic media, while neutral and slightly basic media favour formation of the  $Fe^{II}$  species with  $L'_A$  and  $L'_B$ .

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## Introduction

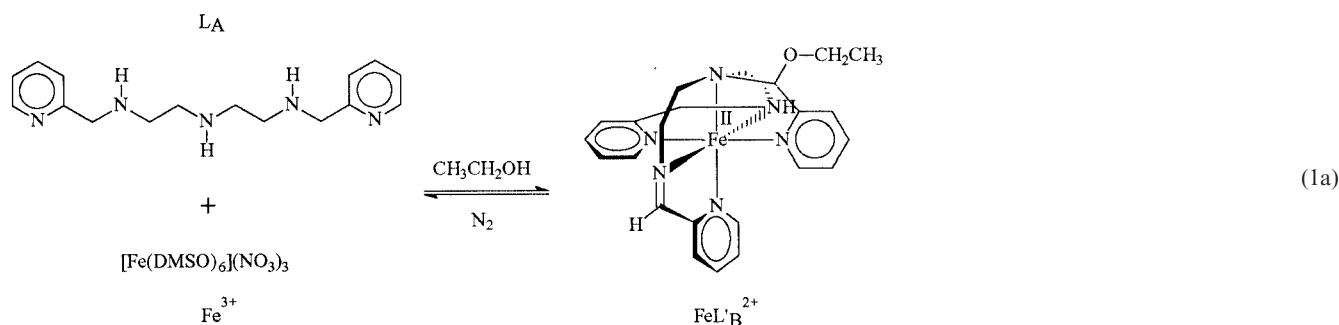
Oxidative dehydrogenation reactions of alcohols and amines are of great interest in biochemistry (e.g., alcohol dehydrogenase enzymes, galactose oxidase, amine oxidase) as well as in systems related to the protein degradation that contributes to aging. In addition, this type of reaction is of great importance in combustion cell operation. The nature of the products obtained in these reactions and the rates of their formation may vary depending on the reaction conditions, and are particularly strongly influenced by the presence of metallic ions. In the above-mentioned biochemical processes, the  $Zn^{II}$  is present in the active site of alcohol dehydrogenase enzyme, whereas  $Cu^{II}$  is found in galactose oxidase<sup>[1]</sup> and amine oxidase.<sup>[2]</sup> The  $Fe^{II}$  of metal-catalyzed oxidation (MCO) systems contributes to enzyme deterioration through dehydrogenation.<sup>[3]</sup> Amine oxidation may give

rise to different products (including nitriles, nitro species and carbonylic compounds formed by insertion of highly reactive imine species formed during oxidation). The oxidation of amines and alcohols coordinated to metallic centers leads to quantitative formation of dehydrogenated products.<sup>[4]</sup> The nature of the metallic center plays a dominant role since the route followed by imine formation depends on it. Metallic ions available in high oxidation states govern the formation of compounds through radicals in a concerted two-electron reaction, with subsequent loss of two protons, as in the reaction of compounds of  $Ru^{II}$  [5–7] and  $Os^{II}$  [8,9] with ethylenediamine. When the metallic ion cannot reach high oxidation states, the reaction takes place only in the presence of strong oxidants, as in the reactions with compounds of  $Ni^{II}$  [10,11] and  $Cu^{II}$ .<sup>[12]</sup>

In the particular case of iron, most oxidation products of amines and coordinated polyamines are coordination compounds containing imines, and in some cases the final product is stable.<sup>[13]</sup> There are very few reports on this kind of compounds in which the ligand not only oxidizes, but also increases its size during the process of final compound formation.<sup>[14]</sup> Despite vast numbers of reports on electrochemical characterization in oxidative dehydrogenation reactions of coordination compounds with polyamines, almost none of them prove the stability of the coordination compounds formed during dissolution.<sup>[15,16]</sup>

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Reports on  $\text{Fe}^{\text{III}}$  systems with polyamine ligands published by Morgenstern–Baradau et al.,<sup>[13]</sup> provide proof of an  $\text{Fe}^{\text{III}}$  system with a tripyridine ligand (TPAA) in which an internal redox reaction proceeds between the metallic ion and the ligand. However, the evidence reported to prove this process is the synthesis of three compounds: two  $\text{Fe}^{\text{II}}$  compounds with TPAA (reduced ligand) and one  $\text{Fe}^{\text{II}}$  compound with  $(\text{py})_3\text{tren}$  (TPAA-oxidized ligand). The compounds were obtained by different procedures from previously isolated starting materials. The evidence presented in the study of possible intermediates formed during the reaction, whether in dissolved or solid form, was inconclusive and in others papers their presence is demonstrated using analytical techniques.<sup>[17,18]</sup> Few publications address iron(III) and iron(II) compounds with the particular case of pentadentate ligands. The high reactivity of iron(III) in this system produces oxidation reactions between the metallic ion and the coordinated ligand. An interesting example of this reactivity occurs between iron(III) and the ligand  $\text{L}_\text{A}$  ( $\text{L}_\text{A}$  = 1,9-bis(2'-pyridyl)-2,5,8-triazanonane), in ethanol. When they are mixed in stoichiometric quantities, a reaction occurs whose final product is a coordination compound with a new hexadentate ligand ( $\text{L}'_\text{B}$ ). A previous work describes synthesis of the compound in detail and the crystal structure of the final product.<sup>[14]</sup> An explanation for the unexpected formation of this compound is shown in the following reaction. In the general reaction [Equation (1a)], an electron exchange occurs between  $\text{Fe}^{\text{III}}$  and  $\text{L}_\text{A}$  to stabilize an iron(II) compound, and a new ligand ( $\text{L}'_\text{B}$ ), which, besides having a double bond, (oxidation product) includes an additional pyridine ring forming a potentially hexadentate compound  $[\text{FeL}'_\text{B}](\text{BPh}_4)_2$ . In this work we describe the key steps of the redox reaction and analyze the electrochemical properties of the species formed in solution during this process.

The following equation summarizes the synthesis of the iron(II) compounds using the ligand  $\text{L}_\text{A}$  in the reaction conditions described (ethanol, 70 °C,  $\text{N}_2$ ).



With:

$\text{L}_\text{A}$  = 1,9-bis(2'-pyridyl)-2,5,8-triazanonane

$\text{L}'_\text{B}$  = 1,9-bis(2'-pyridyl)-5-[(ethoxy)(2''-pyridyl)methyl]-2,5,8-triazanonane

$\text{L}'_\text{B}$  = 1,9-bis(2'-pyridyl)-5-[(ethoxy)(2''-pyridyl)methyl]-2,5,8-triazanon-1-ene

In the proposed reaction [Equation (1)], clarification of the final product of the redox process between the metallic ion and the ligand can be achieved using electrochemical techniques. The characteristics of the intermediates formed in the iron(III)- $\text{L}_\text{A}$  reaction demand a complete study of dissolved species supported by electrochemical techniques. We performed a systematic evaluation using cyclic voltammetry to elucidate the complicated steps occurring during development of the global reaction described in Equation (1b).

## Results and Discussion

Because the reaction in Equation (1) is so complex, it is difficult to perform a direct electrochemical study of the reaction mixture. We therefore proposed electrochemical characterization of the following mixtures: a)  $\text{L}_\text{A} \cdot 3\text{HCl}$  and  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$ , b) equimolar mixtures of  $\text{L}_\text{A} \cdot 3\text{HCl}$  and  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$  and  $\text{L}_\text{A} \cdot 3\text{HCl}$  and  $\text{FeCl}_2$ , c) neutralization of a stoichiometric mixture of  $\text{L}_\text{A} \cdot 3\text{HCl}$  with  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$ , d) an equimolar mixture of  $\text{L}_\text{B}$  and  $\text{FeCl}_2$ , and e) an equimolar mixture of  $\text{L}_\text{B}$  and  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$ .

A half-wave potential ( $E_{1/2}$ ) of 0.504 V vs.  $\text{AgCl}/\text{Ag}$  was obtained from the voltammogram of a ferrocene solution, and this was considered the reference system in all the voltammograms discussed below, according to IUPAC convention.<sup>[19]</sup>

### a) Electrochemistry of a Mixture of $\text{L}_\text{A} \cdot 3\text{HCl}$ and $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$

$\text{L}_\text{A} \cdot 3\text{HCl}$  (15.73  $\mu\text{mol}$ ) was dissolved in 5 mL of electrolyte support (0.1 M  $\text{LiCl}$  in ethanol) and the voltammograms were obtained at 100  $\text{mV} \cdot \text{s}^{-1}$  in the potential interval established by the electroactivity domain. Figure 1 (see a) shows a typical voltammogram for  $\text{L}_\text{A} \cdot 3\text{HCl}$  ( $3.145 \times 10^{-3}$  M) obtained on a platinum electrode. When the potential scan was initiated in the negative direction,  $\text{L}_\text{A} \cdot 3\text{HCl}$  presented three well-defined reduction signals ( $\text{I}_\text{C}$ ,  $\text{II}_\text{C}$  and  $\text{III}_\text{C}$ ), and when the potential scan was reversed, three less-defined oxidation signals ( $\text{I}_\text{A}$ ,  $\text{II}_\text{A}$  and  $\text{III}_\text{A}$ ). When the potential scan was reversed after each cathodic peak, the corresponding anodic peak was well defined (not shown). We

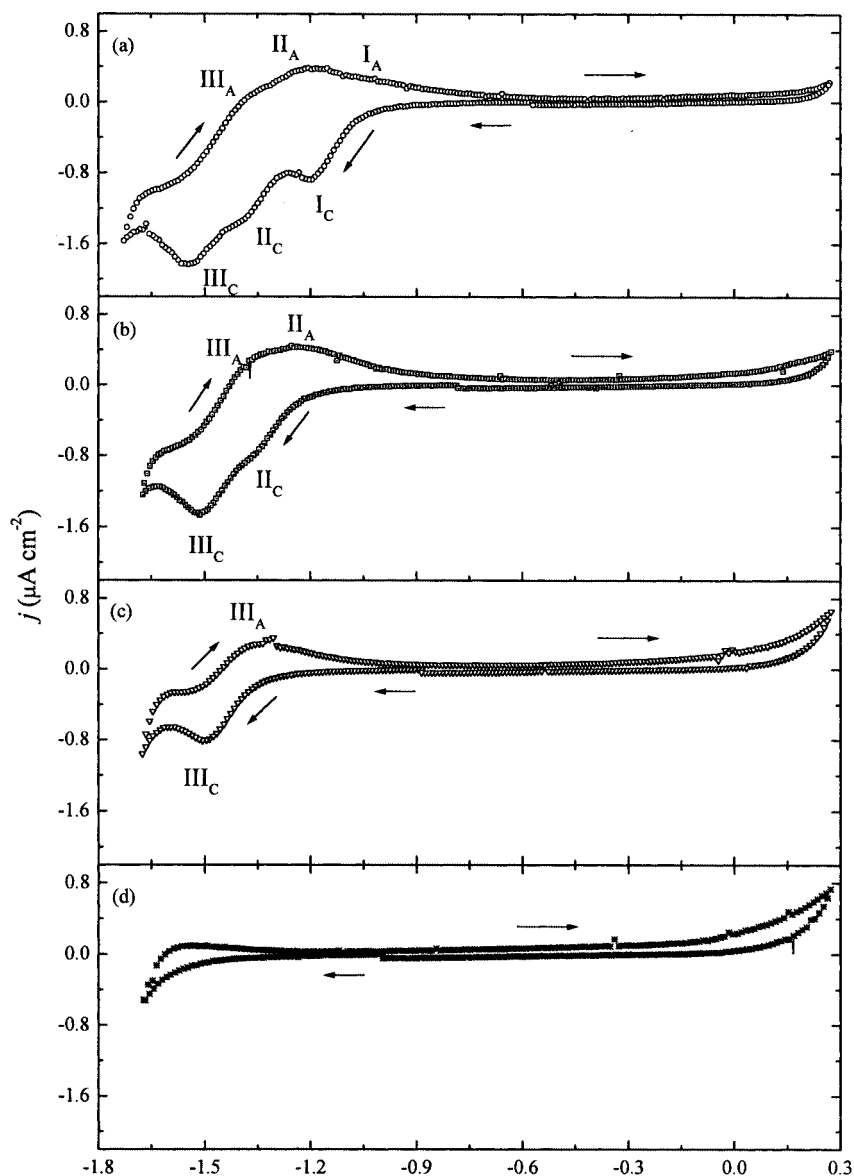
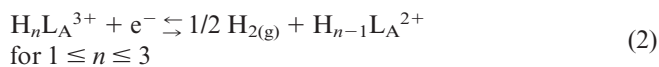


Figure 1. Typical cyclic voltammograms obtained for 15.73  $\mu\text{mol}$   $\text{L}_\text{A}\cdot 3\text{HCl}$  in 5 mL of ethanolic 0.1 M LiCl solution at 100  $\text{mV s}^{-1}$  on a Pt electrode; the potential scan was initiated in the negative direction from  $E_{\text{i}=0}$ ; the voltammograms were obtained after the addition of different quantities of lithium ethoxide: (a)  $\circ$ – 0.0; (b)  $\square$ – 15.72; (c)  $\nabla$ – 31.45 and (d)  $\blacksquare$ – 47.17  $\mu\text{mol}$

propose as a preliminary hypothesis that the reductions are due to protons from the hydrochlorides located at the secondary amines of the ligand. To test this, we gradually added aliquots of a 0.524 M solution of LiOEt to 5 mL of a  $3.145 \times 10^{-3}$  M solution of  $\text{L}_\text{A}\cdot 3\text{HCl}$ . Figure 1 shows the voltammograms obtained when the potential scan was initiated in the negative direction for the  $\text{L}_\text{A}\cdot 3\text{HCl}$  solution and following several additions of LiOEt.

With the first additions of the LiOEt (15 and 30  $\mu\text{L}$ , 15.72 and 31.45  $\mu\text{mol}$ ), the signal  $\text{I}_\text{C}$  decreased until it disappeared. The calculated equivalents added in 30  $\mu\text{L}$  (15.72  $\mu\text{mol}$ ) coincide with neutralization of the first acid equivalent in the ligand (Figure 1, b). This observation was repeated for signals  $\text{II}_\text{C}$  and  $\text{III}_\text{C}$  with aliquot volumes of 60

and 90  $\mu\text{L}$  (31.45 and 47.17  $\mu\text{mol}$ ), respectively (Figure 1, c and d, respectively). After the intensity of the cathodic peaks had diminished, the corresponding anodic peak was better defined (see Figure 1, c). Thus, we effectively proved that the signals observed correspond to the acidic protons of the ligand. We can thereby explain each of the reductions observed based on the following general electrochemical reaction:



This equation confirms that the reduction signals are related to the acidic protons attached to the ligand. In addition, Figure 1 establishes that the neutral ligand is not elec-

troactive as testified by the absence of signals in the voltammogram corresponding to the addition of 90  $\mu\text{L}$  (Figure 1, d). Equation (2) summarizes the different chemical and electrochemical steps and also the different chemical nature of the involved species [i.e.  $\text{H}_{2(\text{g})}$ ], and thus is not a reversible process. The difference of the anodic and cathodic peak current ratio for each peak supports this fact.

An electrochemical study of a  $10^{-3}$  M solution of iron(III) salt  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$ , used for synthesizing the final compound, was performed. A typical voltammogram of a reversible system was obtained, with one cathodic and anodic peak observed (not shown). We analyzed the half-sum of the peak potentials  $[(E_{\text{pC}} + E_{\text{pA}})/2]$  as a function of the logarithm of the scan rate ( $\log v_{\text{B}}$ ), observing a constant behavior, in this way the half-wave potential of  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  ( $E_{1/2} = -0.546$  V vs.  $\text{Fc}^+/\text{Fc}$ ) was obtained. The predominant  $\text{Fe}^{\text{III}}$  species in solution undergoes an electrochemical reaction as shown in the following equation:



#### b) Electrochemistry of an Equimolar Mixture of $\text{L}_\text{A} \cdot 3\text{HCl}$ and $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$ and $\text{L}_\text{A} \cdot 3\text{HCl}$ and $\text{FeCl}_2$

Based on the independent assignment of signals detected for the ligand and iron(III) salt, we proceeded with an electrochemical study with an equimolar mixture of  $\text{L}_\text{A} \cdot 3\text{HCl}$  and  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$  (5  $\mu\text{mol}$ ) at a concentration of  $10^{-3}$  M in 5 mL of electrolyte support. Voltammograms were obtained initiating the potential scan in the positive direction and then in the negative direction while maintaining the same experimental conditions as for the previous experiments. Figure 2, curve a shows a voltammogram obtained for this solution when the potential scan was initiated in the positive direction; in the direct scan no oxidation signal was observed. In the reversed scan two reduction signals were observed ( $\text{I}''_{\text{C}}$ ,  $\text{II}''_{\text{C}}$ ) with cathodic peak potentials ( $E_{\text{pC}}$ ) of  $-0.540$  and  $-1.126$  V vs.  $\text{Fc}^+/\text{Fc}$ , respectively. The value of the current of the peak associated with  $\text{I}''_{\text{C}}$  is approximately one third that for  $\text{II}''_{\text{C}}$ . When the negative switching potential was reached ( $E_{-\lambda} = -1.725$  V vs.  $\text{Fc}^+/\text{Fc}$ ) and the potential scan was performed in the reverse direction, two oxidation signals were observed ( $\text{II}''_{\text{A}}$ ,  $\text{I}''_{\text{A}}$ ) with potential anodic peak values ( $E_{\text{pA}}$ ) of  $-0.913$  and  $-0.401$  V vs.  $\text{Fc}^+/\text{Fc}$ , respectively.

The signals  $\text{I}''_{\text{C}}$  and  $\text{I}''_{\text{A}}$  appear in the potential zone near the half-wave potential of the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  system and for this reason we studied the half sum of the peak potentials  $(E_{\text{pC}} + E_{\text{pA}})/2$  as a function of the logarithm of the scan rate ( $\log v_{\text{B}}$ ). We observed a constant behavior for the  $(E_{\text{pC}} + E_{\text{pA}})/2$  value with  $E_{1/2} = -0.470$  V vs.  $\text{Fc}^+/\text{Fc}$ . In this case,  $\Delta E_{\text{pA}-\text{C}}$  (0.138 V) and the voltammetry function show a similar behavior to that of the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  system.

The information obtained from the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  system in the absence and presence of ligand  $\text{L}_\text{A}$  establishes that the kinetic electron-transfer behavior for both cases is similar, therefore the difference in  $E_{1/2}$  is attributable to the forma-

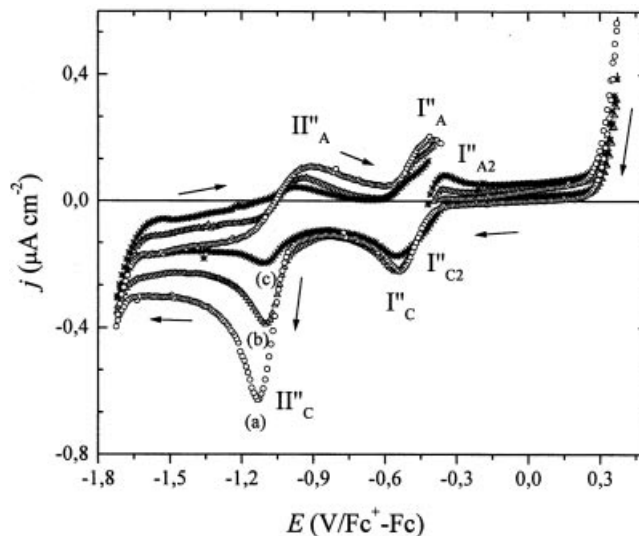


Figure 2. Typical cyclic voltammograms obtained for an equimolar mixture of  $\text{L}_\text{A} \cdot 3\text{HCl}$  and  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$  ( $10^{-3}$  M) in ethanolic 0.1 M LiCl solution on a Pt electrode at  $100 \text{ mV s}^{-1}$ ; the scan potential was initiated in the positive direction from  $E_{\text{f}}=0$ ; the voltammograms were obtained after the addition of different quantities of lithium ethoxide: (a)  $\circ$  0.0; (b)  $\Delta$  6.0 and (c)  $\blacksquare$  12.0  $\mu\text{mol}$

tion of the  $\text{Fe}^{\text{III}}$  complex with  $\text{L}_\text{A}$ . Comparison of the voltammograms of the ligand alone (Figure 1, a) and in the presence of  $\text{Fe}^{\text{III}}$  (Figure 2, a) substantiate this assumption, since three initial reduction signals for the ligand are not observed. The initial complexing reaction could explain the formation of the proposed complex according to the following equation:



According to Equation (4), these signals indicate formation of the coordination compound between  $\text{Fe}^{\text{III}}$  and  $\text{L}_\text{A}$  as formation of the  $\text{FeL}_\text{A}^{3+}$  compound increases the acidity of the protons localized in the ligand, producing a strong acid in solution with a concentration three times that of the compound, explaining the appearance of peak  $\text{II}''_{\text{C}}$  in Figure 2 (a). The new species in solution ( $\text{FeL}_\text{A}^{3+}$ ) undergoes an electrochemical reduction reaction ( $\text{I}''_{\text{C}}$ ) described by the following equation:



As a consequence, the electrochemical reaction for signal  $\text{II}''_{\text{C}}$  occurs according to the following equation:



The proton reduction [Equation (6)] is not reversible under the experimental conditions considered here despite the fact that it is not associated to  $L_A$  ligand. The voltammetric parameters of peak  $II''_C - II''_A$  support this conclusion.

Although we still have to confirm that the species formed at the electrode following the reduction is the compound  $FeL_A^{2+}$ , we can determine that the difference in half-wave potentials for the  $Fe^{III}/Fe^{II}$  system in the absence and presence of  $L_A$  is 0.076 V. The shift toward more positive potentials is probably due to the fact that the complex of  $L_A$  with  $Fe^{II}$  has a greater stability constant than with  $Fe^{III}$ . This effect in the  $Fe^{III}/Fe^{II}$  system has been described previously when varying the ligand  $\pi$  acceptor and analyzing the effects on  $E_{1/2}$  in different compounds.<sup>[20]</sup> A shift in the half-wave potential for this system can explain whether this is the effect of the ligand in the compound. The presence of strong  $\pi$ -acceptors in the ligand (two pyridine rings) allows the central metal ion to resist a greater electron density due to the cooperative effect of this type of ligand. Therefore, we expect coordination compounds with lower oxidation states to have greater formation constants ( $K_f$ ). According to the Nernst law, we can predict a new half-wave potential for a system in which both species of the redox pair form stable coordination compounds [Equation (7)]

$$FeL_A^{3+} + 1e^- \rightleftharpoons FeL_A^{2+}$$

$$E'_{1/2} = E^\circ_{1/2} - 0.058 \log \left[ \frac{K_f^{Fe^{III}L_A}}{K_f^{Fe^{II}L_A}} \right] \quad (7)$$

Where  $E^\circ_{1/2}$  corresponds to the conditional half-wave potential for the  $Fe^{III}/Fe^{II}$  redox pair in 0.1 M lithium chloride and in the absence of the ligand ( $L_A$ ). Thus the values of  $E_{1/2}$  for  $Fe^{III}/Fe^{II}$  and  $FeL_A^{III}/FeL_A^{II}$  allow us to determine the following equation.

$$\frac{K_f^{Fe^{III}L_A}}{K_f^{Fe^{II}L_A}} = 10^{0.95}$$

Under our experimental conditions (room temperature, ethanol,  $N_2$  atmosphere), the compound  $FeL_A^{3+}$  is stable in solution. Nevertheless, the different methods used in attempting to separate out the solid product were unsuccessful.

Equation (5) proposes that the complex  $FeL_A^{2+}$  generated electrochemically is stable in solution and, therefore, it is important to use a mixture of  $L_A \cdot 3HCl$  with an  $Fe^{II}$  salt in this study in order to corroborate the presence of this complex.

As electrochemical proof of the formation of the  $FeL_A^{2+}$  complex, voltammograms were performed on a solution containing an equimolar mixture of  $FeCl_2$  and  $L_A \cdot 3HCl$  ( $10^{-3}$  M; voltammograms not shown). As in Figure 2, curve a, we observed the same number of signals with very similar peak potentials; this confirms the stability of the  $FeL_A^{2+}$  species in solution. This conclusion is very important since there are no reports of coordination compounds of  $Fe^{III}$  and  $Fe^{II}$  with  $L_A$  and this could represent a feasible alternative for studying such compounds. The chemical structure of this compound (availability at the sixth position) lets us

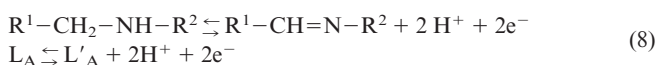
consider this redox pair for use in catalytic processes in homogeneous phase.

### c) Electrochemistry of the Neutralization of an Equimolar mixture of $L_A \cdot 3HCl$ with $[Fe(DMSO)_6](NO_3)_3$

During the synthesis reaction,  $L_A \cdot 3HCl$  is neutralized. We therefore performed a group of experiments with 5 mL of an equimolar metal-ligand mixture at  $10^{-3}$  M (5  $\mu$ mol) to which was added successive quantities of a 0.10 M LiOEt solution. Figure 2 shows the voltammograms for the initial mixture and after adding 60 and 120  $\mu$ L (6 and 12  $\mu$ mol) of LiOEt; in all cases the scan potential was initiated in the positive direction. When the base is added to the solution, the intensity of the reduction signals  $I''_C$  and  $II''_C$  decreases with increasing amounts of added base, with a greater decrease for the signal  $II''_C$  (Figure 2, b and c). We also observe an oxidation signal ( $I''_{A2}$ ) corresponding to the formation of a new species in solution with an anodic peak potential of  $-0.351$  V vs.  $Fc^+/Fc$ . The current values for some signals change as the quantity of added base increases. The oxidation signal  $I''_{A2}$  increases while the signals  $I''_C - I''_A$ , corresponding to the  $FeL_A^{3+}/FeL_A^{2+}$  pair, decrease. The changes in the current values for signal  $II''_C$  are explained by consumption of the  $H^+$  species during neutralization. The peak-potential value of signal  $I''_{A2}$  is more positive than for the  $FeL_A^{3+}/FeL_A^{2+}$  system, and for this reason the new signal  $I''_{A2}$  suggests formation of a new iron complex with a more positive redox potential under the new acidic conditions. The voltammogram obtained in the absence of added LiOEt shows no oxidation signals of  $Fe^{II}$  in the potential interval  $-0.35$  to  $1.00$  V vs.  $Fc^+/Fc$  (Figure 2, a), confirming that only  $Fe^{III}$  is present initially in solution as the species  $FeL_A^{3+}$ .

Since the study was carried out under an inert atmosphere in the absence of oxygen and only the compounds  $FeL_A^{3+}$  and LiCl in ethanol were present in solution, we propose that the ligand  $L_A$  is responsible for the reduction via an intramolecular redox reaction. The formation of imines (oxidation) in coordination compounds with this type of ligand has been described in the literature, with a subsequent reduction of the different metal ions, for example cobalt,<sup>[21]</sup> copper,<sup>[17]</sup> iron,<sup>[13,15,22]</sup> nickel,<sup>[10,23–27]</sup> osmium,<sup>[8,9,28–31]</sup> platinum<sup>[32]</sup> and ruthenium.<sup>[5–7,16,33–45]</sup> To explain this global process we must consider the following:

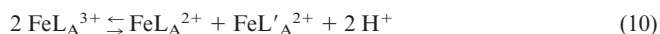
a) Oxidation of the ligand is a process requiring two electrons. The following equation expresses the general form of the reaction:



b) The reduction of the  $Fe^{III}$  species is a single-electron process described by the reaction below:



c) The reaction explaining the overall neutralization process must consider that the  $\text{FeL}_A^{3+}$  species contains the oxidant ( $\text{Fe}^{\text{III}}$ ) and the reductant ( $\text{L}_A$ ). The stoichiometry of the reaction is 2:1 ( $\text{Fe}^{\text{III}}:\text{L}_A$ ) such that the general form of the intramolecular redox reaction can be represented by the following equation:



The above equation describes a disproportionation reaction that is similar to that reported previously,<sup>[46,47]</sup> and justifies the observed changes, demonstrating that the equilibrium shifts to favour formation of the  $\text{Fe}^{\text{II}}$  species as the  $\text{H}^+$  concentration decreases (neutralization). It also explains the transformation of the  $\text{Fe}^{\text{III}}$  species to give rise to two new  $\text{Fe}^{\text{II}}$  species. To confirm this mechanism, we added a slight excess of  $\text{LiOEt}$  (18  $\mu\text{mol}$ ) relative to the initial  $\text{H}^+$  concentration (15  $\mu\text{mol}$ ) and performed voltammograms under the same conditions as before. The initial scan of the voltammogram obtained in the negative direction (Figure 3, a) shows no reduction signals in the interval  $-0.40$  to  $-1.00$  V vs.  $\text{Fc}^+/\text{Fc}$ . The inverse scan shows only two signals, one for oxidation  $\text{I}''_{\text{A}2}$  and the other for reduction  $\text{I}''_{\text{C}2}$ . The absence of reduction signals in the initial scan confirms the hypothesis proposed in Equation (10) for the quantitative transformation of the initial  $\text{FeL}_A^{3+}$ . When the voltammogram is performed initiating the potential scan in the positive direction (not shown), two signals were also observed

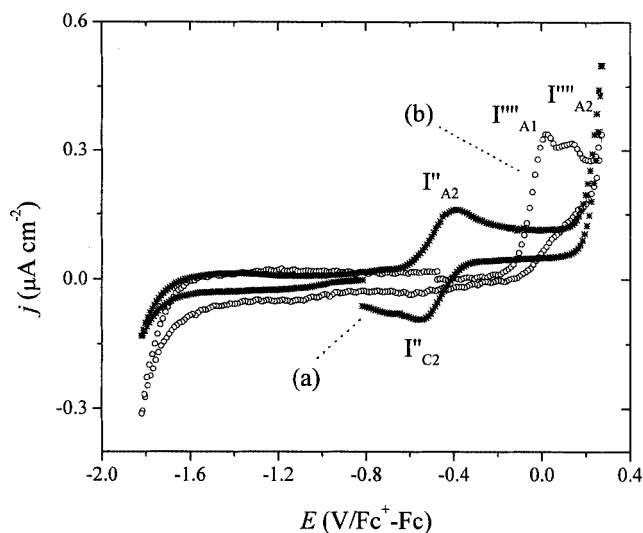
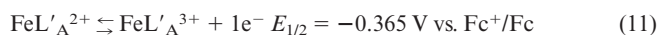


Figure 3. Typical cyclic voltammograms obtained in 5 mL of ethanolic 0.1 M  $\text{LiCl}$  solution on a Pt electrode at  $100 \text{ mV s}^{-1}$ ; the voltammograms were obtained when the scan potential was initiated from  $E_{\text{f}}=0$  for different solutions: (a) —■— a mixture of 5  $\mu\text{mol}$  of  $\text{L}_A \cdot 3\text{HCl}$ , 5  $\mu\text{mol}$  of  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$  and 18  $\mu\text{mol}$  of  $\text{LiEtO}$  (the scan potential was initiated in the negative direction), and (b) —○—  $10^{-3}$  M of  $[\text{FeL}'_B](\text{BPh}_4)_2$  (the scan potential was initiated in the positive direction)

( $\text{I}''_{\text{A}2}$ ,  $\text{I}''_{\text{C}2}$ ) as in Figure 3 (a). A comparison of Figure 3 (a) and Figure 2, curve b–c, demonstrates that, under these conditions, only the  $\text{Fe}^{\text{II}}$  complex is present in solution.

We can therefore conclude that the decrease in the intensity of signal  $\text{I}''_{\text{C}}$  is due to neutralization of the protons formed as products of the complexation reaction. The simultaneous disappearance of the  $\text{Fe}^{\text{III}}$  reduction signal and the appearance of oxidation signals prove that the compound  $\text{FeL}_A^{3+}$  is chemically transformed into two new  $\text{Fe}^{\text{II}}$  species through a redox process in solution. The redox pair responsible for signals  $\text{I}''_{\text{A}}$  and  $\text{I}''_{\text{C}}$  is  $\text{FeL}_A^{3+}/\text{FeL}_A^{2+}$ , and the electrochemical process is described by Equation (5). The signals  $\text{I}''_{\text{A}2}$  and  $\text{I}''_{\text{C}2}$  are explained by the formation of the new species,  $\text{FeL}'_A{}^{2+}$ , through the electrochemical oxidation process described in the following equation:

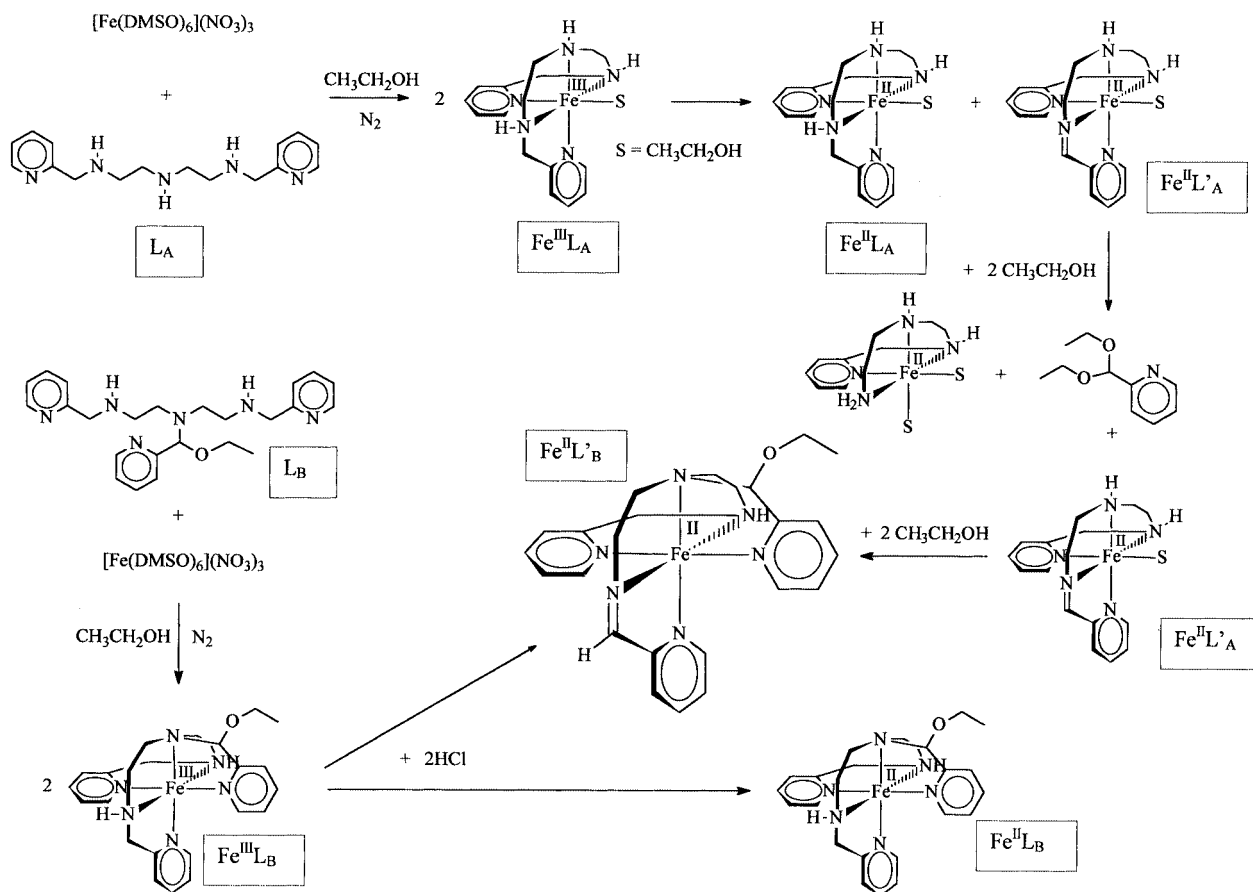


In the new species,  $\text{FeL}'_A{}^{2+}$ ,  $\text{L}'_A$  represents oxidized picdien (containing an imine group). According to Equation (5) and (11), the half-wave potential for the redox pairs resulting from the disproportionation are very close in value. This explains the breadth of the signal and the observation of a single peak for both species  $\text{FeL}_A^{2+}$  and  $\text{FeL}'_A{}^{2+}$  in the voltammogram of Figure 3 (a).

Thereby, the increase in half-wave potential observed for the final product  $\text{FeL}'_A{}^{2+}$  results principally from an increase in the  $\pi$ -acceptor character of the new ligand ( $\text{L}'_A$ ), giving a conjugated double bond  $\pi$  system between the imine and the pyridine ring. We thus conclude that  $\text{FeL}_A^{3+}$  is the precursor to  $\text{FeL}'_A{}^{2+}$  produced by a disproportionation reaction [Equation (10)], favoured at neutral and slightly alkaline pH where the compound  $\text{FeL}'_A{}^{2+}$  is thermodynamically favored.

To prove that  $\text{FeL}'_A{}^{2+}$  indeed corresponds to the coordination compound of  $\text{FeL}'_B{}^{2+}$  ( $\text{L}'_B$  = oxidized form of ligand  $\text{L}_B$ ), we performed an additional experiment. Figure 3, curve b shows the voltammogram of 5  $\mu\text{mol}$  of  $[\text{FeL}'_B](\text{BPh}_4)_2$  dissolved in 5 mL of electrolyte support;  $[\text{FeL}'_B](\text{BPh}_4)_2$  is the final product isolated in the original synthesis. When the potential scan was initiated in the positive direction, two irreversible oxidation signals,  $\text{I}'''_{\text{A}1}$  and  $\text{I}'''_{\text{A}2}$ , appeared with peak-potential values of 0.075 and 0.158 V vs.  $\text{Fc}^+/\text{Fc}$ , respectively. There is a huge difference between this voltammogram and the one obtained for the neutralized mixture of  $\text{Fe}^{\text{III}}\text{-L}_A$  (Figure 3, a), establishing that the  $\text{FeL}'_A{}^{3+}/\text{FeL}'_A{}^{2+}$  system is far from being the final product isolated in the  $[\text{FeL}'_B](\text{BPh}_4)_2$  synthesis process and should be considered an intermediate under the general reaction [Equation (1)].

The end product of the synthesis displays a very different electrochemical behaviour and the voltammograms of the neutralized mixture evolve a wide variety of signals over time which are extremely difficult to explain. Therefore, we used an analogous system to complement our studies in the hope of reproducing this electrochemical behaviour. We proceeded to characterize the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  system electrochemically with a ligand similar in characteristics to that obtained as the major product of the reaction, in this case ligand  $\text{L}_B$ , (see Scheme 1).



Scheme 1

Synthesis of the ligand  $L_B$  begins with formation of the ketal of 2-pyridinecarboxylaldehyde in situ followed by addition of the neutral ligand  $L_A$  in ethanol to form the compound  $L_B$ . This synthetic strategy shows that  $L_B$  has a similar reactivity with  $\text{Fe}^{\text{III}}$  as that discussed up to now for  $\text{Fe}^{\text{III}}$  and  $L_A$ . We describe the details of these experiments below. Unlike the previous experiments with  $L_A \cdot 3\text{HCl}$ , the new ligand  $L_B$  was used in its neutral form.

#### d) Electrochemistry of an Equimolar Mixture of $L_B$ and $\text{FeCl}_2$

We performed a cyclic voltammetric study using 5 mL of a  $3 \times 10^{-3} \text{ M}$   $\text{FeCl}_2$  solution (15  $\mu\text{mol}$ ) in electrolyte support to which 250  $\mu\text{L}$  of a 0.06 M  $L_B$  (15  $\mu\text{mol}$ ) solution was added. The cyclic voltammogram (not shown) obtained when the potential scan was initiated in the positive direction showed a reversible redox system with  $E_{1/2} = -0.409 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ . Voltammograms for the mixture were performed initiating the potential scan in the negative direction; none of the voltammograms show a reduction signal for any  $\text{Fe}^{\text{III}}$ -containing species at the start of recording ( $-0.500$  to  $-1.100 \text{ V}$ ). In this case the reversible redox system is assigned to the complex  $\text{Fe}L_B^{2+}$  formed in solution. The new species in solution follows the electrochemical reaction described below:



The  $\text{Fe}L_B^{2+}$  species is stable under the experimental conditions and no change in the oxidation state of the initial  $\text{Fe}^{\text{II}}$  species in solution is observed. The half-wave potential difference between the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  and  $\text{Fe}L_B^{3+}/\text{Fe}L_B^{2+}$  systems produces a value of 0.121 V, with the  $\text{Fe}L_B^{3+}/\text{Fe}L_B^{2+}$  system potential shifting toward more positive values. Nonetheless, the electrochemical behavior of the new system does not explain the signals observed for the compound  $[\text{Fe}L_B](\text{BPh}_4)_2$  (Figure 3, b), and for this reason we carried out further experiments with  $L_B$  and  $\text{Fe}^{\text{III}}$ .

#### e) Electrochemistry of an Equimolar Mixture of $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$ and $L_B$

The electrochemical study was carried out with an equimolar mixture of  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$  and  $L_B$  (5 mmol) in 5 mL of electrolyte support. Voltammograms were obtained beginning the potential scan in the negative direction (Figure 4, a) and then in the positive direction (Figure 4, b). The signals assigned to the system  $\text{Fe}L_B^{3+}/\text{Fe}L_B^{2+}$ , ( $I'_{A3} - I'_{C3}$ ) present a half-wave potential of  $-0.428 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ .

When the potential scan is initiated in the positive direction (Figure 4, b), unlike the previous recording, an oxidation signal,  $I'_{A3}$ , was observed indicating the presence of an

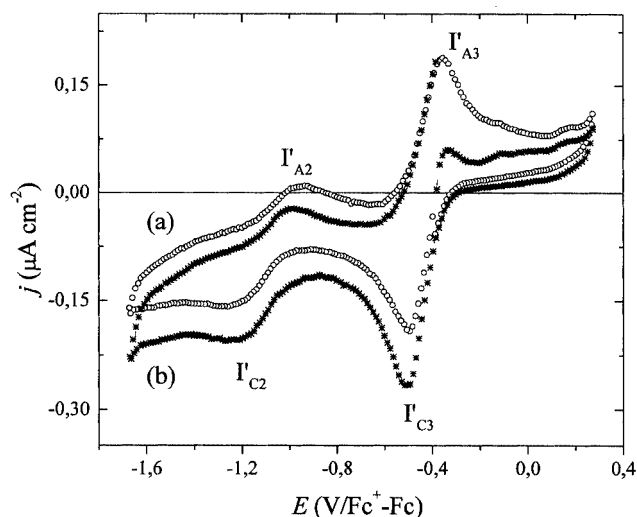
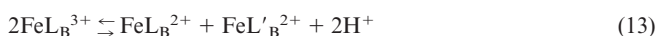


Figure 4. Typical cyclic voltammograms obtained for a fresh equimolar mixture of  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$  and  $\text{L}_\text{B}$ , ( $10^{-3}$  M) in ethanolic 0.1 M LiCl solution on a Pt electrode at  $100 \text{ mV s}^{-1}$ ; the potential was initiated from  $E_{j=0}$  in different directions: (a)  $-o-$  negative direction and (b)  $-■-$  positive direction.

$\text{Fe}^{\text{II}}$  species in solution. In addition, a reduction signal ( $\text{I}'_{\text{C}2}$ ) was present at a peak potential of  $-1.246 \text{ V}$ , with its corresponding oxidation signal  $\text{I}'_{\text{A}2}$  at  $-0.976 \text{ V}$ . The presence of an  $\text{Fe}^{\text{II}}$  species is more obvious (signal  $\text{I}'_{\text{A}3}$ ). Although it is not clearly observed, we propose the existence of additional oxidation signals within the  $-0.10$  to  $0.2 \text{ V}$  potential interval.

These observations and the proposal of Equation (10) suggest that the  $\text{FeL}_\text{B}^{3+}$  species undergoes a similar disproportionation reaction as the  $\text{FeL}_\text{A}^{3+}$  species, involving an oxidation of the ligand  $\text{L}_\text{B}$  with a simultaneous reduction of  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$ . The equation below describes this disproportionation.



In this case  $\text{L}_\text{B}'$  represents the oxidized ligand (imine), and the species  $\text{H}^+$ , appearing as a product of the reaction, explains the reduction signal ( $\text{I}'_{\text{C}2}$ ) at  $-1.246 \text{ V}$ . A decrease of the  $\text{Fe}^{\text{III}}$  reduction signal along with the presence of oxidation signals demonstrates that the compound  $\text{FeL}_\text{B}^{3+}$  is chemically transformed into two new  $\text{Fe}^{\text{II}}$  species by a redox process in solution. The electrochemical reaction for the redox pair  $\text{FeL}_\text{B}^{3+}/\text{FeL}_\text{B}^{2+}$  occurs according to Equation (12).

For the  $\text{Fe}^{\text{III}}-\text{L}_\text{B}$  system, the variation in the concentration of species in solution over time determines the evolution of the voltammograms. To study these variations, an electrochemical study was performed 12 hours after preparing the mixture, initiating the potential scan in the positive direction (Figure 5, a). The recording shows the oxidation signal  $\text{I}'_{\text{A}3}$  and two new oxidation signals,  $\text{I}''''_{\text{A}1}$  and  $\text{I}''''_{\text{A}2}$ , at peak-potential values of  $0.075$  and  $0.158 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$  (Figure 5, a). When the cycle was complete, the signals described coincided with those described previously in

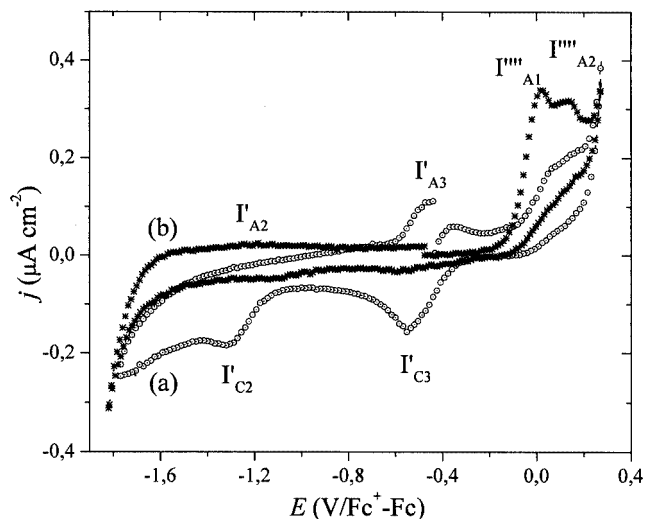


Figure 5. Typical cyclic voltammograms obtained in ethanolic 0.1 M LiCl solution on a Pt electrode at  $100 \text{ mV s}^{-1}$ ; the scan potential was initiated in the positive direction from  $E_{j=0}$ ; the voltammograms were obtained for different solutions: (a)  $-o-$  mixture of  $\text{L}_\text{B}$  and  $[\text{Fe}(\text{DMSO})_6](\text{NO}_3)_3$  ( $10^{-3}$  M each one), 12 h further mixing and (b)  $-■-$   $10^{-3}$  M  $[\text{FeL}'_\text{B}][\text{B}(\text{Ph})_4]_2$

Figure 4. The reduction signal  $\text{I}'_{\text{C}2}$  at  $-1.246 \text{ V}$  increased its current over time while the signal corresponding to the  $\text{FeL}_\text{B}^{3+}/\text{FeL}_\text{B}^{2+}$  system decreased. These observations confirm the reaction proposed in Equation (13) and, in this particular case, the products of the disproportionation reaction have very different electrochemical properties. It is therefore possible to distinguish the two  $\text{Fe}^{\text{II}}$  species formed. For the  $\text{FeL}_\text{B}^{2+}$  species, the half-wave potential is  $-0.428 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$ . The signals with  $E_{\text{pA}} = 0.075$  and  $E_{\text{pA}} = 0.158 \text{ V}$  vs.  $\text{Fc}^+/\text{Fc}$  are assigned to the  $\text{FeL}'_\text{B}^{2+}$  species. To prove this, this voltammogram was compared with the one shown in Figure 3 (b), where the signals assigned to the complex ion  $\text{FeL}'_\text{B}^{2+}$  (Figure 5, b) coincide sufficiently well with the peak-potential values of the isolated product  $[\text{FeL}'_\text{B}][\text{B}(\text{Ph})_4]_2$ .

We have thus shown that the reactivity of ligands  $\text{L}_\text{A}$  and  $\text{L}_\text{B}$  in the presence of  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  is very similar, and that for  $\text{Fe}^{\text{III}}$  an intramolecular reaction occurs involving a redox process in solution between the ligand and the metal. Scheme 1 shows the key steps proposed for the formation of  $[\text{FeL}'_\text{B}][\text{B}(\text{Ph})_4]_2$  based on the stability of the species demonstrated in this work.

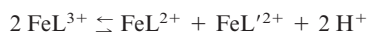
## Conclusions

A systematic study based on evolution of voltammograms following addition of ligand ( $\text{L}_\text{A}$ ,  $\text{L}_\text{B}$ ) or base ( $\text{LiOEt}$ ) to solutions containing  $\text{Fe}^{\text{III}}$ ,  $\text{Fe}^{\text{II}}$  or stoichiometric metal-ligand mixtures was performed. This study provides evidence for the nature of the intermediate species in the process of formation of  $[\text{FeL}'_\text{B}][\text{B}(\text{Ph})_4]_2$ . An intramolecular redox process between  $\text{Fe}^{\text{III}}$  and the ligand is demonstrated when the cyclic voltammograms are initiated in the null current potential and by comparing voltammograms when the po-

tential scan is initiated in both positive and negative directions.

The stability of the  $\text{FeL}_A^{3+}$  and  $\text{FeL}_A^{2+}$  species in acidic media and under nitrogen atmosphere was confirmed. Since no prior evidence exists of solid state compounds existing with the complex ions mentioned here, the electrochemical technique used herein to demonstrate their existence and stability is fundamental.

The reactivity of the systems  $\text{FeL}_B^{3+}$  and  $\text{FeL}_A^{3+}$  was shown to be very similar and the products of the reduction are  $\text{Fe}^{\text{II}}$  species with simultaneous oxidation of the ligand, which, in both cases, produces the formation of an imine double bond, giving rise to an intramolecular redox reaction. The following equation describes the general form of this process.



The oxidation is verified by formation of the double bond in  $\text{L}_A$  and  $\text{L}_B$  giving rise to  $\text{L}_A'$  and  $\text{L}_B'$  as explained by the general equation below.



The reduction revealed by the change in oxidation state from  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  due to a single-electron process establishes the proportion of metal to ligand at 2:1 to complete the exchange and thus justify the presence of two different  $\text{Fe}^{\text{II}}$  species. For  $\text{L}_B$  the compounds identified show very different electrochemical behaviors.

The disproportionation reaction depends on the acidity level of the reaction medium. When this medium is acidic, the disproportionation of the  $\text{FeL}_A^{2+}$  and  $\text{FeL}_B^{2+}$  species cannot be verified, while neutral and slightly basic media favor formation of the  $\text{Fe}^{\text{II}}$  species with  $\text{L}'_A$  and  $\text{L}'_B$ .

## Experimental Section

### Synthesis of $[\text{FeL}'_B](\text{BPh}_4)_2$

The reaction was carried out as described in a previous paper.<sup>[14]</sup> 20% product yield.  $\text{C}_{72}\text{H}_{70}\text{B}_2\text{FeN}_6\text{O}$ : calcd. C 77.71, H 6.34, N 7.55; found C 77.21, H 6.55, N 7.39.

**Synthesis of Ligand  $\text{L}_B$ :** This reaction was carried out by mixing three equivalents of lithium hydroxide in ethanol with one equivalent of the ligand trihydrochloride ( $\text{L}_A \cdot 3\text{HCl}$ ). After neutralization, one equivalent of 2-pyridylcarboxaldehyde was added while maintaining the reaction mixture temperature at 60–70 °C for one hour. Thin-layer chromatography was performed for the mixture, eluting with methanol/chloroform/hexane (1:5:3), to verify that the aldehyde had reacted completely.

**Electrochemistry:** 0.10 M LiCl dissolved in absolute ethanol was used as electrolyte support in the electrochemical studies. A Pt disc (0.0314 cm<sup>2</sup>) was used as the working electrode, a Pt wire as the auxiliary electrode and  $\text{KCl}_{(\text{sat})}/\text{AgCl}_{(\text{s})}/\text{Ag}$  was used as the reference electrode. The working electrode (Pt) was polished with alumina assuring the absence of surface residues. All voltammograms were initiated from the null current potential ( $E_{j=0}$ ) and the scan was initiated in both positive and negative potential directions. In order to report the potentials used according to IUPAC convention,<sup>[19]</sup> voltammograms were obtained for approximately  $10^{-3}$  M

ferrocene (Fc) in electrolyte support. For the working conditions, the electroactive domain was between –1.726 and 0.274 V vs.  $\text{Fc}^+/\text{Fc}$ .

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