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Electrochemistry of phosphaferrocenes

III *. Reaction of nucleophiles with the phosphaferrocenium cations

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Abstract

A comparative electrochemical study of the oxidation of ferrocene and three phosphaferrocene complexes: 1,1′-diphosphaferrocene, 3,3′-dimethyl-1-phosphaferrocene and 3,3′,4,4′-tetramethyl-1,1′-diphosphaferrocene in the presence of nucleophilic reagents (X = Cl, Br; L = *o*-phen, bipy) has shown that phosphaferrocenium cations are less stable than ferrocenium cation towards nucleophilic attack. It has been shown that the electron-withdrawing groups on the (η^5-C_5H_5) ligands are responsible for ligand exchanges on the oxidized species. The main products of the ligand exchange have been identified, and a general reaction scheme is proposed.

Introduction

Under oxidative conditions, ferrocene (hereafter refered as Fc) is unstable. This was first related [1] to the decomposition of the ferrocenium cation $[(\eta^5\text{-}C_5H_5)_2Fe]^+$ (hereafter refered as Fc^+). This cation was found [2] to be stable in acetonitrile, acetone, or nitromethane solutions, for at least a few hours. Furthermore, tetraalkylammonium salts (BF_4^-, NO_3^-, ClO_4^-) used as supporting electrolytes, did not react with the Fc^+ salts [2]. However, the Fc^+ cation is known to be decomposed by nucleophilic reagents in the following sequence of reactions [2]:

$$3Fc^+ + 4X^- \rightarrow 2Fc + [FeX_4]^- + 2C_5H_5 (X = Cl, Br)$$

$$2Fc^+ + 6S \rightarrow Fc + [FeS_6]^{2+} + 2C_5H_5$$

S = DMSO, HMPTA, DMF (for which the reaction is slow)

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* For Part II see Ref. 11.

$$2\mathrm{Fc}^{+} + 3\mathrm{Phen} \rightarrow \mathrm{Fc} + [\mathrm{Fe(Phen)_3}]^{2+} + 2\mathrm{C_5H_5}$$

Phen = 2,2′-bipy or *o*-phen

These results can be interpreted by assuming that a preliminary ligand exchange step involves the $\mathrm{Fe^{III}}$ ion of Fc^{+}, according to:

$$[\mathrm{Fe(C_5H_5)_2}]^{+} + n\mathrm{L} \rightleftarrows [\mathrm{FeL}_n]^{3+} + 2\mathrm{C_5H_5}^{-}$$

(L = solvent or nucleophilic reagent or X^{-} anion)

Because of the high reducing power of the $(\mathrm{C_5H_5})^{-}$ anion generated, reduction of $\mathrm{Fe^{III}}$ complexes will take place, as follows:

$$(\mathrm{C_5H_5})^{-} + [\mathrm{Fe(C_5H_5)_2}]^{+} \rightleftarrows \mathrm{C_5H_5^{\cdot}} + \mathrm{Fe(C_5H_5)_2}$$

$$(\mathrm{C_5H_5})^{-} + [\mathrm{FeL}_n]^{3+} \rightleftarrows \mathrm{C_5H_5^{\cdot}} + [\mathrm{FeL}_n]^{2+}$$

Finally, the $\mathrm{C_5H_5^{\cdot}}$ radical which undergo dimerization and/or H abstraction from the solvent molecules, leading to $\mathrm{C_{10}H_{10}}$ or $\mathrm{C_{10}H_{12}}$. These irreversible reactions will shift the equilibrium position for the overall reaction to the right. In the solid state, crystallographic studies showed that the bonding between the iron ion and the $(\mathrm{C_5H_5})^{-}$ anion is not much weakened by the oxidation of Fc [see ref. 1, 8 and 9].

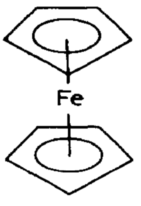
These results provide explanations of why (i) $\mathrm{Fe^{II}}$ species are found in Fc^{+} solutions which contain donor reagents, and (ii) the $\mathrm{Fc/Fc^{+}}$ redox couple is not totally electrochemically reversible [3]. In non-aqueous solvents, four oxidation states are known for ferrocene: +2, +1, 0, −1 [4]. The ferrocene/ferrocenium couple is used as an internal standard for electrochemical measurements [5]. Whereas the electrochemical oxidation of Fc is largely iron-centered [6], recent results show that this is not the case for the parent cation $[\mathrm{(C_5H_5)Fe(CH_3CN)_3}]^{+}$ [7a]. This species, which is only stable at −40 °C in $\mathrm{CH_3CN}$, undergoes an irreversible oxidation at $E_{\mathrm{p,a}} = +0.64$ V vs. Ag/AgCl which is assigned to the oxidation of the bound ligand $(\mathrm{C_5H_5})^{-}$ to the $\mathrm{C_5H_5^{\cdot}}$ radical accompanied by concomitant ligand decomplexation, as follows:

$$[\mathrm{(C_5H_5^{-})Fe(CH_3CN)_3}]^{+} \xrightarrow{+0.64\mathrm{V}} [\mathrm{(C_5H_5^{\cdot})Fe(CH_3CN)_3}]^{2+} + \mathrm{e}$$

$$[\mathrm{(C_5H_5^{\cdot})Fe(CH_3CN)_3}]^{2+} \xrightarrow[\mathrm{CH_3CN}]{\text{fast}} \mathrm{C_5H_5^{\cdot}} + [\mathrm{Fe(CH_3CN)_6}]^{2+}$$

Photolysis of $[\mathrm{(C_5H_5)Fe(CO)_3}]^{+}\mathrm{PF_6}^{-}$ in the presence of 1-phenyl-3,4-dimethylphosphate (P) produced exclusively the air-stable orange complex $[\mathrm{(C_5H_5)Fe(P)_3}]^{+}$ $\mathrm{PF_6}^{-}$ in 94% yield [7b].

In the case of titanocene also it has been claimed that the HOMO (highest occupied molecular orbital involved in oxidation) is based on the $\mathrm{C_5H_5}$ ligand [8]. Evidence for the instability of the Fc^{+} cation can be found in the literature. For instance, electrochemical studies of the $\mathrm{Fc/Fc^{+}}$ couple have been carried out in an $\mathrm{AlCl_3}$-*N*-1-butylpyridinium chloride ionic liquid at 40 °C as a function of melt composition. In basic melts (an excess of BuPyCl) ferrocene is stable, while the Fc^{+} cation is decomposed by Cl^{-} to Fc and $[\mathrm{FeCl_4}]^{-}$ [9]. Also, the relatively strong low-field ESR signal of Fc^{+} is believed to be from Fe^{3+} ions formed by decomposition of Fc^{+} [10]. In the light of these results, it seemed of interest to extend the studies of Fc and derivatives to phosphaferrocenes in order to examine the effect of replacing a CH group by a phosphorus atom in the η^5-C_5H_5 ligands. We have shown previously [11] that the first electrochemical oxidation step for three different phosphaferrocenes hereafter refered as **1**, **2**, and **3** is solvent dependent.



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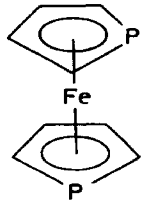
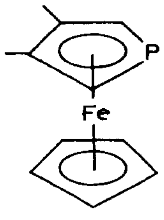


(1)



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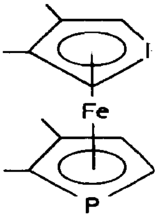


(3)

For instance, the electrochemical oxidation of complex **3** is only reversible in a poor donor solvent such as CH_2Cl_2, whereas it becomes irreversible in a good donor solvent such as DMSO (DN = 29.8 [12]). The criteria of reversibility are the existence of a return reduction peak in triangular sweep cyclic voltammetry and the current peak ratio value. In moderately donor solvents (CH_3CN for which DN = 14.1, or DMF for which DN = 26.6 [12]), the current peak ratio is less than one, indicating that chemical reaction occurs after electronic transfer. In order to understand these subsequent reactions, the electrochemical oxidation of complexes **1**, **2** and **3** were studied in the presence of nucleophilic reagents ($X^- = Cl^-, Br^-$) (L = 1,10-orthophenanthroline (*o*-phen)); 2,2′-bipyridine (bipy). As the phospholyl ring is a weaker donor than the cyclopentadienyl ring, phosphaferrocenes are easier to reduce and more difficult to oxidize than ferrocene [11]. This aim of the present work is to compare the reactivity of the electrogenerated phosphaferrocenium cations toward nucleophilic reagents with that of ferrocenium cations under the same conditions.

Experimental

The electrochemical oxidation of complexes **1** to **3** (which were prepared by published procedures [13]) was carried out in a three electrodes cell, in propylene carbonate (DN = 15.1 [12]) containing 0.1 *M* recrystallized $(C_2H_5)_4NClO_4$ as supporting electrolyte. The working electrode was a Pt microelectrode (3.14 mm^2 area), the auxiliary electrode was a Pt wire, and the reference electrode a saturated calomel electrode (SCE) [11]. We found the $E_{1/2}$ value for the Fc/Fc^+ couple to be $+0.40 \pm 0.01$ V under these conditions. A Bruker E 130 M potentiostat was linked with a high-impedance millivoltmeter (Tacussel, Minisis 6000) and an X-Y IFELEC 3802 recorder. Potential-controlled coulometry was carried out with a PAR 173 potentiostat and a digital coulometer PAR 179. The studies were on freshly prepared solutions handled under pure argon.

In a typical experiment, a triangular potential sweep at 0.1 V s^{-1} from -1.5 to $+1.5$ V was made on a $\sim 10^{-3}$ *M* solution of complex **3**. The nucleophilic reagent ($\sim 10^{-3}$ *M*) was then added and a new potential sweep made from -1.5 to $+1.5$ V. The oxidation peak of the complex was modified and the return scan exhibited new peaks which were analyzed.

All peak potentials are given for potential scan rates of 0.1 V s^{-1}. The first oxidation step for complexes **1**, **2** and **3** occurs at $E_{1/2} = +0.78$, $+0.52$ and $+0.57$ V vs. SCE, respectively. Previous results [11] indicate that a quasi-reversible one-electron oxidation occurs for these complexes in propylene carbonate. The associated reduction peaks on the return potential sweep are modified by the presence of nucleophilic reagents and the product of reaction of complexes $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{3}^+$ cations with nucleophiles were identified by comparison with data for authentic samples.

Results

Oxidation of the phosphaferrocene complexes in the presence of X^- anions (X = Cl, Br)

Whereas the oxidation of ferrocene is not affected under our conditions by the presence of X^- anions, that of the phosphaferrocene oxidation is greatly modified, as shown in Fig. 1. The Cl^- anions were added to the phosphaferrocene solution as 10^{-3} *M* Et_4NCl solutions, and the Br^- anions as 10^{-3} *M* Me_4NBr solutions. In a typical experiment the cyclic voltammetric curve for the one-electron reversible oxidation of complex **3** is changed in the following way in the presence of Et_4NCl (see Fig. 1): (i) the oxidation peak-current of complex **3** is increased; (ii) the associated cathodic peak on the return scan falls to zero; and (iii) two new cathodic peaks appear on the return scan, at 0 and -0.35 V vs. SCE.

We confirmed that under the same conditions $Fe(ClO_4)_3 \cdot 9H_2O$ in the presence of Et_4NCl gives the same reduction peaks at 0 and -0.35 V. A previous study

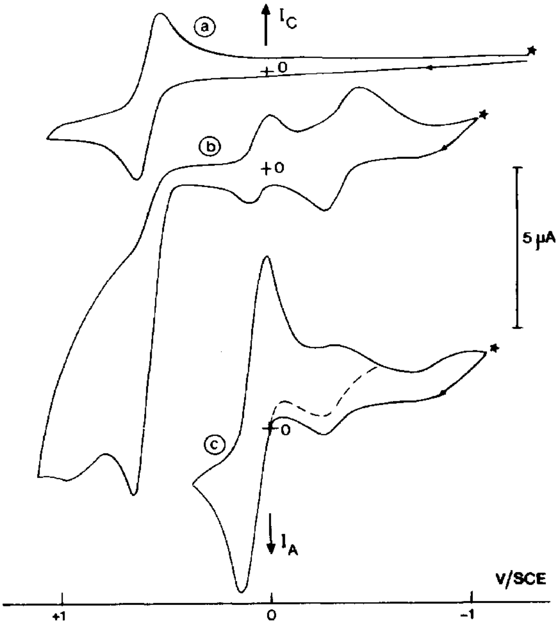


Fig. 1. Single-scan cyclic voltammograms of 10^{-3} *M* $[((CH_3)_2C_4H_2(P))_2Fe]$ in propylene carbonate containing 0.1 *M* TEAP at a scan rate of 0.1 V s^{-1} and 20 °C. The CV peaks of the reactant (R) and product (P) are indicated for solutions containing (a) none, (b) 5 equivalent of added Et_4NCl, (c) $FeClO_4 \cdot 9H_2O + 9$ equivalent Et_4NCl, ★ start of the scan.

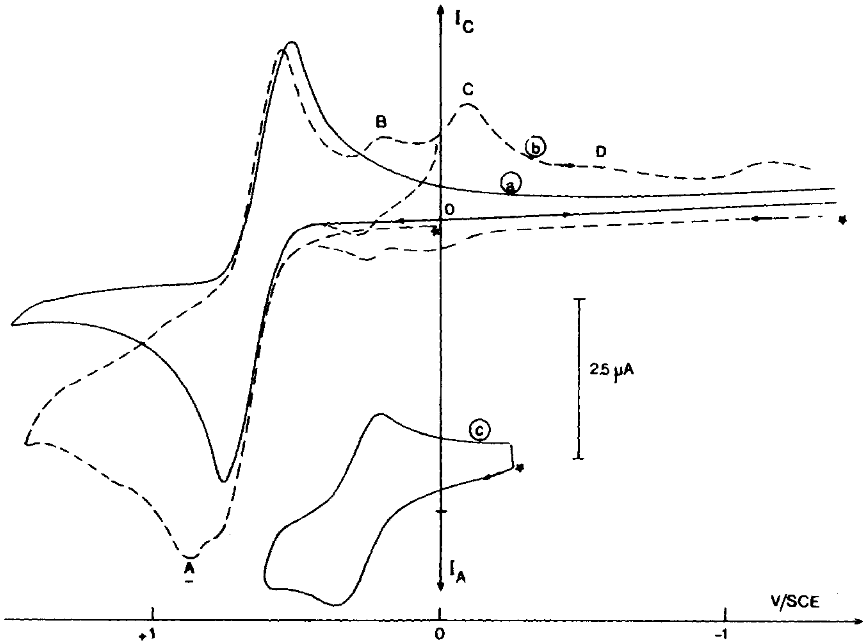
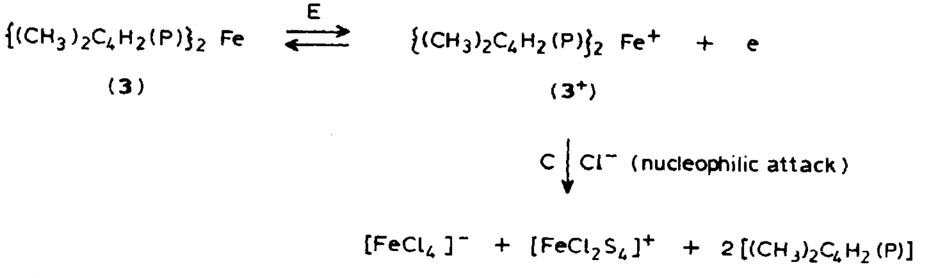


Fig. 2. Single triangular scan cyclic voltammograms of 10^{-3} *M* $[((CH_3)_2C_4H_2(P))_2Fe]$ in propylene carbonate containing 0.1 *M* TEAP at a scan rate of 0.1 V s^{-1} and 20 ° C. The CV peaks of reactant (R) and products (P) are indicated for solutions containing (a) none, (b) 9 equivalent of added Me_4NBr and (c) $FeClO_4 \cdot 9H_2O + Me_4NBr$ in excess, ★ start of the scan.

[14–16] showed that these can be attributed to the following redox couples: $FeCl_4^-/[FeCl_4]^{2-}$, which undergoes a reversible one-electron reaction at 0 V vs. SCE, and $[FeCl_2S_4]^+$ cation, which undergoes an irreversible reduction at −0.35 V/SCE. These results are consistent with an electrochemical-chemical sequence in which, after the uptake of one electron of complex 3 to give 3^+, subsequent chemical reactions take place as follows:



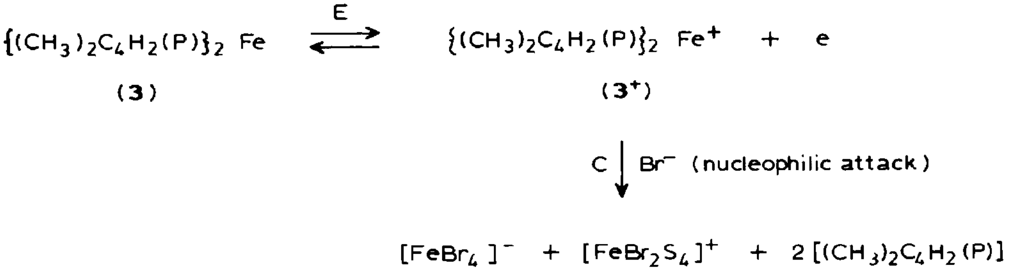
$$\underset{(3)}{\{(CH_3)_2C_4H_2(P)\}_2\,Fe} \overset{E}{\rightleftarrows} \underset{(3^+)}{\{(CH_3)_2C_4H_2(P)\}_2\,Fe^+} + e$$

$$\downarrow \text{C} \quad Cl^- \text{ (nucleophilic attack)}$$

$$[FeCl_4]^- + [FeCl_2S_4]^+ + 2\,[(CH_3)_2C_4H_2(P)]$$

As can be seen from Fig. 2, similar behaviour is observed for complex 3 in the presence of Br^- anion. In Fig. 2, peak A corresponds to the oxidation of free Br^- anion, as shown by comparison with the oxidation of NMe_4Br under the same conditions. Peak B ($E_{1/2} = +0.2$ V vs. SCE) corresponds to the reversible one-electron reduction of the complex $[FeBr_4]^-$, and peak C to the irreversible reduction (at $E_{1/2} = -0.05$ V) of the cationic complex $[FeBr_2S_4]^+$. Studies on $Fe(ClO_4)_3 \cdot 9H_2O$

containing NMe_4Br gave the same reduction peaks under the same conditions. Thus, the following reaction scheme is proposed:



Complexes 1^+ and 2^+ reacted with X^- in the same way as complex 3^+. As the ferrocene oxidation is not modified by the presence of X^- in propylene carbonate, the ferrocenium cation must be more stable than the phosphaferrocenium cations, under the conditions used. After the subsequent chemical reactions there is no change in the formal oxidation state of the central iron(III) ion, showing that the reducing power of $[(CH_3)_2C_4H_2P]^-$ ligand is inferior to that of the corresponding $[C_5H_5]^-$ ligand in ferrocene. The latter is sufficiently reducing to convert Fe^{III} into Fe^{II}, as was noted in the Introduction.

The reaction of I^- and CN^- anions on the phosphaferrocenium cations could not be studied by this method as I^- and CN^- are more readily oxidized (+0.2 and +0.4 V vs. SCE, respectively) than the phosphaferrocenium complexes. When F^- anions are added to a solution of phosphaferrocene as $Bu_4NF \cdot 3H_2O$, modifications of the cyclic voltammetric curves of the oxidation of phosphaferrocene complexes similar to those in the presence of Cl^- and Br^- were observed, but the reaction products could not be identified by comparison with authentic samples.

Oxidation of phosphaferricinium complexes in the presence of chelating ligands L (L = o-phenanthroline, 2,2′-bipyridine)

The electrochemistry of the chelating ligands L has been studied previously [17], as has that of the complexes $[FeL_3]^{3+}$, $[FeL_3]^{2+}$ and $[FeL_3]^+$ [18]. In the presence of a chelating ligand L, for instance 2,2′-bipyridine, the following modifications of the cyclic voltammetric oxidation curve of complex 3 (see Fig. 3) are observed in a typical triangular potential sweep from −1.5 to +1.5 V:

(i) The current peak of complex 3 increases, and the product formed at the electrode is immediately oxidized at that potential.

(ii) The associated return reduction peak disappears, in keeping with a reaction of 3^+ with the nucleophilic reagent.

(iii) A weak reversible oxidation peak appears beyond +1 V vs. SCE, and corresponds to the oxidation of $[FeL_3]^{2+}$ to $[FeL_3]^{3+}$ [18].

(iv) In the return cathodic scan, a new reduction peak appears at −0.5 V, corresponding to the reduction of $[FeL_2S_2]^{3+}$ [19] (S = solvent).

(v) The reduction peaks of $[FeL_3]^{2+}$, $[FeL_3]^+$ and $[FeL_3]$ also appear above −1.3 V vs. SCE in the reverse cathodic scan, and were identified by comparison with data obtained from an authentic sample of $[FeL_3]^{2+}$, which were in keeping with literature data [18]. These modifications are apparent in Fig. 3. Independent studies of ferrous and ferric salts in the

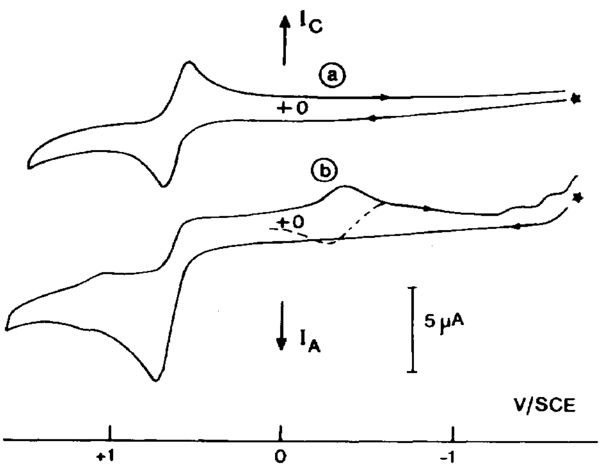


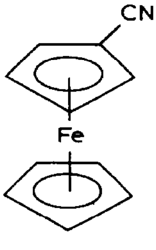
Fig. 3. Cyclic voltammetry at 0.1 V/s of 10^{-3} *M* complex **3** in propylene carbonate with 0.1 *M* tetraethylammonium perchlorate at 20 ° C. (a) complex **3** alone, (b) complex **3** plus 2×10^{-3} *M* bipy. Pt electrode, V vs. SCE, ★ start of the scan.

presence of L confirmed the above assignment of the peaks observed in cyclic voltammetry as a result of the nucleophilic ligand substitution.

We have verified independently that under our experimental conditions the ferrocene oxidation is not affected by the presence of nucleophilic reagents, and that complexes $\mathbf{1}^+$ and $\mathbf{2}^+$ show the same reactivity toward nucleophiles as complex $\mathbf{3}^+$. A $^{31}P\{^1H\}$ NMR spectrum of a totally oxidized solution at +0.7 V vs. SCE (controlled potential coulometry on a Pt wire) of complex **3** in the presence of an excess of bipy in propylene carbonate containing $CDCl_3$ exhibited the signals at $\delta = +52.5$ and $+51.3$ ppm. The first singlet is probably attributable to the anion $[Me_2C_4H_2P]^-$, previously observed at +58.9 ppm for $[Me_2C_4H_2(P)]Li$ in THF [20] (^{31}P NMR chemical shifts are somewhat solvent, concentration, and temperature dependent). Thus in the presence of chelating ligand L, the electrogenerated cations $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{3}^+$ are decomposed, and ligand exchange occurs. The major product of these reactions is $[FeL_3]^{2+}$ (as shown by peak (iii) and (v)), and a minor product is $[FeL_2S_2]^{3+}$ or $[FeLS_4]^{3+}$ [19] (S = solvent). The anion $[Me_2C_4H_2P]^-$ is liberated, as shown by the ^{31}P NMR data. It is important to note that the cation $[FeL_3]^{3+}$, if produced, is reduced to $[FeL_3]^{2+}$ at the potential of +0.6 V (for instance with L = bipy, the reduction of $[Fe(bipy)_3]^{3+}$ occurs at +1.1 V). Similar results were obtained in a poor donor solvent such as $1,2\text{-}C_2H_4Cl_2$ containing 0.1 *M* Bu_4NClO_4, the only difference being that the peak potential for species (iv) appeared at −0.9 V for L = bipy. The oxidation of the phosphaferrocene complexes also becomes irreversible in the presence of pyrazine.

Discussion

Electrochemical experiments show that while the oxidation of ferrocene is only slightly affected by the presence of nucleophilic reagents, the oxidation of phosphaferrocene complexes becomes totally irreversible in their presence. The electrogenerated ferrocenium cation is thus more stable toward nucleophilic substitution than the phosphaferrocenium cations $\mathbf{1}^+$, $\mathbf{2}^+$ and $\mathbf{3}^+$. This contrasts with the generalization that a given phosphametallocene is always less reactive in chemical processes than the corresponding metallocene, owing to the overall electron-withdrawing effect of phosphorus [20]. The phosphorus atoms replacing the CH group in the η^5-cyclopentadienyl ligands are responsible for this situation; they are strong electron-attractors, and are thus especially effective as π-acceptors [21]. In order to generalize this conclusion, we also studied two complexes containing electron-withdrawing groups (monocyano and monoaldehyde groups) bonded to the η^5-C_5H_5 ligands in ferrocene, and found complexes **4** and **5** to show similar effects to those observed for phosphaferrocene.



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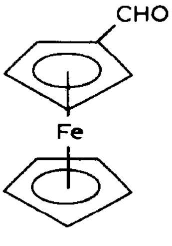

(5)

Under our usual conditions, complexes **4** and **5** undergo a reversible one-electron oxidation at $E_{1/2} = +0.85$ and $+0.68$ V, respectively. In the presence of an excess of 2,2′-bipyridine their oxidation in each case becomes irreversible, and a new signal corresponding to the complex $[Fe(bipy)_3]^{2+}$ affects, as indicated by their potentials: oxidation peak at +1.1 V, reduction peaks at −1.34 and −1.50 V. The complex $[Fe(bipy)_2S_2]^{3+}$ was also identified from its reduction peak at −0.5 V vs. SCE. In contrast, with diphenylphosphinoferrocene, no effect of nucleophilic reagents was apparent in the cyclic voltammetric curves and this is not surprising since phosphaferrocene complexes contain an iron atom directly bound to the phosphorus donor site, which is contained in an heterocyclic aromatic ring [21]. Thus, an electron-attracting group on the C_5H_5 ligand is responsible for the enhanced dissociation of both ferrocenium and phosphaferrocenium cations, in the presence of nucleophilic reagents. A scheme accounting for the observed experimental data for complex **3** is as follows:

$$[(CH_3)_2C_4H_2(P)]_2Fe \rightleftarrows [(CH_3)_2C_4H_2(P)]_2Fe^+ + e$$

$$[(CH_3)_2C_4H_2(P)]_2Fe^+ \rightarrow Fe^{3+}_{(solv)} + 2[(CH_3)_2C_4H_2(P)]^-$$

$$Fe^{3+}_{(solv)} + L \xrightarrow[\substack{(L = \text{bipy,}\\ o\text{-phen})}]{} [FeL_3]^{3+} + [FeS_4L]^{3+} \text{ or } [FeL_2S_2]^{3+}$$

At a potential below +1.1 V, the species $[FeL_3]^{3+}$ are reduced to $[FeL_3]^{2+}$. In ferrocenium solutions containing nucleophiles, the presence of ferrocene has been explained [2] in terms of the high reducing power of the anion $(C_5H_5)^-$ which can reduce the ferrocenium cation to ferrocene. In the light of our observation that the phospholyl anion $[(CH_3)_2C_4H_2(P)]^-$ is a decomposition product of the phosphaferrocenium cation, the reducing power of this anion must be inferior to that of its analogous [$C_5H_5^-$]. Our results can be interpreted in terms of a preliminary ligand exchange involving the Fe^{III} cation of the phosphaferrocenium cations in the presence of nucleophiles. With X = Cl or Br, the complex $[FeX_4]^-$ and $[FeX_2S_4]^+$ are obtained, and the formal oxidation state of the iron atom is unchanged, while with L = bipy or *o*-phen, the $[FeL_3]^{3+}$ cations are reduced at potentials below +1.1 V to $[FeL_3]^{2+}$. Further electrochemical studies on phosphaferrocene and phosphacymantrene complexes are in progress.

Acknowledgement

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