tribution of $d_{x^2-y^2}$ to the SOMO is less than 1% of that from d_{z^2}.

Of the remaining principal axes, one of them (x) necessarily lies along the crystal b axis, and the other (y) is then forced to lie in ac perpendicular to the Fe–P bond. The fact (see Table VI) that these directions nearly coincide with certain Fe–C vectors is purely accidental. Crystal forces evidently dictate the orientation of the x and y tensor components in this case.

Some site splitting may, of course, be hidden in the linewidth (~20 G). This is a likely possibility in a system where one principal axis and turning point is close to a crystal symmetry axis. In other words, Mn($3d_{z^2}$) may lie precisely along the Fe–P vector of the crystal with x directed 2° from b, yet site splitting would not be detected.

Registry No. Fe(η-C_4H_6)$_2$PMe$_3$, 87922-45-0; Mn(η-C_4H_6)$_2$PMe$_3$, 82963-75-5.

Supplementary Material Available: Tables of anisotropic temperature factors and observed and calculated structure factors for Fe(η-C_4H_6)$_2$PMe$_3$ (9 pages). Ordering information is provided on any current masthead page.

Electrochemistry of Phosphaferrocenes. 1. Comparison of the Redox Properties of Ferrocene, Diphosphaferrocene, 3,4-Dimethyl-1-phosphaferrocene, and 3,3′,4,4′-Tetramethyl-1,1′-diphosphaferrocene

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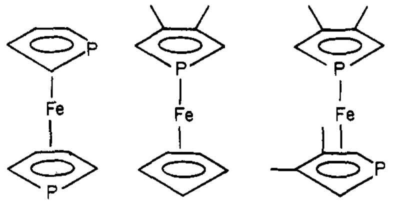
The redox behavior of three phosphaferrocenes (hereafter referred to as **1**, **2**, and **3**) has been investigated on both solid (Pt, Au, vitreous carbon) and dropping mercury electrodes in solvents with varying donicities and compared with the redox behavior of ferrocene (Fc). It was found that the replacement of a CH group by a phosphorus atom strongly modifies the reduction potential. Reversible one-electron reductions in propylene carbonate occur at $E_{1/2}$ = −2.15 V vs. SCE for **1**, at −2.33 V for **3**, and at −2.55 V for **2** compared to −2.93 V for Fc. The phosphaferrocenes also undergo one-electron oxidations at potentials near that for the oxidation of Fc (Fc (+0.40 V), **1** (+0.78 V), **3** (+0.57 V), **2** (+0.52 V)). The stability of the derived phosphaferricinium cations depends upon the solvent nature. In general, the phosphaferricinium cations are less stable than the ferricinium cation, but the ESR spectrum of the $\mathbf{3}^{+\cdot}$ cation has been obtained and it displays no hyperfine coupling. The unpaired electron is localized largely on iron. The redox potentials display additivity and can be predicted by assigning group contributions to the P and CH_3 groups. Complexes **2** and **3** also exhibit an irreversible two-electron oxidation that is attributed to oxidation on ligands of $\mathbf{2}^+$ and $\mathbf{3}^+$ by comparison with the oxidation of an analogous phosphole. The experimental results are discussed in terms of the HOMO and LUMO levels as determined by recent quantum mechanical calculations. The heterogeneous rate constants of the electron transfer are calculated.



1 **2** **3**

Introduction

In the recent years, the Fc/Fc$^+$ couple and derivatives[2-24] (Fc = ferrocene, (η^5-C_5H_5)$_2$Fe) attracted much interest owing to the ability of Fc/Fc$^+$ to function as a reference system in nonaqueous media in the general context of the steep

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increase in organic and organometallic electrochemistry.

Among the redox couples that more or less possess similar characteristics (viz., cobaltocene/cobaltocinium, tris(2,2′-bipyridine)iron(I)/tris(2,2′-bipyridine)iron(0), bis(biphenyl)chromium(I)/bis(biphenyl)chromium(0)), the Fc/Fc$^+$ redox couple is the reference system recommended by IUPAC for organic electrochemistry in nonaqueous solvents.[19] Yet, a previous study[20] revealed that its oxidation is in fact only quasi-reversible and that electron transfer from Fc is followed by a slow and irreversible decomposition of Fc$^+$ in solvents like ethanol, dimethylformamide, and propylene carbonate.

On the other hand, previous studies have shown that the ferricinium cation Fc$^+$ is decomposed under oxidative conditions by nucleophilic reagents into ferric or ferrous complexes as[22]

$$3[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})_2]^+ + 4\mathrm{X}^- \xrightarrow{\mathrm{X\ =\ Cl,\ Br}} 2\ \mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})_2 + \mathrm{Fe\ X_4}^- + 2\mathrm{C_5H_5}$$

$$2[\mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})_2]^+ + 6\mathrm{S} \xrightarrow{\mathrm{S\ =\ DMF}} \mathrm{Fe}(\eta^5\text{-}\mathrm{C_5H_5})_2 + \mathrm{Fe\ S_6}^{2+} + 2\mathrm{C_5H_5}$$

Ferrocene also undergoes a one-electron reduction[18] on a mercury electrode at a very cathodic potential that was observed in DMF containing 0.2 M Bu$_4$NI below 10 °C ($E_{1/2}$ = −2.93 V vs. SCE). Similarly, methylferrocene has been reduced at −3.07 V at −35 °C and diferrocenylmethane reduced at −3.02 V at −30 °C under the same conditions. While methylferrocene is more difficult to reduce than ferrocene, it is more easily oxidized.[26]

The aim of the present work was to compare the redox behavior of ferrocene (Fc) and of **1**, **2**, and **3** in order to establish the contribution of the phosphorus to the observed changes. The molecules **1**, **2**, and **3** are the only heterocyclic C–P compounds for which an aromatic chemistry has been developed.[27]

Table I. Electrochemical Results[a]

compd	working electrode: platinum[b]: first oxidatn	working electrode: platinum[b]: second oxidatn	working electrode: mercury: first oxidatn	working electrode: mercury: reductn	k_s,[g] cm·s^{-1}
ferrocene	$E_{1/2}$ = +0.40 V $E_{3/4} - E_{1/4}$ = 90 mV	c	$E_{1/2}$ = +0.43 V	d	$k_s^{ox.}$ = (Pt, Hg) 0.008 ± 0.003[i] $k_s^{red.}$ = 0.001[h]
dimethylferrocene	$E_{1/2}$ = + 0.30V	c	$E_{1/2}$ = +0.32 V	e	
2	$E_{1/2}$ = +0.52 V $E_{3/4} - E_{1/4}$ = 80 mV	E_p = +1.50 V[f]	$E_{1/2}$ = +0.50 V $E_{3/4} - E_{1/4}$ = 50 mV	$E_{1/2}$ = −2.55 V $E_{3/4} - E_{1/4}$ = 60 mV	$k_s^{ox.}$ = 0.003 ± 0.002 (Pt) $k_s^{red.}$ = 0.02 ± 0.01 (Hg)
3	$E_{1/2}$ = +0.57 V $E_{3/4} - E_{1/4}$ = 90 mV	E_p = +1.80 V[f]	$E_{1/2}$ = +0.53 V $E_{3/4} - E_{1/4}$ = 51 mV	$E_{1/2}$ = −2.33 V $E_{3/4} - E_{1/4}$ = 60 mV	$k_s^{ox.}$ = 0.006 ± 0.004 (Pt) $k_s^{red.}$ = 0.02 ± 0.01 (Hg)
1	$E_{1/2}$ = +0.78 V $E_{3/4} - E_{1/4}$ = 110 mV	c	$E_{1/2}$ = +0.61 V $E_{3/4} - E_{1/4}$ = 70 mV	$E_{1/2}$ = −2.15 V $E_{3/4} - E_{1/4}$ = 55 mV	$k_s^{ox.}$ = 0.0008 ± 0.0003 (Pt) $k_s^{red.}$ = 0.04 ± 0.03 (Hg)

[a] In propylene carbonate containing 0.1 M TEAP; potentials relative to SCE. [b] The measured $E_{1/2}$ values were independent of the nature of the solid electrode (Pt, Au, Cu). [c] No second oxidation was observable up to 2 V vs. SCE. [d] $E_{1/2}$ = −2.93 V vs. SCE at 10 °C in dimethylformamide containing 0.2 M Bu$_4$NI.[18] [e] No reduction was observable down to −3 V vs. SCE. [f] Potential determined at 0.1 V/s by cyclic voltammetry only. [g] Heterogeneous rate constants for reduction, $k_s^{red.}$, and for the first oxidation, $k_s^{ox.}$, determined by the Nicholson–Shain method.[33] Pt, on a Pt electrode; Hg, on a Hg electrode. The reported values are an average of the values derived from series of curves recorded at different scan rates in CV (0.05–1 V/s on Pt electrode for oxidation and 10–100 V/s on Hg electrode) at 20 °C. [h] Determined at −45 °C.[35] [i] From ref 36 and 25 and this work.

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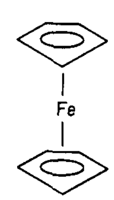

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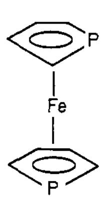

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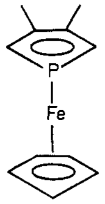

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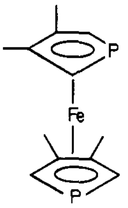

3

Experimental Section

The experimental results were obtained on solid rotating disk electrodes (RDE) made of Pt, Au (area = 3.14 mm^2 for both), and vitreous carbon (area = 6.15 mm^2) and on a dropping mercury electrode (DME) (τ = 1 s, m = 0.170 mg·s^{-1}, 60 cmHg) in organic solvents: CH_2Cl_2 + 0.1 M tetrahexylammonium perchlorate (THAP), propylene carbonate (PC) + 0.1 M tetraethylammonium perchlorate (TEAP), acetonitrile (CH_3CN) + 0.1 M TEAP, dimethyl sulfoxide (Me_2SO) + 0.1 M TEAP, and dimethylformamide (DMF) + 0.1 M tetrabutylammonium perchlorate (TBAP). Before use the solvents were distilled twice under argon as already described.[28] Cyclic voltammetry was used with both electrodes, whereas RDE voltammetry (ω = 2000 rpm) was used on solid electrodes only, and normal or differential pulse polarography was used on DME only. Redox measurements were performed with a Tacussel PRG 4 multipurpose device (on DME), whereas solid electrodes measurements were carried out with a Bruker E 130 M potentiostat associated with a high-impedance millivolt meter (Tacussel, Minisis 6000, and an X-Y IFELEC 3802 recorder). Potentiostatic coulometries were performed with a PAR 173 potentiostat and a digital coulometer, PAR 179.

Three electrode cells were used throughout, involving the working electrode (solid or DME), a Pt wire as auxiliary electrode, and a saturated calomel electrode as reference, the latter being in electrical contact with the cell through a junction bridge filled with the same organic solvent and supporting electrolyte as the solution studied. No Ohmic drop correction was made as preliminary experiments on Fc/Fc$^+$ demonstrated that cyclic voltammetry led to acceptable values of k_s (see Table I and references therein). The studied species were freshly prepared compounds[37] handled under argon only. All solvents and solutions were also handled under argon. The X band ESR spectra were recorded on a Bruker ER 200 D.

Results

I. Electrochemical Oxidation of 1, 2, and 3. Complexes 1, 2, and 3 undergo a first oxidation step at $E_{1/2}$ = +0.78, +0.52, and +0.57 V vs. SCE, respectively (Table I). A further ill-defined oxidation step is found at more positive potentials (≥1.5 V vs. SCE) for 2 and 3.

The first oxidation step is diffusion controlled for the three compounds. Potentiostatic coulometry and comparisons of limiting currents between 1, 2, and 3, respectively, with Fc indicate a one-electron exchange in this first oxidation step. The CV curves in PC + 0.1 M TEAP reveal that the electron transfer involved in this step is quasi-reversible: at low scan rates, the peak separation $\Delta E_p = E_{p_a} - E_{p_c}$ being 60 ± 3 mV (for $2 \rightleftarrows 2^+$ and for $3 \rightleftarrows 3^+$) and 120 ± 3 mV (for $1 \rightleftarrows 1^+$), at 0.02 V/s^{-1}. These ΔE_p increase with the potential scan rate, enabling the calculation of heterogeneous electron-transfer rates k_s[33] (Table I). The so-calculated k_s do not exhibit significant differences with that obtained for Fc (Table I) except for 1 where k_s is about 10 times smaller.

When the 3^+ cation is generated at −40 °C (in 1,2-dichloroethane + 0.1 M TBAP) by exhaustive oxidation at +1 V on Pt, the solution turns from red to orange. The frozen solution (148 K) of 3^+ gives two ESR signals ($g_\parallel$ = 2.72 and $g_\perp$ = 1.99; Figure 1). These values compare to those reported for ferricinium picrate[23] ($g_\parallel$ = 3.18 and $g_\perp$ = 1.84). No hyperfine coupling is observed, suggesting that the unpaired electron resides largely on iron.

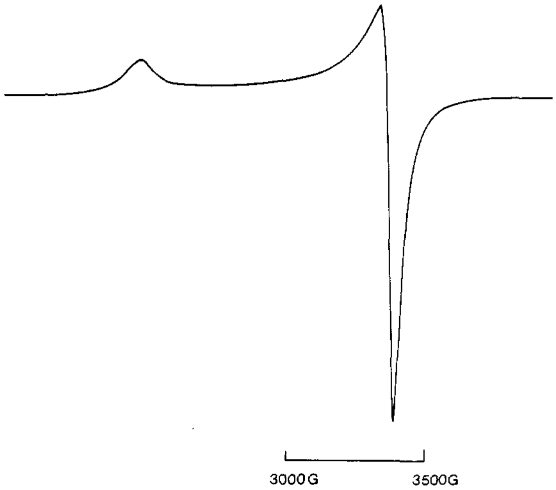

Figure 1. ESR spectrum of 3^+ in 1,2-dichloroethane at 148 K.

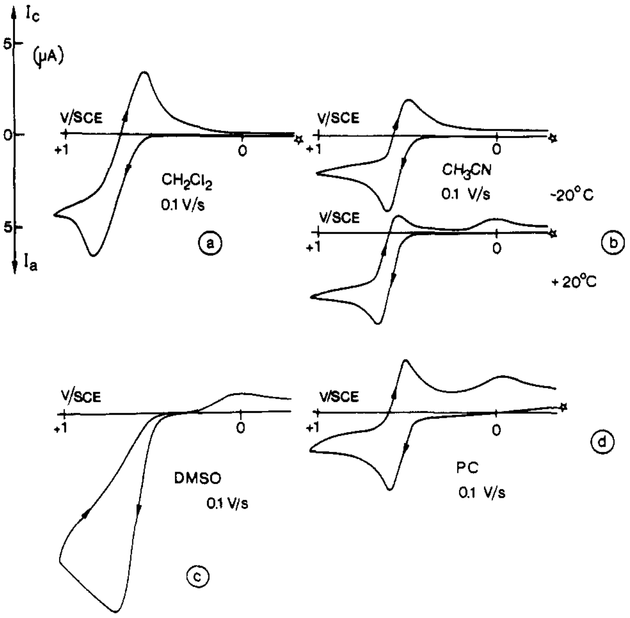

Figure 2. Electrochemical oxidation of 3 (first step) on a platinum electrode at 0.1 V/s in (a) dichloromethane containing 0.1 M THAP (~10^{-3} M), (b) acetonitrile containing 0.1 M TEAP (~10^{-3} M), (c) Dimethyl sulfoxide containing 0.1 M TEAP (~2 × 10^{-3} M), and (d) propylene carbonate containing 0.1 M TEAP (~10^{-3} M).

The stability of 2^+ and 3^+ is critically solvent dependent (Figure 2 and 3) whereas 1^+ undergoes fast decomposition in all studied solvents, except PC. From CV curves, the ratios i_{p_c}/i_{p_a} (i_{p_c} = cathodic return peak current; i_{p_a} = anodic peak current) indicate that the chemical step corresponding to the decomposition of 2^+ and 3^+ species is accelerated as the solvent donicity[29] increases: the ratio i_{p_c}/i_{p_a} is unity in CH_2Cl_2 and decreases to zero in Me_2SO. On the contrary, the decomposition of 1^+ is such that i_{p_c}/i_{p_a} is about zero in all studied solvents, except in PC where a return reduction peak is observed (at v ≥ 0.02 V/s^{-1}). On cyclic voltammograms where the oxidation products of 1, 2, and 3 respectively undergo significant chemical decomposition (e.g., in PC + 0.1 M TEAP), a new reduction peak appears near 0 V vs. SCE on the cathodic return scan, of

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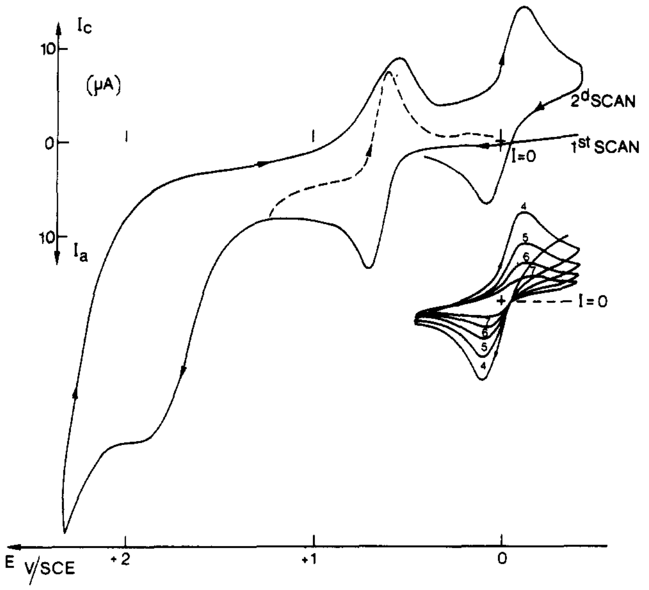
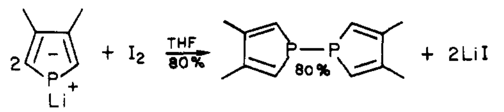


Figure 3. Electrochemical oxidation of 3 (2×10^{-3} M) on a platinum electrode at 0.1 V/s in propylene carbonate containing 0.1 M TEAP. The numbers on the curves indicate the successive multiple scans following the initial anodic sweeps.

which the peak potential is only slightly solvent dependent. The corresponding redox couple is reversible, and multiple scans clearly demonstrate that the electroreducible species is confined to the electrode surface (Figure 3). In order to identify this redox system detected around 0 V vs. SCE, the redox behavior of $Fe(ClO_4)_3{\cdot}9H_2O$ (Fluka product) and of 1-phenyl-3,4-dimethylphosphole respectively were investigated on Pt in PC containing 0.1 M TEAP.

The reduction of Fe^{III} to Fe^{II} is observed at $E_{1/2} = -0.05$ V vs. SCE. Also 1-phenyl-3,4-dimethylphosphole is oxidized at $E_{1/2} = +1.35$ V vs. SCE and the generated species decomposes into a product that is reversibly reduced at 0 V vs. SCE. We speculate that this species might be the dimer previously reported[30,31] in the chemical oxidation of lithium phospholide:



Of course, this scheme implies that, following the first oxidation of phosphaferrocenes, the phospholyl radical might be liberated and further dimerized[32] to form the biphospholyl, reducible at 0 V under these conditions.

Addition of chelating ligands to the solution of the three phosphaferrocenes modifies significantly the CV curves obtained for the first oxidation step. On CV, we observe that, in the presence of 2,2′-bipyridine (bpy) or *o*-phenanthroline (*o*-phen), the above-mentioned reduction peak (near 0 V vs. SCE) disappears, beside the expected accelerating effect on the decomposition of 1^+, 2^+, or 3^+.

These results are much consistent with an electrochemical (EC) mechanism in the oxidation of 1, 2, and 3. The reduction peak of Fc^+ remains unaffected in the presence of bpy or *o*-phen, and no further reduction peak is obtained.

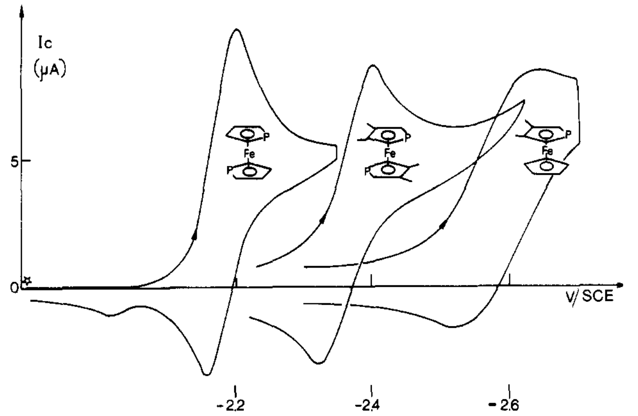


Figure 4. Electrochemical reduction of 10^{-3} M solutions of 1, 2, and 3 on a mercury electrode in propylene carbonate containing 0.1 M TEAP at 10 V/s.

A second oxidation step is observed for 2 and 3 only by CV in PC + 0.1 M TEAP. The second oxidation step of 1 is not observed as the electrode surface is passivated after the first oxidation step. This second oxidation of 2 and 3 is an irreversible, likely two-electron process on the basis of the peak current values compared with those of the first step.

This second oxidation likely involves the species generated in the first oxidation step, as the corresponding peak is not significantly modified at low temperature (−20 °C). We think that this second oxidation step involves the phospholide coordinated to Fe^{III}, as 1-phenyl-3,4-dimethylphosphole is also oxidized at +1.8 V vs. SCE under these conditions (second oxidation).

II. Electroreduction of the Complexes. In PC + 0.1 M TEAP, the species 1, 2, and 3 are reversibly reduced on DME at $E_{1/2} = -2.15$, −2.55, and −2.33 V/SCE, respectively, all three potentials being less negative than the reduction potential of Fc[18] (−2.93 V/SCE). Also, the reduction product of 1 is less stable than those of 2 or 3 (Figure 4). For all three species, the cathodic and the first anodic polarographic waves exhibit equal height, thus indicating that the reduction process is a one-electron step, as also illustrated by comparison of the cathodic limiting currents with that corresponding to oxidation of Fc. The reduction processes of 1, 2, and 3 are diffusion controlled. The rate constants (Table I) were calculated from cyclic voltammograms recorded on DME at different scan rates (from 10 to 100 V/s for 1, 2, and 3).[33] The calculated k_s do not differ significantly.

Discussion

According to previous studies[2-23] ferrocene (Fc) exhibits the following redox behavior:

$$\text{oxidation:}\quad Fc \rightleftarrows Fc^+ + e^- \xrightarrow{\text{chemical step}} \text{products}$$

$$\text{reduction:}\quad Fc + e^- \rightleftarrows Fc^- \xrightarrow[\text{chemical step}]{} \text{products}$$

The three phosphaferrocenes studied herein (1, 2, and 3) show an analogous redox behavior but with some differences introduced by the substitution of a phosphorus atom for a CH fragment. As for ferrocene, oxidation of the three phosphaferrocenes leads to phosphaferricinium cations whose stability is solvent dependent. Each of the phosphaferrocenes is more difficult to oxidize than the ferrocene is (Table I), despite the fact that 2 and 3 both possess methyl substituents that should facilitate their

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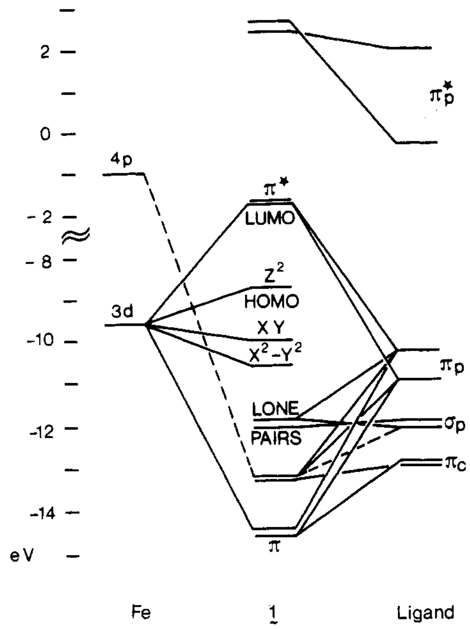
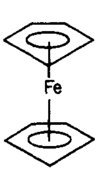


Figure 5. Molecular orbital energy level diagram for $(C_4H_4P)_2Fe$ (1) after ref 34a.

oxidation. Clearly the presence of the phosphorus atom(s) overwhelms the effects of methyl substitution. According to earlier results,[12-14,26] each methyl group facilitates the oxidation of a metallocene by about 50 mV, a result which has been verified on $(C_5H_4CH_3)_2Fe$ (Table I). Therefore we thus expected 3, which possesses four methyl groups, to be oxidized at a potential approximately 200 mV less anodic than that of 1 in concert with the experimental observation. Furthermore, comparison of the oxidation potentials of 3 (570 mV) and Fc (400 mV) leads to the conclusion that the net effect of the four methyl groups and two phosphorus atoms is to shift the ferrocene oxidation potential 170 mV anodically. Thus, each phosphorus atom gives rise to an anodic shift of 185 mV. Using these incremental group contributions, it is possible to calculate the oxidation potentials of the phosphaferrocenes using ferrocene as a standard. On this basis we make the following predictions for oxidation potentials compared to the observed values in parentheses.



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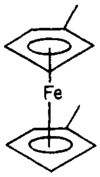
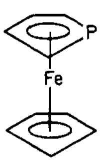
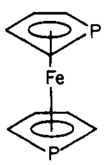


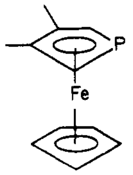
0.30 V
(0.30 V)



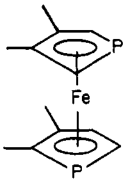
0.58 V
(· · ·)



0.77 V
(0.78 V)

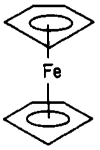


0.48 V
(0.52 V)

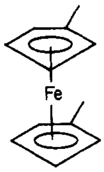


0.57 V
(0.57 V)

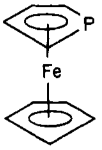
A similar analysis of the reduction potentials (Table I) leads to the conclusion that methyl groups would shift the reduction potential by 46 mV cathodically and phosphorus groups 390 mV anodically. On this basis, we make the following predictions for the reduction potentials compared to the observed values in parentheses.



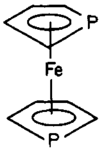
(−2.93 V)



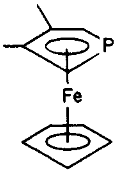
−3.02 V
(· · ·)



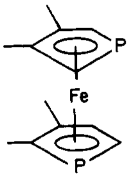
−2.55 V
(· · ·)



−2.15 V
(−2.15 V)



−2.64 V
(−2.55 V)



−2.33 V
(−2.33 V)

Recent quantum mechanical calculations[34] on phosphaferrocenes support these electrochemical results. A simplified molecular orbital diagram for 1 is shown in Figure 5. This diagram demonstrates that the phosphorus lone pairs are at low energy, that the HOMO is localized largely on iron (89%), and that the LUMO is a π-antibonding mixture of iron d orbitals (58%) and ligand orbitals (35%). Comparison of the HOMO and LUMO orbital energies for $(C_4H_4P)Fe(C_5H_5)$ and $(C_4H_4P)_2Fe$ shows that the HOMO is destablized by phosphorus substitution and the LUMO is stabilized.

In addition, the quantum mechanical results suggest that oxidation of phosphaferrocenes should occur by removal of an electron from a molecular orbital that is largely of iron d character in concert with the ESR results. The informations provided by quantum mechanical chemistry are much consistent with the cathodic behavior of 2 and 3 as the observed facilitated reduction for 3 compared with 2 parallels the stabilization of the LUMO. However, in the oxidation process, the predicted[34] easier oxidation for 3 (compared with 2) is not observed experimentally.

Further studies on the electrochemistry of phosphaferrocene complexes are in progress.

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Registry No. 1, 73153-27-2; 2, 63287-56-9; 3, 67887-86-9; 3⁺, 90414-58-7; ferrocene, 102-54-5; dimethylferrocene, 1291-47-0.

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(37) Aged samples of 3 gave no reproducible signals, probably due to oxidation as evidenced by the appearance of ν(P=O) near 1200 cm⁻¹ in IR spectra.