

Articles

Electron-Transfer Properties of Cp*FeP₅: Evidence for Dimerization Reactions following both Oxidation and Reduction

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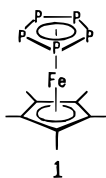
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The redox reactions of Cp*Fe(η^5 -P₅) (**1**; Cp* = η^5 -C₅Me₅) have been characterized in nonaqueous solvents by electrochemical methods. As anticipated by analogy with ferrocene, **1** may be both oxidized and reduced in one-electron processes. Both processes are irreversible by cyclic voltammetry but reversible by bulk electrolysis. In CH₂Cl₂ complex **1** oxidizes initially to 17-electron **1**⁺ ($E_{p,a} = 0.57$ V vs Fc), which rapidly equilibrates to give the dimeric dication [**1**₂]²⁺. An ESR spectrum attributed to **1**⁺ is consistent with a d⁵ iron sandwich complex. A dimerization rate constant for **1**⁺ of $k_{D(17)} = 1.4 \times 10^4$ M⁻¹ s⁻¹ was determined from cyclic voltammetry (CV) data. The dimeric dication quantitatively re-forms neutral **1** upon rereduction. Complex **1** undergoes reduction ($E_{1/2} = -2.00$ V) to 19-electron **1**⁻, which also appears to dimerize in THF; $k_{D(19)} = \text{ca. } 6 \times 10^5$ M⁻¹ s⁻¹. Reoxidation of the diamagnetic dimer [**1**₂]²⁻ regenerates **1**. The shifts in potential induced when replacing a cyclopentadienyl ring by a pentaphosphacyclopentadienyl ring, explicable in terms of the weaker electron-donating ability of the latter, are greater for the reductions than the oxidations, implying an increased P₅ character to the LUMO of **1** compared to the HOMO. Possible structures of the dimeric ions are discussed in terms of known structural analogues and previously published molecular orbital descriptions.

Introduction

The redox properties of Cp*Fe(η^5 -P₅) (**1**; Cp* = C₅Me₅)^{1–4} are of interest because of the close analogy between this compound and ferrocene.⁵ Molecular or-



bital calculations indicate that the HOMO of **1** is a_g, in contrast to the e_{2g} HOMO of ferrocene.⁶ Although electrochemical studies of monophosphacyclopentadi-

enyl analogues have appeared,^{7,8} no information has been published concerning the ionization potentials and/or the redox potentials of **1** or other mononuclear complexes containing the pentaphosphacyclopentadienyl ligand^{9a} (the electron-transfer properties of the triple-decker complexes Cp*₂M₂(P₅) (M = Cr, Mo, W, V) were characterized by Kaim and co-workers).^{9b}

The present study shows that complex **1** undergoes one oxidation and one reduction, each involving one electron, within the usual potential window in nonaqueous solutions. In terms simply of the number of one-electron processes, its behavior mirrors that of ferrocene and a number of sandwich complexes containing one or two monophosphacyclopentadienyl complexes (vide infra). The chemical fates of the one-electron products are strikingly different, however. Both the 17-electron cation **1**⁺ and the 19-electron anion **1**⁻ are short-lived and undergo reactions that are second-order in the iron complex. The apparently dimeric products can each be re-electrolyzed to give back the starting material **1**. It

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(1) Scherer, O. J.; Brueck, T. *Angew. Chem.* **1987**, *99*, 59; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 59.

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(9) (a) CV data on **1** was obtained elsewhere: Elvers (Elvers, A. Ph.D. Dissertation, Erlangen, Germany, 1998) reports $E_{p,a} = 1.19$ V for oxidation and $E_{p,c} = -1.67$ V for reduction in CH₂Cl₂ (vs SCE). (b) Scherer, O. J.; Schwalb, J.; Swarowsky, H.; Wolmershaeuser, G.; Kaim, W.; Gross, R. *Chem. Ber.* **1988**, *121*, 443.

is significant that throughout both chemically reversible redox sequences, namely the *oxidation* of **1** followed by rereduction of the product and the *reduction* of **1** followed by reoxidation of the product, the cyclic P₅ ring remains coordinated to the metal.

Experimental Section

All operations were conducted under an atmosphere of dinitrogen using standard Schlenk and drybox procedures. Solvents were distilled from drying agents before use, and electrochemical experiments were conducted with solvents that were vacuum-distilled from drying agents into flasks that were transferred into the drybox. Complex **1** was obtained from Dr. T. Mohr and Prof. O. J. Scherer (University of Kaiserslautern) and used as received. Tris(*p*-bromophenyl)ammonium hexafluorophosphate was prepared according to the literature.¹⁰

Reagent-grade dichloromethane was twice distilled from CaH₂, and THF was subjected to successive distillations from CaH₂, K, and (deep purple) K/benzophenone. 1,2-Difluorobenzene (Strem) was stirred over and vacuum-distilled from activated alumina. The supporting electrolyte was generally 0.1 M [NBu₄][PF₆], recrystallized from 95% EtOH and dried at 373 K under vacuum for at least 2 days. For subambient-temperature work in THF, [NBu₄][CF₃SO₃] was employed as supporting electrolyte for solubility reasons. Prepared by the procedure of Dolphin et al.,¹¹ the salt was successively recrystallized from Et₂O and a 3/1 CH₂Cl₂/Et₂O mixture to yield a waxlike white solid which was finely crushed and dried at 351 K under vacuum. Although a silver/silver chloride electrode was used as the experimental reference electrode, all potentials in this paper are referred to the ferrocene/ferrocenium couple; on a practical basis, the latter was obtained by adding ferrocene as an internal standard at an appropriate point in each experiment. Since the electrochemical behavior of **1** appeared to be identical on Pt, Au, and glassy C electrodes, only the results on Pt are presented here. Homemade Pt disks of diameter 125, 250, or 625 μm were employed for cyclic voltammetry (CV) scans, the choice of electrode depending on scan rate. Steady-state voltammograms were recorded at a Pt electrode rotating at 1800 rpm. The area of a larger Pt disk (*A* = 0.35 cm²) used for chronoamperometry studies was calibrated using the diffusion coefficient reported for ferrocene in CH₃CN by Hershberger et al.^{12a}

Voltammetric measurements were performed using a PARC Model 173 potentiostat interfaced to home-written software. Along with the electrochemical cell, the electrometer monitor was housed inside the drybox in order to minimize noise. Solution temperatures were controlled to better than 1 °C by immersion of the electrochemical cell in a temperature-controlled (FTS Systems) heptane bath. Bulk electrolyses were conducted in a cell having two compartments separated by a 20 mm fine frit; a Pt-gauze cylinder was used as the working electrode, and coulometry was monitored with a PARC Model 276 plug-in. Mechanistic criteria for diffusion control, reversibility, etc. were applied as described earlier.¹³ Measurement of the peak potential shifts for **1** in THF as a function of the CV scan rate utilized an internal standard of decamethylferrocene in order to account for resistive losses. The anodic peak height of the standard was equal to the cathodic peak height of **1** in these experiments.

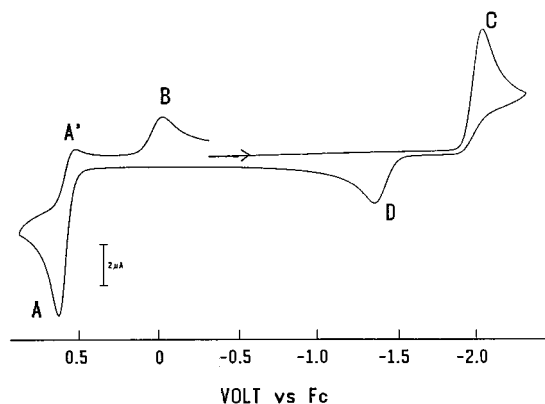


Figure 1. Cyclic voltammogram of 0.5 mM **1** in CH₂Cl₂/0.1 M [NBu₄][PF₆] at 260 K (*v* = 0.5 V/s, Pt electrode).

ESR spectra were measured with a modified Varian E-4 spectrometer using dpph as a standard. Samples were transferred from electrolyzed solutions into ESR tubes, capped with a rubber septum, removed from the drybox, and immediately frozen at 77 K until ESR analysis.

Results and Discussion

It will be shown below that both the anodic and cathodic reactions of **1** proceed through ECEC mechanisms; that is, fast chemical reactions follow each electron-transfer step observed for this complex and its electrode products. Peaks A and B (Figure 1) comprise a chemically reversible oxidation/reduction couple, and peaks C and D constitute a chemically reversible reduction/oxidation couple. The fully oxidized and fully reduced products are very reactive and have resisted our efforts to isolate them. ESR measurements and voltammetric mechanistic studies shed light, however, on their probable structures.

Oxidation of 1. Complex **1** has a single anodic wave (peak A in Figure 1) in CH₂Cl₂ which is irreversible at slow scan rates, *n* (except at very low concentrations, vide infra), apparently involving one electron (constant current function from 0.1 to 1 V/s; diffusion coefficient at 269 K 1.80 × 10⁻⁵ cm²/s; cf. diffusion of ferrocene in CH₂Cl₂ at 1.4 × 10⁻⁵ cm²/s;^{12b} *E_p* - *E_{p/2}* = 46–48 mV at 250 K compared to 48 mV expected for a Nernstian one-electron process).¹³ Qualitatively similar behavior was observed when the solvent was 1,2-difluorobenzene. The presence of a coupled cathodic wave (peak A', Figure 1) at higher scan rates established the *E*_{1/2} value as 0.57 V vs Fc and gave evidence for at least transient **1**⁺. Since the single product wave (B, *E_{p,c}* = -0.03 V) found at lower scan rates is ascribed to reduction of the dimer [**1**₂]²⁺ on the basis of concentration studies, the oxidation mechanism of **1** is written as a dimerization following reversible electron transfer (eqs 1 and 2; the dimerization rate constant is designated as *k*_{D(17)} since the reaction involves the 17-electron cation **1**⁺).



The potentials for oxidation and reduction of **1** are given in Table 1 along with those for related complexes that are compared below.

(10) (a) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577. (b) See also references in: Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

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Table 1. Redox Potentials ($E_{1/2}$, V vs Ferrocene) of Phosphaferrocenes and Selected Ferrocenes

complex	0/1+	0/1-	$\Delta E_{1/2}^a$	conditions
Cp*FeP ₅ (1)	0.57	-2.00	2.57	this work
(PC ₄ H ₄) ₂ Fe	0.38	-2.55	2.93	PC, room temp ^b
(2,5-Me ₂ PC ₄ H ₂) ₂ Fe	0.23	-2.84	3.07	glyme, 233 K ^c
(3,4-Me ₂ PC ₄ H ₂) ₂ Fe	0.17	-2.73	2.90	PC, room temp ^b
CpFe(3,4-Me ₂ PC ₄ H ₂)	0.12	-2.95	3.07	PC, room temp ^b
(PC ₄ Me ₄) ₂ Fe	0.08	-3.00	3.08	glyme, 233 K ^c
Cp ₂ Fe	0	-3.43 ^d	3.43	
Cp(Me ₂ C ₅ H ₃)Fe	-0.10	not obsd	<i>e</i>	
Cp*CpFe	-0.25	not obsd	<i>f</i>	

^a Difference of $E_{1/2}$ potentials of the two columns. ^b Reference 7: PC = propylene carbonate, room temp = ambient temperature. ^c Reference 8. ^d Reference 23b. ^e ^f The potential of this compound is extrapolated from the value for Cp(Me₂C₅H₃)Fe, subtracting 50 mV per methyl group added.

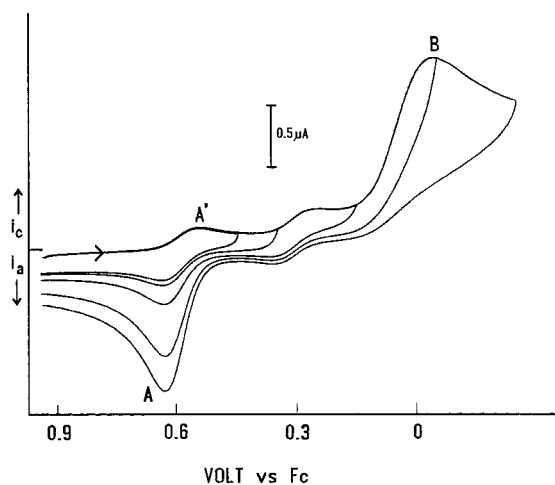


Figure 2. CV scans taken after bulk anodic oxidation of **1** (scan rate 0.2 V/s). Scans were initiated positive of 0.9 V and taken to increasingly negative values. The reduction waves for 1^+ (wave A') and $[1_2]^{2+}$ (wave B) are observed along with a small unassigned cathodic feature at about 0.3 V.

Bulk oxidation of **1** was accomplished in several trials at temperatures between 250 and 260 K with $E_{\text{appl}} = 0.8$ V. The original pale green solution turned orange-brown in the process, and the major electroactive product had a reduction wave (Figure 2, peak B) at -0.03 V. Exhaustive reduction of the orange-brown solution negative of peak B ($E_{\text{appl}} = -0.5$ V) regenerated the original green solution of **1** (coulometry: 1.1 faradays/equiv) with overall yields of 85–93% (CV peak heights, steady-state voltammograms).¹⁴

A closer inspection of CV scans taken after the bulk oxidation reveals the apparent presence of a minor quantity of 1^+ in solution. In Figure 2, scans initiated at a quiescent potential positive of the initial wave A are taken to increasingly negative values. The small cathodic wave A' arising from reduction of 1^+ is clearly

(14) Bulk anodic coulometry on **1** was complicated by the slow regeneration of **1** under the conditions of the oxidation. The electrolysis current did not drop below about 5% of the initial value even after long electrolysis times. After about 1 h, the charge passed was consistent with approximately 2 faradays/equiv. This type of behavior is frequently encountered when oxidations are performed at very positive potentials and is usually ascribed to the tendency of the oxidized form to react with adventitious nucleophiles such as trace water. The electrolytic behavior is consistent with our observation that attempts to isolate the oxidation product always led to solids highly contaminated with **1**.

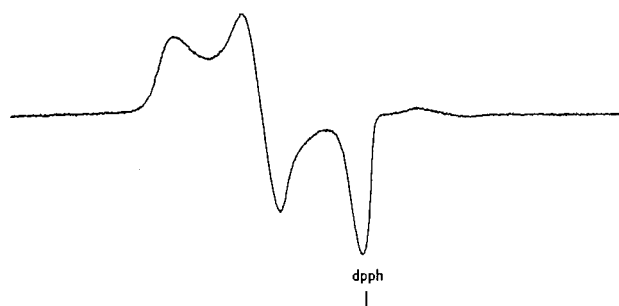


Figure 3. ESR spectrum at 77 K of 1^+ in 1/1 CH₂Cl₂/C₂H₄-Cl₂ produced by reaction of **1** with equimolar [(*p*-BrC₆H₄)₃N]⁺.

observed at about 0.5 V. As will be shown below, these data are consistent with the presence of 1^+ as the minor component and the dimeric dication $[1_2]^{2+}$ as the major component. An estimate of the equilibrium constant for eq 2 can be obtained if it is assumed that the cathodic peak heights reflect a "frozen" condition, $K_{\text{dim}} = \text{ca. } 2 \times 10^4 \text{ M}^{-1}$.

The oxidized solution displayed an ESR signal at 77 K with a rhombic *g* tensor ($g_1 = 2.1961$, $g_2 = 2.1095$, $g_3 = 2.0071$) which was also observed when **1** was chemically oxidized with [(*p*-BrC₆H₄)₃N]⁺ in 1/1 CH₂Cl₂/C₂H₄-Cl₂ at 196 K and then frozen (Figure 3). Although these solutions could be repeatedly warmed to room temperature and refrozen to give virtually the same signal intensity, fluid solutions were always ESR-silent.

The marginal stability of the oxidation product frustrated our attempts to isolate it. For example, oxidation of **1** by [(*p*-BrC₆H₄)₃N]⁺ gave solutions that appeared to be stable for 24 h at 243 K, but workup always gave solids contaminated significantly with **1** (NMR and voltammetry evidence) even when the isolation procedures were conducted below 250 K. The oxidation product was found to be unreactive to either hexamethylbenzene or triphenyl phosphite (20- to 100-fold excesses) over 30 min, suggesting that it does not contain a coordinatively unsaturated metal.

Relatively few reactions can be envisioned which may give rise to an efficient chemically reversible process coupled to the oxidation of **1** in these media. The most likely of these are a structural reorganization, H-atom abstraction and loss, and dimerization.¹⁵ Since only the last of these is higher order in reactant, a test of the anodic response as a function of the concentration of **1** was undertaken.

Cyclic voltammograms were obtained on a series of solutions at five different concentrations of **1** between the limits of 0.11 and 1.47 mM at 252 K. A large effect of concentration on the reversibility of the anodic wave was observed, with a scan rate of 75 V/s being required to achieve full chemical reversibility at the highest concentration, in contrast to 2 V/s at the lowest. Representative CV curves from these experiments are given in Figure 4. Table 2 gives the ratio of the reverse to forward peak currents¹⁶ for a single scan rate (1 V/s) at various concentrations. These ratios as well as those

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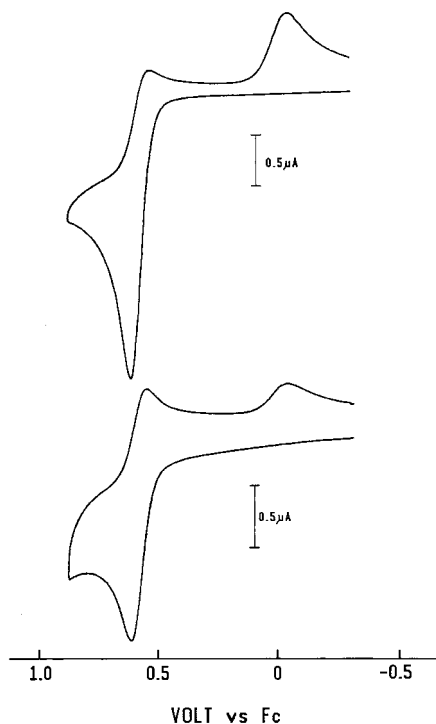


Figure 4. CV scans of oxidation of **1** in $\text{CH}_2\text{Cl}_2/0.1 \text{ M} [\text{NBu}_4][\text{PF}_6]$ at 252 K (Pt electrode, $\nu = 0.5 \text{ V/s}$) at two different concentrations: (top) 1.47 mM; (bottom) 0.42 mM.

Table 2. Reversibility Values^a for the Couple $1/1^+$ and Dimerization Rate Constants $k_{\text{D}(17)}$ as a Function of Concentration ($\nu = 1.0 \text{ V/s}$)^a

concn (mM)	reversibility ^b	$10^{-4}k_{\text{D}(17)} (\text{M}^{-1} \text{ s}^{-1})^c$
0.11	0.96	0.9(0.2)
0.27	0.91	1.3(0.2)
0.42	0.71	1.4(0.4)
0.54	0.69	1.4(0.2)
0.77	0.62	1.3(0.2) ^d
0.88	0.58	1.7(0.3)
1.47	0.48	2.1(0.5)

^a Conditions: 252 K, $\text{CH}_2\text{Cl}_2/0.5 \text{ M} [\text{NBu}_4][\text{PF}_6]$, Pt electrode.

^b The value i_c/i_a for the couple A/A' of Figure 4 was measured by the method of Nicholson.¹⁶ These are given for illustrative purposes to show how the chemical reversibility of the oxidation of **1** decreases with increasing concentration. ^c Rate constant calculated from reversibility values as a function of scan rate within a range in which i_c/i_a varied between 0.5 and 0.9, using the method of Lasia.¹⁷ The values in parentheses are standard deviations from determinations at a minimum of six scan rates. ^d This value was obtained in an experiment separate from the others in the table.

at other scan rates were used to extract the second order rate constant, $k_{\text{D}(17)}$ in eq 2, according to the procedure of Lasia,¹⁷ the results being collected in Table 2. The average value of $k_{\text{D}(17)}$ was $[1.4 (\pm 0.3)] \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. With this estimate of $k_{\text{D}(17)}$ in hand we then calculated theoretical voltammograms for comparison with the entire CV curve, getting good overall agreement (Figure 5) with $k_{\text{D}(17)} = 1.28 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ over the entire concentration range. The voltammetric data are therefore entirely consistent with the oxidation product being a dimeric dication, which we designate $[\mathbf{1}_2]^{2+}$. We defer a discussion of its probable structure until later in the paper.

Reduction of 1. Remarkably, the reduction of **1** mirrors the behavior of its oxidation: a single cathodic

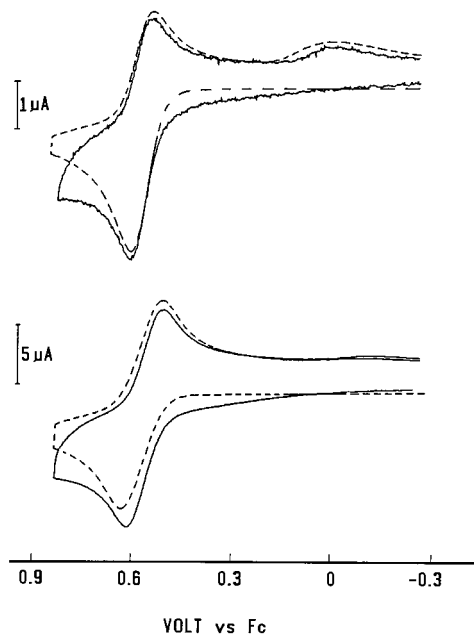


Figure 5. Comparison of experimental (solid line) and calculated (dashed line) cyclic voltammograms for oxidation of **1** in CH_2Cl_2 at 252 K: (top) concentration 0.42 mM, $\nu = 2.5 \text{ V/s}$; (bottom) concentration 1.47 mM, $\nu = 50 \text{ V/s}$. Simulation parameters were $E_{1/2}(\mathbf{1}) = 0.57 \text{ V}$, $k_s(\mathbf{1}) = 1 \text{ cm s}^{-1}$, $1 - \alpha = 0.32$; $E_{1/2}(\mathbf{1}_2^{2+}) = 0.02 \text{ V}$, $k_s = 0.03 \text{ cm s}^{-1}$, $\alpha = 0.25$, dimerization $K_{\text{eq}} = 100$, $k_{\text{D}(17)} = 1.28 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $R_u = 8000 \Omega$, $C_{\text{dl}} = 0.02 \mu\text{F}$.

wave (peak C) is observed ($E_{\text{p,c}} = -2.05 \text{ V}$ at $\nu = 0.2 \text{ V/s}$) with a single anodic product wave (peak D) on the reverse scan at $E_{\text{p,a}} = -1.34 \text{ V}$ (Figure 1). Identical results are found in THF, dichloromethane, and 1,2-difluorobenzene. A number of facts establish that the cathodic wave is a one-electron process, most notably bulk coulometry (1.01 faradays/equiv), peak height (0.9 times that of the one-electron oxidation wave of **1**, discussed above, in CH_2Cl_2), and peak breadth ($E_{\text{p}/2} - E_{\text{p}} = 45 \text{ mV}$ at 236 K compared to 47 mV for ferrocene). Assuming a one-electron process, a diffusion coefficient of $8.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was calculated from chronoamperometry data for **1** in THF at 238 K.

The reduction wave at -2.05 V (peak C) and the oxidation wave at -1.34 V (peak D) constitute a chemically reversible couple. Double-potential step chronoamperometry (5 s step time) between step potentials of -1.1 and -2.3 V gave reverse-to-forward current ratios exactly the same as that of ferrocene/ferrocenium, and bulk electrolysis demonstrated the overall reversibility on a longer time scale. Concerning the latter, coulometric reduction at $E_{\text{appl}} = -2.3 \text{ V}$ gave a deep green solution with the major anodic product wave at $E_{\text{p,a}} = -1.3 \text{ V}$, consistent with CV experiments (wave D), and a smaller wave at $E_{\text{p,a}} = -1.05 \text{ V}$. Scanning negative to positive through the product wave(s) (Figure 6) demonstrates that **1** is regenerated from the reoxidation scans. Bulk reoxidation at $E_{\text{appl}} = -0.7 \text{ V}$ gave back the starting material **1** in 80–90% yield in several replicates at ca. 270 K. The final reoxidized solution also showed a small reversible wave at $E_{1/2} = -0.5 \text{ V}$ which is most likely due to Cp^*_2Fe . The reduced solutions were ESR-silent when frozen at 77 K, and they did not react with an excess of hexamethylbenzene.

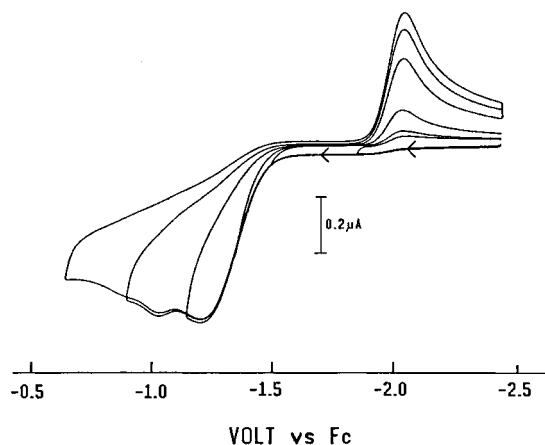
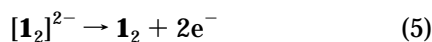
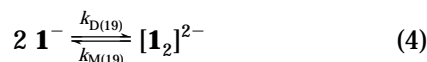


Figure 6. CV scans of $\mathbf{1}_2^{2-}$ in THF/0.1 M [NBu₄][PF₆] ($\nu = 0.5 \text{ V s}^{-1}$) from -2.45 V to increasingly positive potentials at 252 K. $\mathbf{1}_2^{2-}$ was prepared from bulk electrolytic reduction of a solution of $\mathbf{1}$ at $E_{\text{appl}} = -2.3 \text{ V}$.

Mechanistic information is obtained from the manner in which the peak potentials of the cathodic wave of $\mathbf{1}$ (peak C) and of the anodic product wave D vary with CV scan rate at 236 K. Over the range $0.05 \text{ V/s} < \nu < 10 \text{ V/s}$, $E_{\text{p,c}}$ (peak C) shifted negative by 20 mV per 10-fold increase in ν and $E_{\text{p,a}}$ (peak D) shifted positive by 56 mV ($T = 240 \text{ K}$). The cathodic behavior is consistent with a fast chemical reaction following electron transfer (i.e., an EC mechanism), but the data are not sufficiently precise to distinguish between a first-order reaction (expected shift 24 mV)¹⁸ and a dimerization reaction (expected shift ca. 20 mV).¹⁹ (We show below that concentration variations support a dimerization model).

The anodic behavior (peak D) is diagnostic, however, of a one-electron *irreversible* charge transfer (expected peak potential shift vs $\log \nu$ for $\alpha = 0.5$ system, 48 mV; observed shift of 56 mV consistent with system having $1 - \alpha = 0.42$).²⁰ The increased *breadth* of the product wave D ($E_{\text{p,a}} - E_{\text{p,a/2}} = 70 \text{ mV}$ at room temperature) is also consistent with irreversible electron transfer, ($1 - \alpha = \text{ca. } 0.4$).

All electrochemical data on the reduction of Cp*FeP₅ may therefore be understood in terms of eqs 3 and 4, which describe a reversible one-electron reduction of $\mathbf{1}$ (eq 3), followed by a fast dimerization reaction (rate constant $k_{\text{D}(19)}$, eq 4) giving the dianion $[\mathbf{1}_2]^{2-}$ for the cathodic process; the coupled anodic process involves an irreversible (slow charge transfer) oxidation of the dimeric dianion (eq 5) followed by rapid cleavage of the neutral dimer (eq 6) to give back $\mathbf{1}$.



Although the anodic reaction of eq 5 has a net stoichiometry of two electrons, the voltammetric peak

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(20) We write the transfer coefficient as $1 - \alpha$ for an oxidation and as α for a reduction.



breadth shows that a single electron is involved in its rate-determining step.

The dimerization of the 19-electron system $\mathbf{1}^-$ was further probed by investigating the concentration dependence of the chemical reversibility of the couple $\mathbf{1}/\mathbf{1}^-$ (eq 3). These experiments verified the dimerization hypothesis, albeit less quantitatively than achieved in the case of the 17e⁻ system. Some chemical reversibility was observed for $\mathbf{1}/\mathbf{1}^-$ at $\nu = 10 \text{ V/s}$ ($E_{1/2} = -2.00 \text{ V}$) with a concentration of 0.2 mM. Because of the combination of high scan rates, low concentrations, low temperature, and a highly resistive solvent, we performed only semiquantitative simulations of the CV curves. These calculations allow a conclusion that the dimerization rate for $\mathbf{1}^-$ must be between 5×10^5 and $6 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, i.e., about 40 times higher than observed for the 17-electron system $\mathbf{1}^+$.

Analysis of Redox Potentials. The $E_{1/2}$ potentials for the oxidation and reduction processes of $\mathbf{1}$ may be compared with those observed for analogues including ferrocene derivatives and sandwich complexes with one or two monophosphacyclopentadienyl rings (Table 1). Although the values were obtained under different conditions, the potentials of $\mathbf{1}$ appear to be explicable in terms of a more or less additive substituent effect when P is substituted for CH in the five-membered cyclic ligand.

When the oxidation potential of $\mathbf{1}$ ($E_{1/2} = 0.57 \text{ V}$) is compared with that of Cp*CpFe ($E_{1/2} = -0.25 \text{ V}$), a positive shift of 820 mV is noted with the change of five groups (P for CH), an average of 164 mV per substitution. Previous work by other groups demonstrated similar shifts for *single* substitutions in monophosphacyclopentadienyl complexes. Thus, Lemoine et al. found the oxidation of (PC₄H₄)₂Fe at $E_{1/2} = 0.38 \text{ V}$ vs ferrocene, a shift of 190 mV per P-for-CH substitution.⁷ Similarly, the potential for oxidation of (2,5-Me₂PC₄H₂)₂-Fe measured by Elschenbroich et al. (Table 1) is shifted by 430 mV from a ferrocene with four Me groups, a change of 215 mV per P-for-CH substitution.⁸ Lemoine et al.'s measurement on the isomer (3,4-Me₂PC₄H₂)₂Fe gives a value of 185 mV per substitution. The average shift for a single substitution from these previous studies is 196 mV. We conclude therefore that the more positive oxidation potential of $\mathbf{1}$ compared to that of ferrocene can be understood qualitatively as arising from the weaker electron-donating ability of phospholyl rings compared to Cp rings^{21,22} and quantitatively as an approximately additive effect of this electron-donating ability as several ring substitutions are involved. The overall shift for five P atoms (820 mV) is somewhat less than 5 times the single shift ($5 \times 196 = 980 \text{ mV}$), but the point of deviation from additivity cannot be discerned from the presently available data.

Similar arguments are useful to rationalize the potentials of the *reductions* of phosphacyclopentadienyl vs cyclopentadienyl complexes. We assume a reduction potential for Cp*CpFe of $E_{1/2} = -3.68 \text{ V}$ by taking into account the observed value of -3.43 V for ferrocene (in

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glyme)^{23b} and subtracting 0.25 V for the substitution of Cp* for Cp. Then the reduction of **1** ($E_{1/2} = -2.00$ V) is seen to be easier by 1680 mV, or -336 mV per P-for-CH ring substitution. This compares to values of about -390 mV for the mono-P complexes in Table 1 arrived at by considerations similar to those in the previous paragraph. The fact that the P-for-CH shifts are substantially greater for the reductions as compared to the oxidations is consistent with molecular orbital calculations that indicate increased P₅ character to the LUMO of **1** as compared to its HOMO.^{6,24}

It is also worth noting that the separation of $E_{1/2}$ oxidation ($18e^-/17e^-$) and reduction ($18e^-/19e^-$) potentials decreases steadily from 3.4 V for ferrocene to ca. 3.0 V for monophosphacyclopentadienyl complexes to 2.57 V for **1** (Table 1). This is consistent with a diminished HOMO/LUMO gap for complexes of increased P-for-CH substitution.

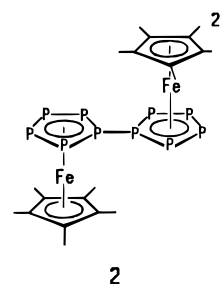
ESR Characterization of 1^+ . The ESR characteristics of anodically electrolyzed **1** (vide supra) confirm the presence of the 17-electron system 1^+ in solutions containing $[1_2]^{2+}$ as the major product. The two most likely electronic configurations for a d^5 metal in a sandwich ligand field are $(a_{1g})^2(e_{1g})^1$ and $(e_{1g})^2(a_{1g})^1$.²⁵ The ferrocenium ion has the former electronic configuration,²⁶ whereas some ferrocenium analogues (e.g., [(2,4-dimethylpentadienyl)CpFe]⁺) are known to possess the latter.²⁷ The symmetry labels used here are not strictly correct, of course, since they refer to the idealized cylindrical symmetry of sandwich complexes. In actuality the e_{1g} pair is split by ligand field distortion and is usually referred to as a "quasi-degenerate" pair.²⁸ The metal orbitals involved are d_{xy} and $d_{x^2-y^2}$ for the " e_{1g} " pair and d_z for the a_{1g} state.

d^5 Complexes having d_{xy} or $d_{x^2-y^2}$ ground states in sandwich-type ligand fields are generally characterized by very large g -value anisotropies and rapid relaxation rates, often requiring use of temperatures below 77 K for spectral detection. By contrast, d^5 systems with pure d_z ground states have small g -value anisotropies and may even display fluid-solution ESR spectra if excited states are sufficiently removed in energy.²⁹ The data for 1^+ are clearly *inconsistent* with a ground-state having e_{1g} parentage. Consistent with theoretical calculations which place the a_{1g} orbital above the e_{1g} for **1**,⁶ the primary metal contribution must be d_z . There must be significant mixing, however, of the d_z orbital with other metal orbital(s) to explain the fact that there is no g -value below the free-spin value.²⁵ Finally we note that the large deviation from axial symmetry in 1^+ suggests a significant lowering of its effective ligand field symmetry as opposed to the C_{5v} symmetry of **1**.

Likely Structures of Dimeric Dications and Dianions. Seventeen-electron metal sandwich cations are known to dimerize through coupling at either the

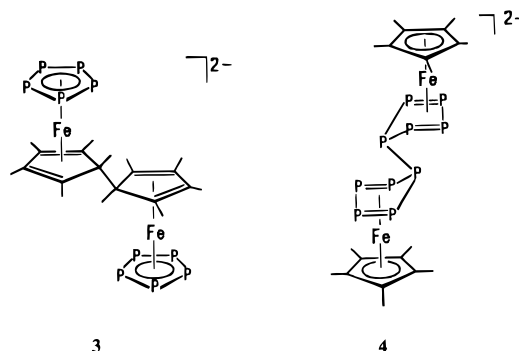
metal or the ligands.^{30,31} Metal-metal coupling is extremely unlikely in the present system. The isoelectronic osmocene monocation dimerizes at the metal, forming a long Os-Os bond,³⁰ but the smaller radius of Fe compared to Os is expected to preclude this route, owing to steric hindrance. It also appears that coupling involving the Cp* rings is unlikely, owing to an apparent lack of C₅Me₅ character in the SOMO of 1^+ . Calculations have consistently indicated that the a_g -type orbitals in mixed-sandwich phosphoferrocenes (with C₅R₅ and C_{*n*}R_{*n*}P_{5-*n*} ligands) are devoid of cyclopentadienyl character.^{6,7,24}

From these considerations and since mixing of both π_P and σ_P occurs with the metal d_z orbital in the SOMO of 1^+ , the coupling reactions of the $17e^-$ system likely involve the two P₅ rings. Coupling might occur through $\pi_P-\pi_P$, $\sigma_P-\pi_P$, or $\sigma_P-\sigma_P$ interactions, an idealized drawing of the latter being shown as structure **2**. In this case,



removal of σ_P electron density from a phosphorus sp^2 orbital leads to a fulvalenyl-type structure. The apparent diamagnetism of $[1_2]^{2+}$ (recall that the ESR activity of its solutions may be ascribed simply to 1^+) is consistent with **2**, since efficient electronic coupling of the two metal centers is reasonably expected in such a structure.

The coupling possibilities for the 19-electron anion, forming diamagnetic $[1_2]^{2-}$, are also limited to the ligand centers. Since the LUMO of **1** contains significant amounts of π character from both the C₅Me₅ and P₅ ligands,⁶ the dimer $[1_2]^{2-}$ likely has the structure **3** or **4**, in which the two metal centers are once again 18-



electron Fe(II), consistent with the apparent diamagnetism of the dimer dianion. A considerable number of analogues of **3** are known. Sandwich complexes having 19 valence electrons have been shown to form similar structures through coupling at one of their cyclic

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hydrocarbons, representative examples being Cp₂Rh,³² CpFe(arene),³³ and (η^4 -C₄R₄) complexes of CpNi³⁴ and (arene)Co.³⁵ There is also precedent, however, for the P₅-P₅ coupled structure in the complex [(Cp''Rh)₂(P₅-P₅)(RhCp'')₂]³⁶ (Cp'' = 1,3-di-*tert*-butylcyclopentadienyl). This complex possesses a Rh₂P₁₀ core that is isoelectronic with the [Fe₂P₁₀]²⁻ core of **4**.

Summary

The sandwich complex Cp*FeP₅ has reduction and oxidation properties similar in one sense to those of

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ferrocene and analogous phosphacyclopentadienyl complexes: a 19-electron anion and a 17-electron cation are accessible within normal potential limits. The two odd-electron species derived from **1** react, however, by a route unknown in the analogues, namely by dimerization. The resulting charged dimeric species re-form the original complex **1** in reverse electrolyses.

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