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# Anodic Electrochemistry of Multiferrocenyl Phosphine and Phosphine Chalcogenide Complexes in Weakly Nucleophilic Electrolytes

Frédéric Barrière,[†,‡] Rein U. Kirss,[*,§] and William E. Geiger[*,†]

*Departments of Chemistry, University of Vermont, Burlington, Vermont 05405, and*
*Northeastern University, Boston, Massachusetts 02115*

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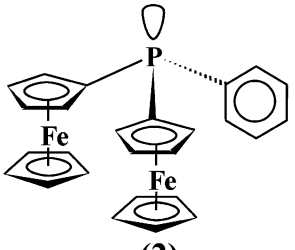
The anodic electrochemistry of several compounds containing two or three ferrocenyl moieties linked by a phosphine or phosphine chalcogenide group has been studied in dichloromethane containing $[NBu_4][TFAB]$, where TFAB is the tetrakis(perfluoroaryl)borate anion, $[B(C_6F_5)_4]^-$. In two cases, namely $[CpFe(C_5H_4)]_3P$ (**3**) and $[CpFe(C_5H_4)]_2P{=}O(Ph)$ (**6**), the first one-electron-oxidation product is stable on the cyclic voltammetric (CV) time scale and subsequent oxidations at more positive potentials are also observed. The oxidations of $[CpFe(C_5H_4)]_2PPh$ (**2**) and $[CpFe(C_5H_4)]_3P{=}Se$ (**7**) are not reversible, and their monocations undergo follow-up reactions that are first-order and second-order, respectively, in the neutral compound. The results are consistent with a model in which the initial oxidation always involves a largely ferrocenyl-based HOMO which, nevertheless, has significant phosphine or phosphine chalcogenide character, allowing radical-type reactions, including dimerizations, at the linking group. The traditional nonaqueous supporting electrolyte anions such as $[PF_6]^-$ and $[BF_4]^-$ are shown to be responsible for many of the earlier difficulties in interpreting the anodic electrochemistry of this oft-studied class of compounds.

## Introduction

Owing in part to the widespread utility of ferrocenyl "redox labels", there is considerable interest in the electron-transfer properties of ferrocenes containing an exocyclic amine or phosphine moiety.[1,2] A number of studies have described the oxidation of ferrocenyl-substituted phosphine complexes. The electrochemically most well-behaved member of this group is ferrocenyldiphenylphosphine, $FeCp(C_5H_4)PPh_2$ (**1**), which is reported by a number of authors to undergo a reversible one-electron oxidation.[3−5] Oxidation of the diferrocenyl−phenylphosphine system $[FeCp(C_5H_4)]_2PPh$ (**2**) is considerably more complex. Originally said to involve simple sequential oxidation of the two ferrocenyl groups,[3b] it was later reported to first oxidize at the PPh group, followed by two subsequent ferrocenyl oxidations.[6,7] A further study concluded that the first oxidative feature was merely an adsorption wave and concentrated on the two reversible waves which followed at more positive potentials.[8] The most recent paper categorized the first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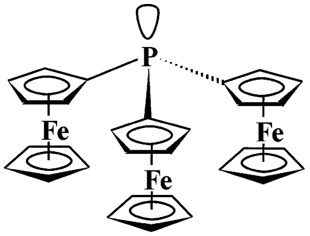
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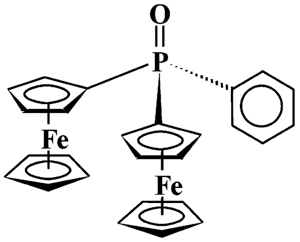
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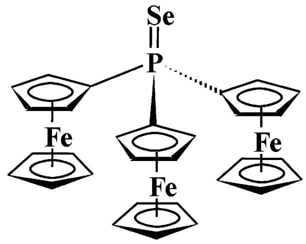
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[*] To whom correspondence should be addressed. E-mail: r.kirss@neu.edu (R.U.K.); wgeiger@zoo.uvm.edu (W.E.G.).

[†] University of Vermont.

[‡] Current address: Université de Rennes I, Rennes, France. E-mail: frederic.barriere@univ-rennes1.fr.

[§] Northeastern University.

(1) Leading references in: (a) Ihara, T.; Nakayama, M.; Murata, M.; Nakano, K.; Maeda, M. *J. Chem. Soc., Chem. Commun.* **1997**, 1609. (b) Horie, M.; Sakano, T.; Osakada, K.; Nakao, H. *Organometallics* **2004**, *23*, 18. (c) Patolsky, F.; Weizmann, Y.; Wilner, I. *J. Am. Chem. Soc.* **2002**, *124*, 770. (b) Stone, D. L.; Smith, D. K.; McGrail, P. T. *J. Am. Chem. Soc.* **2002**, *124*, 856.

(2) Leading references to ferrocenes having Lewis-base substituents: (a) Herberhold, M. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1996; Chapter 5. (b) Arjun, M.; Barlow, S.; Day, M. W.; Marder, S. R. *Organometallics* **1999**, *18*, 454. (c) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 3978.

(3) (a) Kotz, J. C.; Nivert, C. L. *J. Organomet. Chem.* **1973**, *52*, 387. (b) Kotz, J. C.; Nivert, C. L.; Lieber, J. M. *J. Organomet. Chem.* **1975**, *91*, 87.

(4) Gref, A.; Diter, P.; Guillaneux, D.; Kagan, H. B. *New J. Chem.* **1997**, *21*, 1353.

(5) Durfey, D. A.; Kirss, R. U.; Frommen, C. Reiff, W. M. *Inorg. Chim. Acta* **2004**, *357*, 311.

(6) Britton, W. E.; Kashyap, R.; El-Hashash, M.; El-Kady, M.; Herberhold, M. *Organometallics* **1986**, *5*, 1029.

(7) Houlton, A.; Bishop, P. T.; Roberts, R. M. G.; Silver, R. J.; Herberhold, M. *J. Organomet. Chem.* **1989**, *364*, 381.

(8) Butler, I. R.; Griesbach, U.; Zanello, P.; Fontani, M.; Hibbs, D.; Hursthouse, M. B.; Abdul Malik, K. L. M. *J. Organomet. Chem.* **1998**, *565*, 243.

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anodic process as highly irreversible but showed that the chemical oxidation of this compound by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave a clean conversion to the 1:1 salt [**2**][DDQ].[5]

We wondered if these apparently discordant results arose from effects of the solvent/electrolyte medium on the redox mechanism. Therefore, we have investigated the oxidation of **2** in $CH_2Cl_2$/[$NBu_4$][TFAB] (TFAB = $[B(C_6F_5)_4]^-$), a medium that generally lowers the tendency of positively charged oxidation products to undergo electrode adsorption and also minimizes nucleophilic attack on those products.[9−13]

Additional interest in this system arises from the varied findings for other ferrocenyl−phosphine anodic reactions. The voltammetry of tris(ferrocenyl)phosphine, $[FeCp(C_5H_4)]_3P$ (**3**), displays three irreversible oxidation waves in either $CH_3CN$[1b] or $CH_3CN/CH_2Cl_2$[14] solutions containing either $[PF_6]^-$ or $[BF_4]^-$ electrolyte anions, but $[\{FeCp(C_5H_4)\}_3P][DDQ]$ is readily obtained from the reaction of **3** with DDQ in benzene.[5] Downard and coworkers studied the oxidation of $FeCp(C_5H_4)CH_2PPh_2$ (**4**) and showed that the initially formed cation radical undergoes a follow-up reaction at the phosphine.[15] Much of the interest in this series of compounds can be traced back to the importance of the related diphosphine complex $Fe(C_5H_4(PPh_2))_2$ (dppf, **5**).[16] A number of studies have appeared on the electrochemical behavior of **5**,[4,17−19] the most definitive being those of Pilloni et al.[18] and Nataro et al.,[19] in which dimerization of the original radical cation was evident. The latter paper, which utilizes $[B(C_6F_5)_4]^-$ as the electrolyte anion, summarizes the published electrochemistry of dppf.[19] Voltammetry of polymers based on ferrocenylphosphines has also been reported.[20] Questions common to this collection of work are whether the initial oxidation is phosphine-based or ferrocenyl-based and in what way the chemical follow-up reactions are related to this point. This question is relevant not only to ferrocenylphosphine redox chemistry but also to the broader anodic chemistry of metallocenyl groups to which substituents having oxidizable lone pairs have been attached. The present work takes advantage of the favorable properties of the $[B(C_6F_5)_4]^-$ anion to better elucidate the redox behavior of this important class of compounds.

## Experimental Section

All procedures were carried out under an atmosphere of nitrogen using either Schlenk techniques or a Vacuum Atmospheres drybox. The following compounds were prepared as previously described: $[FeCp(C_5H_4)]_2PPh$ (**2**),[3a] $[FeCp(C_5H_4)]_3P$ (**3**),[21] $[FeCp(C_5H_4)]_2P{=}O(Ph)$ (**6**), [3a] and $[FeCp(C_5H_4)]_3P{=}Se$[22] (**7**). Dichloromethane was twice distilled from $CaH_2$, the first time under nitrogen and the second time under static high vacuum. Tetrabutylammonium hexafluorophosphate was prepared by metathesis of $[NBu_4]I$ with $[NH_4][PF_6]$ in acetone/water, recrystallized three times from ethanol, and dried under vacuum. $[NBu_4][B(C_6F_5)_4]$ was prepared by metathesis of $[NBu_4]Br$ with $Li[B(C_6F_5)_4]\cdot nOEt_2$ (Boulder Scientific Co.) in methanol and recrystallized at least twice from $CH_2Cl_2$/hexane. A detailed description of the metathesis procedure is available elsewhere.[23] A standard three-electrode configuration was used for voltammetry and coulometry experiments. In the case of bulk electrolyses a three-compartment cell was used in which the working and auxiliary compartments were separated by two fine frits to minimize mixing of the solutions. The experimental reference electrode was a AgCl-coated Ag wire prepared by anodic electrolysis of a silver wire in HCl solution. All potentials in this paper are referenced, however, to the ferrocene/ferrocenium reference couple.[24,25] To accomplish this, decamethylferrocene was added to the solution as an internal standard at an appropriate time in the experiment, and the measured potential was then altered by the difference between the $[FeCp_2]^{0/+}$ and $[FeCp^*_2]^{0/+}$ potentials in these media. Under our conditions, $[FeCp^*_2]^{0/+}$ is −0.61 V vs ferrocene in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6F_5)_4]$ and −0.55 V vs ferrocene in $CH_2Cl_2$/0.1 M $[NBu_4][PF_6]$. The working electrodes were glassy-carbon disks having a diameter of either 1.5 or 2 mm (Bioanalytical Systems), polished on a Buehler polishing cloth with Metadi II diamond paste, rinsed copiously with Nanopure water, and placed under vacuum for drying. Bulk electrolyses were performed at Pt basket electrodes. The diagnostics employed for voltammetric mechanistic analysis have been described in detail.[26] Since none of the redox reactions appeared to exhibit non-Nernstian charge-transfer rates, in this paper the term "reversibility" refers specifically to the chemical reversibility of a couple.

## Results

**Overview: Effect of Electrolyte Anions.** As noted in the Introduction, medium effects play a role in the published electrochemical results on the present class of compounds. It has recently been shown that a combination of $CH_2Cl_2$ and $[NBu_4][B(C_6F_5)_4]$ as solvent and supporting electrolyte, respectively, provides close-to-optimal conditions for anodic electrochemical studies of multiferrocenyl compounds by minimizing nucleophilic attack by the electrolyte anion and improving product solubilities.[13] Cyclic voltammetric (CV) scans of $[FeCp(C_5H_4)]_2PPh$ (**2**) in $CH_2Cl_2$/0.1 M $[NBu_4][PF_6]$ clearly demonstrate the difficulties faced in earlier studies.[3b,6−8] The first oxidation wave, at ca. 0 V vs ferrocene, has poor chemical reversibility and, in subsequent oxidation waves at more positive potentials, product adsorption is encountered (Figure 1). The broad

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[9] LeSuer, R. J.; Geiger, W. E. *Angew. Chem., Int. Ed.* **2000**, *39*, 248.

[10] Camire, N.; Nafady, A.; Geiger, W. E. *J. Am. Chem. Soc.* **2002**, *124*, 7260.

[11] Barrière, F.; Camire, N.; Geiger, W. E.; Mueller-Westerhoff, U. T.; Sanders, R. *J. Am. Chem. Soc.* **2002**, *124*, 7262.

[12] Barrière, F.; LeSuer, R. J.; Geiger, W. E. In *New Trends in Molecular Electrochemistry*; Pombeiro, A. J. L., Amatore, C., Eds.; FontisMedia: Lausanne, Switzerland, 2004, pp 413−444.

[13] Camire, N.; Mueller-Westerhoff, U. T.; Geiger, W. E. *J. Organomet. Chem.* **2001**, *637−639*, 823.

[14] Durfey, D. A.; Kirss, R. U.; Frommen, C.; Feighery, W. *Inorg. Chem.* **2000**, *39*, 3506.

[15] Downard, A. J.; Goodwin, N. J.; Henderson, W. *J. Organomet. Chem.* **2003**, *676*, 62.

[16] (a) Gan, K.-S.; Hor, T. S. A. In ref 2a, Chapter 1. (b) Cullen, W. R.; Woolins, J. D. *Coord. Chem. Rev.* **1981**, *39*, 1.

[17] Miller, T. M.; Ahmed, K. J.; Wrighton, M. *Inorg. Chem.* **1989**, *28*, 2347.

[18] (a) Corain, B.; Longato, B.; Favero, G.; Ajó, Pilloni, G.; Russo, U.; Kreissl, F. R. *Inorg. Chim. Acta* **1989**, *157*, 259. (b) Pilloni, G.; Longato, B.; Corain, B. *J. Organomet. Chem.* **1991**, *420*, 57.

[19] Nataro, C.; Campbell, A. N.; Ferguson, M. A.; Incarvito, C. D.; Rheingold, A. L. *J. Organomet. Chem.* **2003**, *673*, 47.

[20] Foucher, D. A.; Honeyman, C. H.; Nelson, J. M.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709.

[21] Sollott, G. P.; Mertwoy, H. E.; Portnoy, S.; Snead, J. L. *J. Org. Chem.* **1963**, *28*, 1900.

[22] Sollott, G. P.; Petersen, Jr., W. R. *J. Organomet. Chem.* **1965**, *4*, 491.

[23] LeSuer, R. J.; Geiger, W. E. *Anal. Chem.* **2004**, *76*, 6395.

[24] Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.

[25] Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

[26] Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry,* 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1996; Chapter 23.

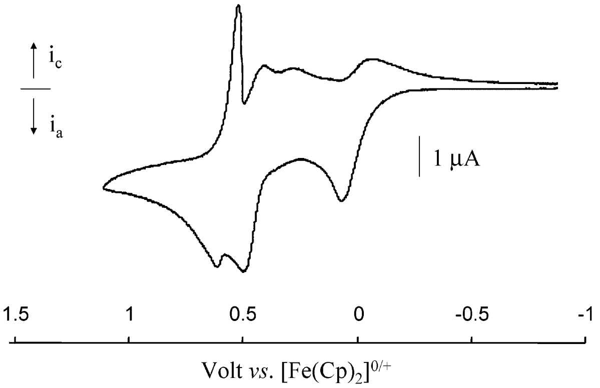

**Figure 1.** CV of 1.0 mM $[CpFe(C_5H_4)]_2PPh$ (**2**) in $CH_2Cl_2$/0.1 M $[NBu_4][PF_6]$ at room temperature ($v = 0.1$ V $s^{-1}$).

**Table 1. Relevant $E_{1/2}$ Potentials in V vs $[FeCp_2]^{0/+}$ for Ferrocenyl (Fc) Derivatives in $CH_2Cl_2/[NBu_4][B(C_6F_5)_4]$**[a]

| | $E_{1/2}$ | | | |
|---|---|---|---|---|
| compd | 0/1+ | 1+/2+ | 2+/3+ | comments |
| $Fc_2PPh$ (**2**) | 0.02 | | | second oxidn not assigned |
| $Fc_3P$ (**3**) | −0.02 | ∼0.5 | | oxidn of 1+ complex |
| $Fc_2P(=O)Ph$ (**6**) | 0.15 | 0.42 | | fully rev |
| $Fc_3P=Se$ (**7**) | 0.16 | 0.45 | 0.77 | rev at high $v$, low concn of **7** |

[a] Table limited to redox couples that can be reasonably assigned. See text for details.

anodic feature at ca. 0.5−0.6 V seemingly arising from the second and third oxidations is subject to electrode history and gives rise to a stripping peak on the reverse scan. Lowering the temperature somewhat improves the chemical reversibility of the first wave but accentuates the adsorption problems. In our hands, bulk electrolysis at 0.25 V ($T = 220$ K) consumed one electron and produced a small amount of what appeared to be $\mathbf{2}^+$ in addition to several unknown follow-up product waves at potentials consistent with those seen at the more positive potentials in CV scans of **2**. As shown below, the electrochemical behavior was simplified in $CH_2Cl_2$ /$[NBu_4][B(C_6F_5)_4]$, owing to greater chemical reversibility of the first oxidation and more consistency in the voltammetric and electrolytic behavior.

**Oxidation of $[FeCp(C_5H_4)]_2PPh$ (2) in $[NBu_4][B(C_6F_5)_4]$.** In this medium the first oxidation ($E_{1/2} =$ 0.02 V, Table 1) displays increased chemical reversibility, although there is a noticeable broadness in the reverse (cathodic) response. If $[PF_6]^-$ is added to the solution, the anodic process becomes irreversible. In the *absence* of $[PF_6]^-$ there is a small "second wave" at ca. 0.3 V (Figure 2) followed by two unresolved anodic features at ca. 0.5 and 0.7 V (not shown). The small wave is assigned to a product arising from decomposition of the primary monocation $\mathbf{2}^+$. Since dimerizations are known to play a role in the follow-up reactions of related radical cations,[15,19] it is important to note that the chemical reversibility of $\mathbf{2}/\mathbf{2}^+$ is *not* sensitive to the concentration of the starting material. To this point, the $i_{rev}/i_{fwd}$ values of the first oxidation of **2** are unchanged at $v = 0.2$ V $s^{-1}$ over a concentration range of 0.15−2.1 mM. This is in contrast to the "decomposition" reactions of both $\mathbf{4}^+$ and $\mathbf{5}^+$ (as well as $\mathbf{7}^+$; vide infra), the rates of which are second order in starting material.[13,19] Bulk anodic electrolysis at the first oxidation wave ($E_{appl} =$ 0.2 V) gave 1 F/equiv but established that $\mathbf{2}^+$ still undergoes long-term follow-up reactions, as evidenced by several product waves in the range −1 to −2 V. Cathodic re-electrolysis of the oxidized solution passed 0.25 F/equiv and resulted in about a 25% yield of original **2**.

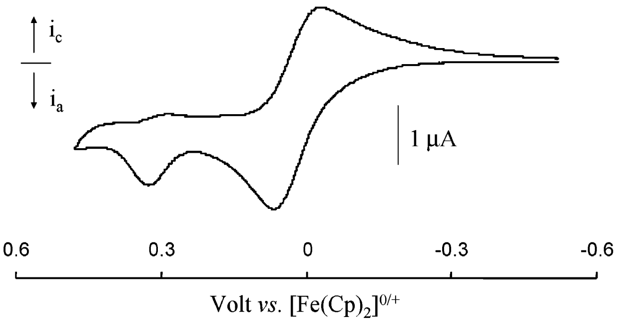

**Figure 2.** CV of 1.0 mM $[CpFe(C_5H_4)]_2PPh$ (**2**), in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6F_5)_4]$ at room temperature ($v = 0.1$ V $s^{-1}$).

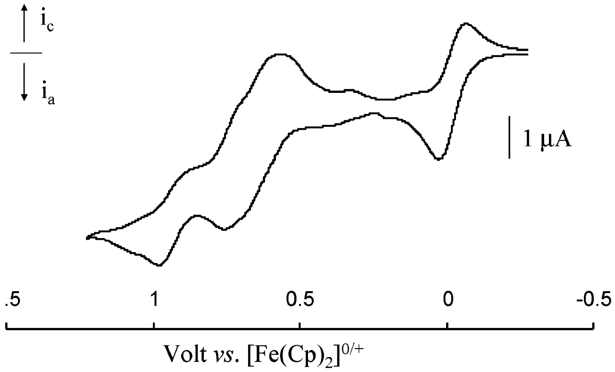

**Figure 3.** CV of 1.0 mM $[CpFe(C_5H_4)]_3P$ (**3**) in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6F_5)_4]$ at room temperature ($v = 0.1$ V $s^{-1}$).

As detailed in the Discussion, these data are consistent with an initial oxidation at a ferrocenyl group followed by a slow follow-up reaction at the nearby phosphine, most likely by an unspecified nucleophile. The much higher stability of the phosphine oxide derivative $\mathbf{6}^+$ (vide infra) supports this interpretation.

**Oxidation of $[FeCp(C_5H_4)]_3P$ (3) in $[NBu_4][B(C_6F_5)_4]$.** The first oxidation of the triferrocenylphosphine **3** is highly reversible by cyclic voltammetry, $E_{1/2} =$ −0.02 V, in contrast to the irreversibility reported earlier in other electrolytes[3b,5] (and confirmed in the present study by CV scans in $CH_2Cl_2$/0.1 M $[NBu_4][PF_6]$). Extending the scan to more positive potentials (Figure 3) reveals a sequence of three or more additional overlapped oxidations from about 0.6 to 0.9 V, several of which have coupled reverse features. Beyond the first one-electron process, the oxidation of **3** appears to be very complex. Bulk oxidation of **3** in $CH_2Cl_2/[NBu_4][B(C_6F_5)_4]$ failed to give $\mathbf{3}^+$, even at 220 K. However, after passage of 1 F/eq ($E_{appl} = 0.2$ V) the strong multipeak activity from 0.6 to 0.9 V is essentially retained. On this basis it appears that the long-term oxidation product of **3** retains three ferrocenyl moieties, most likely having undergone a reaction at the phosphine.

**Oxidation of $[FeCp(C_5H_4)]_2P(=O)Ph$ (6) in $[NBu_4][B(C_6F_5)_4]$.** The phosphine oxide **6** undergoes two highly reversible, ferrocenyl-based, one-electron oxidations to

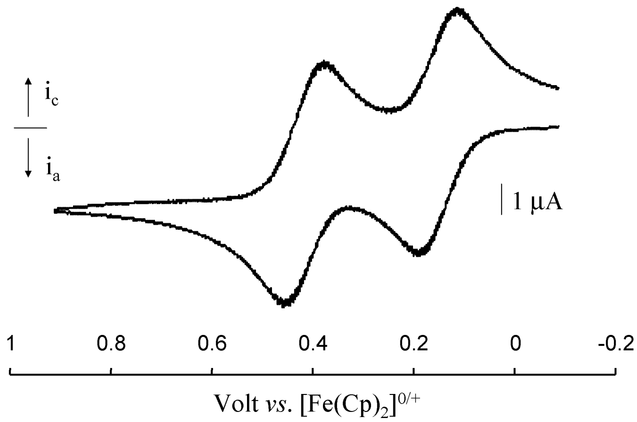

**Figure 4.** CV of 2.2 mM $[CpFe(C_5H_4)]_2P{=}O(Ph)$ (**6**) in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6F_5)_4]$ at room temperature ($v$ = 0.1 V $s^{-1}$).

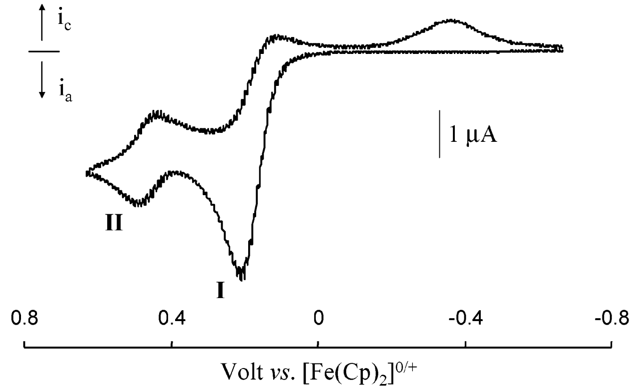

**Figure 5.** CV of 3.8 mM $[CpFe(C_5H_4)]_3P{=}Se$ (**7**) in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6F_5)_4]$ at room temperature ($v$ = 0.1 V $s^{-1}$).

$\mathbf{6}^+$ and $\mathbf{6}^{2+}$ that are separated by 270 mV: $E_{1/2}(1) = 0.15$ V and $E_{1/2}(2) = 0.42$ V (Figure 4). No other waves are observed within the range of +1.5 to −2.0 V. The redox simplicity of the phosphine oxide system contrasts with the complexity of the analogous phosphine complex **2** and lends strong support to the idea that the follow-up reaction of $\mathbf{2}^+$ is likely to take place at the phosphorus atom. The long-term stabilities of the oxidation products of **6** were not explored. There is ample precedent for the reversible oxidation of ferrocenylphosphine oxides, even in the presence of traditional anions such as $[BF_4]^-$ and $[ClO_4]^-$.[4,15]

**Oxidation of $[FeCp(C_5H_4)]_3P{=}Se$ (7) in $[NBu_4][B(C_6F_5)_4]$.** Although the oxidations of multiferrocenyl phosphine sulfides have been reported,[4] we are not aware of anodic studies of the corresponding selenides. The tris(ferrocenyl) derivative **7** displays an interesting series of anodic waves with relative heights and reversibilities that depend on CV scan rate and on analyte concentration. Under conditions of *slow* scan rates and *high* concentrations the first oxidation wave (**I**, $E_{1/2}$ = 0.16 V) is almost completely *ir*reversible (Figure 5, $v$ = 0.1 V $s^{-1}$, concentration 3.8 mM) and gives a cathodic wave due to a follow-up product at −0.35 V. At more positive potentials, two other waves appear, both reversible, but with peak heights that are different from that of the first wave (the second peak (**II**) at $E_{1/2}$ = 0.45 V is smaller and the third peak (**III**) at $E_{1/2}$ = 0.77 V is larger). The heights of the last two features change with increased scan rates until they take on the characteristics of three successive, essentially reversible, processes (Figure 6, $v$ = 10 V/s, concentration 3.8 mM). The faster scan outruns the follow-up reaction after the formation of $\mathbf{7}^+$, allowing measurement of the three separate oxidations of **7** (Table 1) and determination of the separation of the successive redox processes ($E_{1/2}(2) - E_{1/2}(1)$ = 320 mV, $E_{1/2}(3) - E_{1/2}(2)$ = 290 mV). More modest scan rates are needed to obtain chemical reversibility for **7** at lower concentrations (Figure S1, $v$ = 0.5 V $s^{-1}$, concentration 0.2 mM). The follow-up reaction of $\mathbf{7}^+$ is therefore shown to be second order in either **7** or $\mathbf{7}^+$, suggesting possible dimerization at the P=Se moiety.

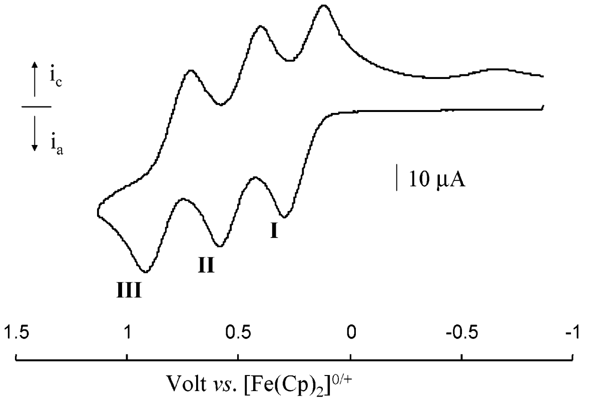

**Figure 6.** CV of 3.8 mM $[CpFe(C_5H_4)]_3P{=}Se$ (**7**) in $CH_2Cl_2$/0.1 M $[NBu_4][B(C_6F_5)_4]$ at room temperature ($v$ = 0.1 V $s^{-1}$).

## Discussion

The use of $[B(C_6F_5)_4]^-$ as the supporting electrolyte anion permits a systematic approach to what has previously been a confusing series of studies on the anodic reactions of multiferrocenyl phosphines and phosphine chalcogenides. Although the first oxidations of $[FeCp(C_5H_4)]_2PPh$ (**2**) and $[FeCp(C_5H_4)]_3P$ (**3**) occur at potentials very close to that of ferrocene, the very un-ferrocenium-like follow-up reactions of $\mathbf{2}^+$ and $\mathbf{3}^+$ suggest that the monocations have a significant radical cation character at the phosphorus atom, making them susceptible to attack by nucleophiles. Supporting electrolyte anions such as $[PF_6]^-$ appear to be active in these reactions, and other weak nucleophiles, possibly even the phosphorus atom of the neutral starting material, must be considered. The fact that these reactions are considerably *slower* than those which follow the oxidation of organic phosphines such as $PPh_3$[27] is ascribed to the charge delocalization intrinsic to the ferrocenyl group(s). The electrochemical results also shed light on recently reported physical data on the oxidation products of **2**, **3**, and $[CpFe(C_5H_4)]_2P^tBu$ by DDQ.[5] In each case the product is shown by Mossbauer spectroscopy to contain low-spin Fe(II), consistent with significant phosphine character in the SOMO of the cations.

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(27) (a) Culcasi, M.; Berchadsky, Y.; Gronchi, G.; Tordo, P. *J. Org. Chem.* **1991**, *56*, 3537. (b) Toshikatsu, T.; Abe, A.; Suda, K.; Ohmori, H. *J. Chem. Soc., Chem. Commun.* **1990**, 1310. (c) Kargin, Yu.; Nikitin, E. V.; Parakin, O. V.; Romanov, G. V.; Pudovik, A. N. *Dokl. Akad. Nauk SSSR* **1978**, *241*, 131; *Chem. Abstr.* **1978**, *89*, 119655. (d) Kargin, Yu.; Nikitin, E. V.; Parakin, O. V.; Mironov, B. S.; Pudovik, A. N. *Dokl. Akad. Nauk SSSR* **1976**, *226*, 1101.

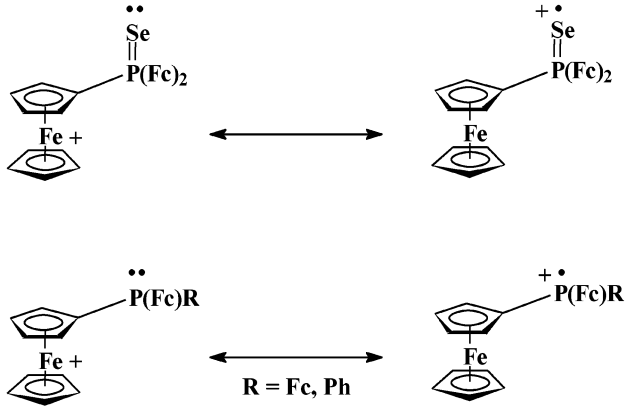

**Figure 7.** Valence isomers of monocationic forms of either phosphine or phosphine chalcogenide complexes.

In the oxide complex $[FeCp(C_5H_4)]_2P{=}O(Ph)$ (**6**) the phosphine is essentially eliminated as a reaction site and the two stepwise oxidations of the ferrocenyl groups are fully reversible. This is consistent again with results on the chemical oxidations of **6** and $[CpFe(C_5H_4)]_2P{=}O(Et)$ by DDQ, which lead to partial oxidation of the ferrocenyl moiety.[28] Interestingly, the oxidation of $[FeCp(C_5H_4)]_3P{=}Se$ (**7**) once again takes on reactive complexity. Under shorter time scale (CV) conditions, the oxidations of all three ferrocenyl groups are observed. The fact that these stepwise oxidations are well-separated in $E_{1/2}$ values (by ca. 300 mV apiece) means that there is some through-bond charge delocalization that must incorporate the phosphorus atom. The partial radical character at the P=Se group is likely responsible for the second-order follow-up reaction of **7**$^+$.

A simple explanation for the different behaviors of **6**$^+$ and **7**$^+$ arises from consideration of the polarity of the phosphorus−chalcogen bond. On the basis of Pauling electronegativities, the P=O bond in **6** has partial negative charge on the oxygen atom. The fact that phosphorus is more electronegative than selenium leads to a reversal of the P=E bond polarity in **7**, giving a more chalcogenide-centered radical that undergoes dimerization, mimicking the behavior of organoselenide radicals.[29] Our interpretations are visually summarized in Figure 7, using valence isomers to depict contributions from both Fe(III) and P or Se radical character in the monocations of this series.

## Summary

Excluding traditional anions such as $[PF_6]^-$ from the supporting electrolyte, in favor of the very weakly nucleophilic and highly lipophilic $[B(C_6F_5)_4]^-$, improves the chemical reversibilities of the redox couples of the title compounds and simplifies the electrochemical mechanistic inquiries. The most facile one-electron oxidation of phosphine or phosphine chalcogenide complexes multiply substituted with ferrocenyl groups involves a HOMO which is predominantly ferrocenyl in character. Reactions which follow the electron-transfer process are, however, generally characteristic of phosphine or phosphine chalcogenide radical cations and may be first order or second order in the complex.

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**Supporting Information Available:** A figure giving the CV of 0.2 mM **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[28] Kirss, R. U. Unpublished data. The Mossbauer spectrum of $[Fc_2P({=}O)(Et)][DDQ]$ at 293 K consists of a doublet at $\delta = 0.498$ mm s$^{-1}$ and DEQ = 2.32 mm s$^{-1}$, typical of low-spin Fe(II). An extremely broad signal at $\delta \approx 0.4$ mm s$^{-1}$ is characteristic of ferrocenium cations. Similar features are seen in [**6**][DDQ], as described in ref 14.

[29] Liotta, D., Ed. *Organoselenium Chemistry*; Wiley: New York, 1987.