

MM2 force field, i.e., type 1 = aliphatic C, type 2 = olefinic C, type 3 = carbonyl C, type 5 = H, type 6 = divalent O, and type 7 = carbonyl O.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this research.

Supplementary Material Available: Details of transition-state modeling calculations including Cartesian coordinates for the RHF/3-21G transition state of the Diels-Alder cycloaddition of *s-trans*-acrolein and butadiene and force-field parameters (4 pages). Ordering information is given on any current masthead page.

Arene Exchange by P Donors in the 19-Electron Complexes $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$: Kinetics, Mechanism, and Salt Effects. Interconversion, Radical-Type Reactions, and Electron-Transfer Chemistry of the New 17-Electron and 19-Electron Radicals $\text{Fe}^{\text{I}}\text{CpL}_n$ (L = Phosphine, Phosphite; $n = 2, 3$)

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Abstract: The 19e complexes $\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{H}_6-n\text{Me}_n)$, 1 ($0 \leq n \leq 6$), react with P donors (PMe_3 , PPh_3 , PPh_2H , PPh_2D , dppe , $\text{P}(\text{OMe})_3$, $\text{P}(\text{OPh})_3$) to give products resulting from arene exchange and radical reactions of the 17e radicals $\text{Fe}^{\text{I}}\text{CpL}_2$, 2 (H or Cl abstraction, Arbuzov-type reaction, P-O cleavage, and coupling with Hg). These reactions are potentially side reactions in the electrocatalytic exchange starting from the 18e complexes 1^+ , but reduction of 1^+ by the 19e species $\text{Fe}^{\text{I}}\text{CpL}_3$, 3 , proceeds faster except for L = $\text{P}(\text{OPh})_3$. Complex 1 was used as an electrocatalyst (1%) for the quantitative synthesis of $[\text{FeCp}(\text{PMe}_3)_3]^+$, $3a^+$, $[\text{FeCp}(\text{P}(\text{OMe})_3)_3]^+$, $3b^+$, $[\text{FeCp}(\text{dppe})(\text{NCMe})]^+$, 13^+ , and $[\text{FeCp}(\text{dppe})(\text{NCMe})]^+$, 10 , in a THF suspension at 20 °C. The 19e complex $3a$ (L = PMe_3) is also formed in stoichiometric reactions of 1 with PMe_3 in the presence of reducible substrates (CO_2 , perylene, *p*-dicyanobenzene, and methyl *p*-cyanobenzoate) as well as in disproportionation reactions of 1 induced by sodium salts. Double ion exchange in the latter reactions gives reactive ion pairs containing the organoiron anion and the Na^+ counter cation. This disproportionation can also be catalyzed by NaPF_6 . The kinetics of the ligand exchange of 1 with P donor is shown to follow a second-order process according to the following rate law: $-\text{d}[\text{FeCp}(\text{toluene})]/\text{dt} = k[\text{FeCp}(\text{toluene})][\text{P donor}]$. The reaction rate depends on the nature of the P donor and on the arene. The associative mechanism is confirmed by the large, negative entropy of activation ($\Delta S^\ddagger = -22 \pm 3 \text{ cal mol}^{-1} \text{ K}^{-1}$ for $\text{P}(\text{OMe})_3$). A fast preequilibrium, $\text{FeCp}(\eta^6\text{-arene}) = \text{FeCp}(\eta^7\text{-arene})$, is proposed, which avoids a high-energy 21e intermediate or transition state. In the course of the reaction of 1 with L = PPh_3 , the 17e species $\text{Fe}^{\text{I}}\text{CpL}_2$ was characterized by its ESR spectrum at 10 K showing three g values around 2 and a characteristic triplet indicating the coupling with two P ligands. Another entry into the 19e species $3a$ is the one-electron reduction of the cathodic precursor. For example, Na/Hg reduction of $[\text{FeCp}(\text{PMe}_3)_3]^+\text{PF}_6^-$, $3a^+$, gives $\text{Hg}[\text{FeCp}(\text{PMe}_3)_2]_2$, 9 , while its reduction on sodium mirror gives $[\text{FeCp}(\text{PMe}_3)_2\text{H}]$, $4a$, as the reactions of 1 with PMe_3 . This confirms the fast equilibrium $\text{Fe}^{\text{I}}\text{CpL}_2 + \text{L} = \text{Fe}^{\text{I}}\text{CpL}_3$ (L = PMe_3).

Organometallic and inorganic radicals might play an important role in material science¹ as well as in catalytic processes.² Their intermediacy in organometallic reactions is now being increasingly recognized.^{2,3} The main focus thus far has been on the structure of main group radicals⁴ and metal sandwich radicals⁵ and on the

reactivity of transition-metal carbonyl radicals.⁶ However, stable 19e radicals are relatively rare, and their reactivity⁷ is not very

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well understood. In performing the exchange of the arene ligand with P donors in the complexes $[\text{Fe}^{\text{I}}\text{Cp}(\text{arene})]$, we have discovered a general route to new organophosphorus radicals and have in hand a rare system for which we can compare both the stoichiometric and electrocatalytic⁸ ligand exchange reactions. The latter type of reaction can generate a catalytically active species from a precatalyst.⁸ⁱ Since side reactions of organometallic radicals are a major problem in electrocatalytic reactions, the comparison of the stoichiometric and catalytic reactions that are reported here should result in a better understanding of electrocatalysis. In these studies, we have scrutinized the dramatic role of the sodium salts. The latter can completely change the course of these reactions, and, in particular, their presence can induce disproportionation.

$[\text{Fe}^{\text{I}}\text{Cp}(\text{arene})]$ complexes have been well-characterized and recognized as true metal-centered 19e radicals.^{5i,j,7,9} Their decomposition to ferrocene, iron, and free arenes in coordinating solvents has been noted.^{10a} The reaction of $[\text{FeCp}^{\text{I}}(\text{C}_6\text{H}_6)]$ with CO has been reported to give $[\text{FeCp}(\text{CO})_2]$, whereas the reaction with $\text{L} = \text{P}(\text{O}^i\text{Ph})_3$ was erroneously proposed to give ferrocene and $[\text{FeCpL}_2]$.^{10b} In 1981, we reported the electrocatalytic decomplexation of the cations $[\text{FeCp}(\text{arene})]^+$, 1^+ , in 95% ethanol and proved the intermediacy of the Fe^{I} intermediate $[\text{Fe}^{\text{I}}\text{Cp}(\text{arene})]$, **1**, in this electrocatalytic process. It was proposed that the Fe^{I} species $[\text{Fe}^{\text{I}}\text{Cp}(\text{S})_n]$ formed reduces the cation 1^+ in a cross redox step which propagates the chain.^{11a} Some years later this reaction was extended to phosphites,^{11b} but no kinetic studies were available.

In this article, a comprehensive investigation of the chemistry of the 17e and 19e radicals $\text{Fe}^{\text{I}}\text{Cp}(\text{PR}_3)_n$ ($n = 2, 3$) is reported including the mechanism of their formation, radical-type and electron-transfer reactions, salt effects, and their role in electrocatalysis.^{11c}

Results and Discussion

1. Stoichiometric Reactions between $[\text{Fe}^{\text{I}}\text{Cp}(\text{arene})]$ and Various P Donors: Evidence for 17e Radicals FeCpL_2 ($\text{L} = \text{PR}_3$). The reactions were performed with arene = C_6H_6 (**1a**) or $\text{C}_6\text{H}_5\text{CH}_3$ (**1b**). The 19e Fe^{I} complexes **1** are stable at -20°C ,^{12a-d} and reactions are performed in THF at this temperature in order to insure a better selectivity (at 20°C , more decomposition giving polycyclopentadiene was observed). The reactions with phosphines $\text{L} = \text{PMe}_3$, PPh_3 , PPh_2H or $\text{L}_2 = \text{dppm}$ or dppe give the iron hydrides $\text{FeCpL}_2(\text{H})$, **4**, which result from H atom abstraction by the 17e radicals FeCpL_2 from the solvent, from impurities, or from a substrate. In the present case, THF, toluene, and residual water are good candidates as H-atom donors. There have been many previous reports of such H-atom abstractions by transition-metal radicals from the medium or from the solvent.^{12e-f} With $\text{Re}(\text{CO})_5^+$, the mechanism of H-atom abstraction from H_2O was subjected to a careful study and was shown to be very complex.^{12g} In our study, the H-atom source may also vary from one case to the other. For instance, the iron-hydride complexes were obtained whatever the nature, benzene or toluene, of the arene ligand. All the reactions were carried out in THF, an excellent H-atom donor.¹²ⁱ

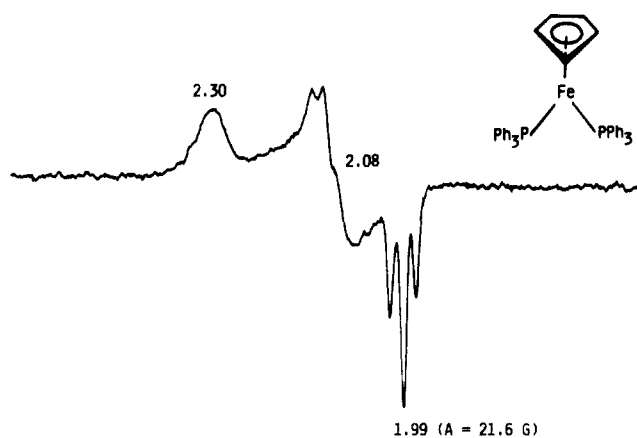
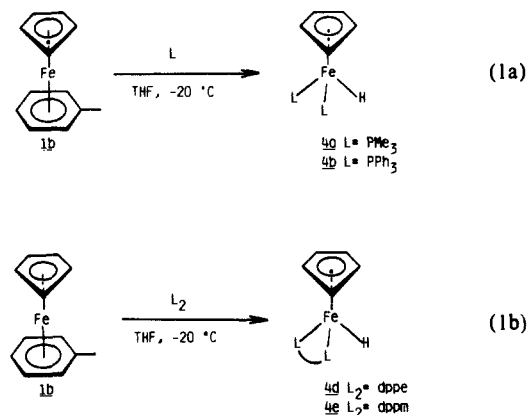


Figure 1. ESR spectrum of the proposed 17e species $\text{Fe}^{\text{I}}\text{Cp}(\text{PPh}_3)_2$ observed from a frozen THF solution at 77 K obtained by reaction of $\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ with PPh_3 in THF at -20°C after 10 min.

These reactions represent a facile route to iron-hydride complexes **4** of this type. The complexes **4a** and **4b** are known from other routes.^{13a} All the hydride complexes were identified by the hydride resonance between $\delta = -13$ and -17 ppm (triplet) in the ^1H NMR spectrum indicating the presence of two P ligands (Table I) and by elemental analysis. In **4e**, additional coupling of the hydride with one of the CH_2 protons (the one at a lower field) is observed, $^4J_{\text{H-H}} = 5$ Hz ($^4J_{\text{H-H}}$ couplings are observed in the M or W conformation^{13b,c}). The X-ray crystal structures of **4b** and **4e** were obtained and will be reported elsewhere.^{13d}



In the reaction with PPh_3 , we attempted to characterize a paramagnetic reaction intermediate by its ESR spectrum. After disappearance of the 19e complex **1**, an ESR spectrum is reproducibly observed (Figure 1) with three g values close to 2 as usually seen for Fe^{I} complexes.^{14a} A triplet is also visible as a result of

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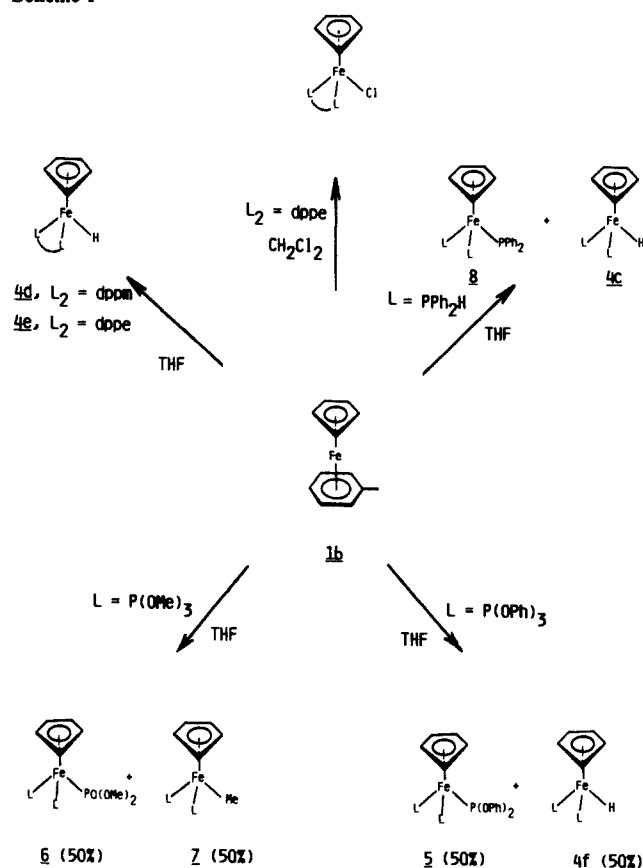
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Scheme 1



the coupling of the electron with the two P atoms bound to iron. Thus we propose the structure Fe¹Cp(PPh₃)₂, **2a**, stabilized by the PPh₃ bulk. On the other hand, the alternative 19e structure Fe¹Cp(PPh₃)₃ is too bulky and cannot form (the 18e cation is unknown). However, the ESR spectrum does not allow us to choose between a piano-stool structure and a pseudo-C_{2v} structure of the CpCoL₂-type. From an empirical basis, a 17e radical usually has the same structure as its 18e analogue bearing the same charge (e.g., CpCoL₂ in the present case).^{14b}

Other radical-type reactions of the 17e radical FeCpL₂ can be observed. For example, we carried out the reaction between FeCp(C₆H₆) and dppe at -20 °C in CH₂Cl₂ instead of THF and found the known purple black chloride FeCp(dppe)Cl^{14c} as the only iron complex, characterized by elemental analysis and ¹H NMR (Scheme 1).

The reactions of **1** with phosphites in THF are different. A report of the reaction of **1** with $L = \text{P(OPh)}_3$ claimed the formation of both ferrocene and the dimer FeCpL₂.^{10b} We repeated this reaction under identical conditions and found neither of these products. Instead we obtained [FeCp{P(OPh)₃}₂P(OPh)₂], (**5**), resulting from P-O cleavage, and the hydride [FeCp{P(OPh)₃}₂(H)], (**4f**), in equal amounts. The Cp signals in ¹H NMR for ferrocene and **4f** are both located at δ 4.1 ppm in CCl₄, which might explain the confusion. Both complexes **5** and **4f** were characterized by elemental analysis (see also Table I for the hydride resonance of **4f**); the ³¹P NMR spectrum of **5** shows a doublet and a triplet indicating the presence of two types of P ligand with two P ligands of one type and one P ligand of the other type (A₂B). Cleavage occurs at the P-O bond not a C-O bond as shown by the number of oxygen atoms left (from the elemental analysis). Consistently, the Arbusov rearrangement is not known with P(OPh)₃.¹⁵

Table I. ¹H NMR Data for the Iron-Hydride Complexes 4^a

FeCpL ₂ (H)	¹ H (ppm)	² J _{P-H} (Hz)
FeCp(PMe ₃) ₂ (H), 4a	-16.20	76.60
FeCp(PPh ₃) ₂ (H), 4b	-13.25	71.35
FeCp(PPh ₂ H) ₂ (H), 4c	-14.81	72.50
FeCp(dppe)(H), 4d	-16.06	71.41
FeCp(dppm)(H), 4e	-12.01	66.36
FeCp{P(OPh) ₃ } ₂ (H), 4f	-13.88	87.70
FeCp{P(OMe) ₃ } ₂ (H), 4g	-14.63	82.50

^a ¹H chemical shifts and coupling constants ²J_{P-H} of the hydride with the phosphorus atoms. The hydride appears as a triplet due to equal coupling with the two phosphorus atoms. For **4e**, see text.

The reaction with P(OMe)₃ gives the radical Arbusov reaction.¹⁵ The complexes [FeCp{P(OMe)₃}₂{P(O)(OMe)₂}], **6**, and [FeCp{P(OMe)₃}₂(Me)], **7**, are formed in 50% yield each. Both complexes were identified by the high-resolution mass spectrum which provides the molecular peak in each case. Also the ¹H NMR spectrum of **7** shows a triplet at $\delta = 0.20$ ppm for the methyl ligand (³J_{P-H} = 5.3 Hz). The ³¹P spectra show one type of P ligand for **7** and again two types (doublet + triplet) for **6**. The ¹H NMR spectrum of **6** shows the two Me groups (6 H) of the phosphonate ligand at $\delta = 3.99$ ppm.

In the presence of PPh₂H, the reaction of Fe¹Cp(C₆H₅Me), **1b**, gives equal amounts of two products: the hydride complex FeCp(PPh₂H)₂(H), **4c**, and the phosphido complex FeCp(PPh₂H)₂(PPh₂), **8**, suggesting that the H-atom source in the hydride complex **4c** might be PPh₂H. The A₂B pattern is found in the ³¹P NMR spectrum of **8**, whereas only one type of P ligand is found for **4c** (see also Table I for the hydride signal). The mass spectrum of **4c** presents a peak at M-2. The same reaction with PPh₂D gave [FeCpP(Ph₂D)₂(D)] characterized analogously by the high-resolution peak at M'-4. The presence of the peak at 370 shows the formation of free Ph₂P-PPh₂. Thus the peaks at M-2 (492) for **4c** and at M'-4 (493) for **4c-d₃** are attributable to FeCpL₂(H), respectively, FeCpL₂(D) with L₂ = Ph₂P-PPh₂. The peak at M'-4 also confirms the formation of the deuteride complex **4c-d₃** and the H-atom source in **4c**.

2. Kinetics and Mechanism of Arene Exchange by P Donors in Fe¹Cp(arene): Associative Mechanism and Fast Preequilibrium with a 17e Species Fe¹Cp(η⁴-arene). Although 17e complexes are known to undergo ligand exchange by an associative mechanism,¹⁶ no mechanistic studies have been reported for 19e complexes. The reactions of Fe¹Cp(arene) with P donors were conveniently monitored by observing the change in optical density at 710 nm of complexes **1** as a function of time. Indeed, in this region, the starting materials have their maximum absorptions, whereas the final products do not absorb at all (**1b**, λ_{max}(THF) = 710 nm (ε = 226 L mol⁻¹ cm⁻¹); **6**, λ_{max}(THF) = 364 nm (ε = 827 L mol⁻¹ cm⁻¹); **7**, λ_{max}(THF) = 372 nm (ε = 768 L mol⁻¹ cm⁻¹)). An extensive kinetic study was carried out with P(OMe)₃. The Fe¹ complexes are thermally unstable above -10 °C and extremely air-sensitive, and all manipulations were carried out under argon. The kinetic runs were conducted under pseudo-first-order conditions, with [P(OMe)₃] > 10[Fe¹Cp(arene)]. The rate of disappearance of Fe¹Cp(C₆H₅Me) varies with the concentration of P(OMe)₃ and the temperature as shown in Figure 2. The substitution follows a second-order process with a rate constant $k = 5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ at -10 °C according to the rate law

$$-d[\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})]/dt = k[\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})][\text{P}(\text{OMe})_3]$$

The reaction rate with PMe₃ is 3 times larger than with P(OMe)₃ and 4.5 times larger than with P(OPh)₃. The nature of

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(16) Typical examples are Re(CO)₅^{26a-c}, Mn(CO)₅^{26d}, V(CO)₆^{26f}, Fe(CO)₄(PPh₃)₃^{27,3f} and MnCp(CO)₂(NCMe)^{27,6d}.

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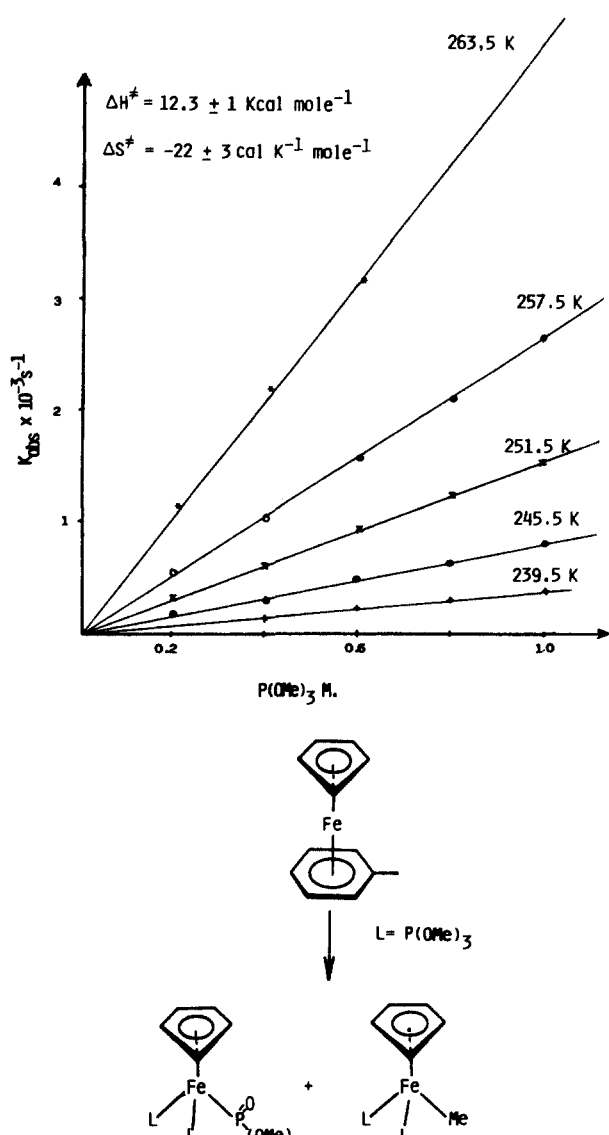
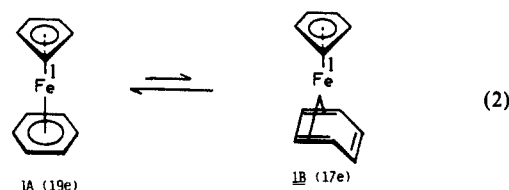


Figure 2. Plot of k_{obs} (s^{-1}) vs $\text{P}(\text{OMe})_3$ concentration (M) for the substitution of $\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})$ in THF solution.

the arene ligand is important as well: displacement of toluene, for example, proceeds 400 times faster than that of hexamethylbenzene. An associative bimolecular mechanism is supported by the observed activation parameters: $\Delta H^\ddagger = 12.3 \pm 1$ kcal mol^{-1} and $\Delta S^\ddagger = -22 \pm 3$ cal $\text{mol}^{-1} \text{K}^{-1}$ for $\text{P}(\text{OMe})_3$. The large negative entropy of activation is known to be indicative of an associative mechanism.^{16,17}

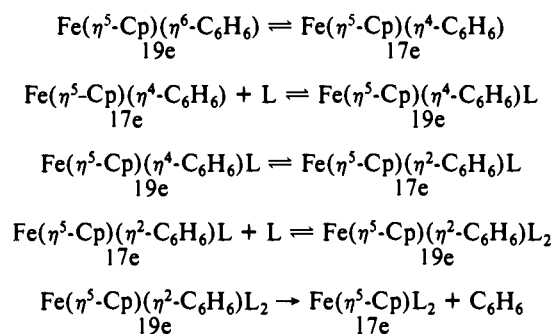
The 18e cation $[\text{Fe}^{\text{II}}\text{Cp}(\text{C}_6\text{H}_5\text{Cl})]^+$ is known to react with $\text{P}(\text{OEt})_3$ at 130 °C.^{18a} Since $\mathbf{1b}^+$ reacts with $\text{P}(\text{OMe})_3$ under analogous conditions, one can estimate that the 19e radical $\mathbf{1b}$ reacts about 10^9 times faster than the 18e isostructural cation.^{18b} An associative mechanism involving coordination of a P donor on a metal center bearing 19 valence electrons would lead to a 21e transition state. At present, only one 21e complex is known, a diphosphine adduct of manganocene.¹⁹ Manganese compounds are very special since they are ionic (manganocene is a high spin complex),²⁰ and the classical electron count has less meaning. Late

transition-metal complexes are highly covalent, and 21e complexes have never been postulated.²¹ On the other hand, it is well-known that 19e complexes rapidly lose a 2e ligand to give 17e species. In the case of $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$ complexes, extended Hückel calculations predict equal energies for both the 19e sandwich structure **1A** and the 17e structure involving a η^4 -arene **1B**,²² while Mössbauer and X-ray data show that the 19e structure is the only one observed in the solid state.^{5f,7}



However, the situation may be slightly different in solution. We propose that the 19e and 17e states are in rapid equilibrium although the 19e one dominates. The small fraction of the 17e species would thus be responsible for the reactivity with P donors. The slow associative step would be preceded by a fast preequilibrium between the 19e and the 17e states. The bulk of the arene ligand in the C_6Me_6 complex slows down the reaction since it sterically inhibits the approach of the P donor to the iron center. The most probable behavior of the 19e transition state bearing the P donor is to lose either the P donor or a second double bond of the arene to give another 17e species. In this way, it is most probable that the mechanism of ligand exchange proceeds by a series of interconversions between the 19e and 17e states, such as in Scheme II. These species are thermodynamically preferred

Scheme II



L = P donor

with respect to 15e and 21e species. The 17e and 19e states often have close energy levels, and interconversion between them is extremely fast. The overall series of equilibria is finally displaced toward the ligand exchange product since the ultimate 17e species $\text{Fe}^{\text{I}}\text{CpL}_2$ (L = P donor) reacts irreversibly in a radical-type process to yield an 18e complex much faster than the starting sandwich compound. In Scheme II, the transition state must have been passed before addition of the second L. Otherwise, the reaction would be second order in [L].

3. Formation of the 17e Radicals $\text{Fe}^{\text{I}}\text{CpL}_2$ (L = PPh_3) by Mono-electronic Reduction of Piano-Stool 18e Cations. It is of interest to compare the behavior of the radicals $\text{Fe}^{\text{I}}\text{CpL}_n$ generated from $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$ with those of the same radicals generated by reduction of $[\text{Fe}^{\text{II}}\text{CpL}_3]^+$ or $[\text{Fe}^{\text{II}}\text{CpL}_2(\text{NCMe})]^+$.²³ The electrochemical reduction of these piano-stool complexes is chemically irreversible at room temperature or even at -20 °C. At fast scan rates and temperatures around -60 °C, very low chemical reversibility ($i_a/i_c = 0.1$) was noted, which allows an inaccurate estimation of the thermodynamic potential of the system $[\text{Fe}^{\text{I}}\text{CpL}_3]^+/\cdot$. Reduction of the piano-stool cations on sodium mirror or the use of the electron-reservoir complex $[\text{Fe}^{\text{I}}\text{Cp}$

(17) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967.

(18) (a) Lee, C. C.; Gill, U. S.; Iqbal, M.; Azogu, C. I.; Sutherland, R. G. *J. Organomet. Chem.* **1982**, *231*, 151. (b) Comparable observations were reported for other transition-metal radicals.^{3f,26f}

(19) Howard, C. G.; Girolami, G. S.; Wilkinson, G.; Pett, M. T.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1984**, *106*, 2033.

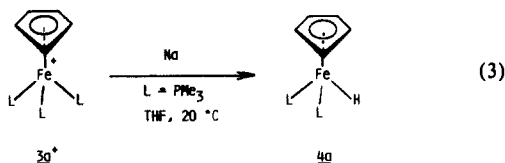
(20) Treichel, P. M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 4, Chapter 29, pp 1-160.

(21) For a relevant discussion, see for instance: Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 2038.

(22) Saillard, J.-Y. Unpublished data. See also ref 35.

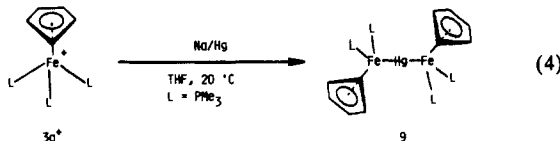
(23) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1984**, *272*, 417.

(C₆Me₆)^{5i,40a} as a one-electron transfer reagent gives the hydrides as does the reaction between [Fe^ICp(C₆H₅Me)] and phosphines.

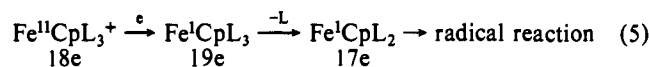


With L = P(OMe)₃, the complex FeCp(L)₂CH₃, **7**, is also found and characterized by ¹H and ³¹P NMR as in section 1. It results from what we believe to be the reduction of the phosphonate complex formed in the radical Arbuzov reaction.

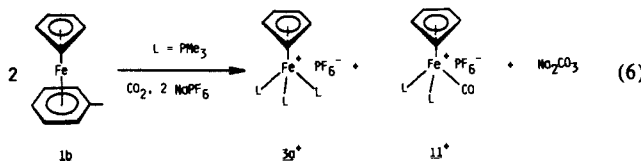
Both the generation of Fe^ICpL_n radicals from the Fe^I sandwiches and from the Fe^{II} piano-stool complexes also lead to small quantities of decomposition products. Reactions must therefore be conducted at -20 °C. When they are conducted at room temperature, large amounts of decomposition products are observed. When the reduction of [FeCp(PMe₃)₃]⁺PF₆⁻, **3a**⁺, was carried out by using Na/Hg in THF, the known trimetallic complex {Hg[FeCp(PMe₃)₂]₂}, **9**,^{10c} was the only reaction product formed as shown by elemental analysis and by the unicity of the ³¹P NMR signal. It results from the coupling of two 17e radicals Fe^ICpL₂ with mercury atoms. This type of behavior has precedence in other systems, especially in mono-electronic oxidation of 18e anions.^{6e,24}



All the one-electron reductions of piano-stool 18e complexes give neutral 19e species Fe^ICpL₃, but the reaction products arise from radical reactions of the 17e species Fe^ICpL₂. This indicates that 19e species Fe^ICpL₃ give 17e species Fe^ICpL₂ whose chemistry is observed.

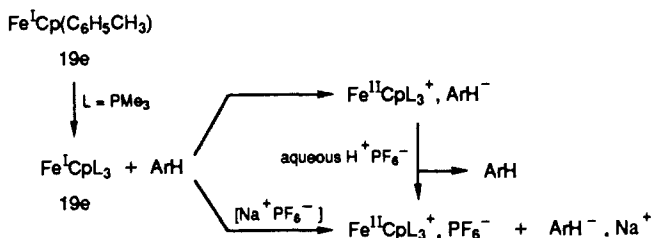


4. The 17e Radicals Fe^ICpL₂ Give 19e Radicals Fe^ICpL₃ (L = PMe₃) Which Can Be Trapped by Electron-Transfer Reactions with CO₂ and Aromatics. We know that the 19e complexes [Fe^ICp(arene)] reduce CO₂²⁵ to CO₃²⁻ and CO giving back their 18e cationic precursors [Fe^{II}Cp(arene)]⁺.^{5i,25e} However, when the reduction is carried out in the presence of PMe₃ and Na⁺PF₆⁻ (0 °C), exchange of the arene ligand by PMe₃ is faster than CO₂ reduction. No sandwich compound remains after the reaction, but known piano-stool cationic complexes are found as PF₆⁻ salts in addition to Na₂CO₃. All the CO produced is incorporated in the piano-stool complex, necessary at the radical level, since, as we have checked, the Fe^{II} complexes are substitutionally inert under the reaction conditions.



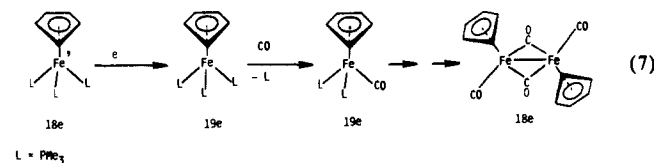
Both the 19e piano-stool radicals Fe^ICpL₃ and Fe^ICpL₂(CO) can reduce CO₂, either by an outer-sphere or by an inner-sphere

Scheme III. Reaction of **3b** with Aromatics in the Presence of PMe₃ (THF, -20 °C) and in the Absence and in the Presence of 1 equiv of Na⁺PF₆⁻



ET. An outer-sphere ET would be endergonic by about 0.2 to 0.3 V, thus still possible. However CO₂ could easily coordinate to the substitutionally labile iron center, which would accelerate the ET by an inner-sphere mechanism. The incorporation of CO indicates that facile phosphine exchange by CO occurs in the 19e species Fe^ICpL₃ (L = PMe₃).²⁶ Thus the 19e species Fe^ICpL₃(CO) is more stable than Fe^ICpL₃, presumably because CO stabilizes low oxidation states.

In order to confirm the exchange of PMe₃ by CO in the 19e species Fe^ICp(PMe₃)₃, we reduced [FeCp(PMe₃)₃]⁺PF₆⁻ by a Na mirror in THF at 20 °C in the presence of 1 atm of CO and found that [Fe₂Cp₂(CO)₄] and PMe₃ are the only reaction products. In the absence of oxidant, ligand exchange proceeds until FeCp(CO)₂⁺ forms and then dimerizes.



Other suitable trapping agents are electron-deficient aromatic derivatives.²⁷ Thus *p*-dicyanobenzene (*E*^o = -1.64 V vs SCE), perylene (*E*^o = -1.64 V vs SCE), and *p*-methylbenzoate (*E*^o = -1.76 V vs SCE) react at -20 °C with Fe^ICp(C₆H₅Me), **1b**, in the presence of PMe₃ in THF to give the intensely colored salt [FeCp(PMe₃)₃]⁺ArH⁻ characterized by a single line in the ESR spectra of frozen solutions (77 K). Metathesis of these salts with Na⁺PF₆⁻ gives [Fe^{II}Cp(PMe₃)₃]⁺PF₆⁻, known^{13d} and characterized by ¹H and ³¹P NMR as in sections 5 and 7. Alternatively, when the reaction is effected in the presence of Na⁺PF₆⁻ in THF, [FeCp(PMe₃)₃]⁺PF₆⁻, **10a**, is formed along with [Na⁺ArH⁻]. Addition of H⁺PF₆⁻ to the aromatic radical anion gives ArH, as shown in Scheme III. Analysis of the organic phase by ¹H and ¹³C NMR did not show any reduction product that could have been formed by disproportionation of the monohydrogenated

(26) Fast ligand exchange processes 17e + L ⇌ 19e ⇌ 17e + L' have been demonstrated. (a) Fawcett, J. P.; Jackson, R. A.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1975**, 733. (b) Fox, A.; Malito, J.; Poë, A. *J. Chem. Soc., Chem. Commun.* **1981**, 1052. (c) Poë, A. *Trans. Met. Chem.* **1982**, 7, 65. (d) Herrinton, T. R.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 5700. (e) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007. (f) Shi, Q.; Richmond, T. g.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032 and **1984**, *106*, 71. (g) Therien, M. J.; Ni, C. L.; Anson, F.; Osteryoung, J. G.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 4037. (h) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032. (i) Goldman, A. S.; Tyler, D. R. *J. Am. Chem. Soc.* **1984**, *106*, 4066. (j) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1985**, *107*, 967. (k) Stiegman, A. E.; Tyler, D. R. *Coord. Chem. Rev.* **1985**, *63*, 217. (l) Hershberger, J. W.; Kochi, J. K. *J. Chem. Soc., Chem. Commun.* **1982**, 212. (m) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61. (n) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (o) Brown, T. L.; Sullivan, R. J. in ref 3g, pp 187-200. (p) Tyler, R. D.; Philbin, C.; Fei, M. *Ibid.* pp 201-210. (q) Rushman, P.; Brown, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 3632. (r) Hepp, A. F.; Wrighton, M. S. *Ibid.* **1983**, *105*, 5934. (s) Amatore, C.; Verpeaux, J. N.; Madonik, A. M.; Desbois, M.-H.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1988**, 200. Verpeaux, J. N.; Desbois, M.-H.; Madonik, A. M.; Amatore, C.; Astruc, D. *Organometallics* **1990**, *9*, 630. Desbois, M.-H.; Astruc, D. *J. Chem. Soc., Chem. Commun.* in press.

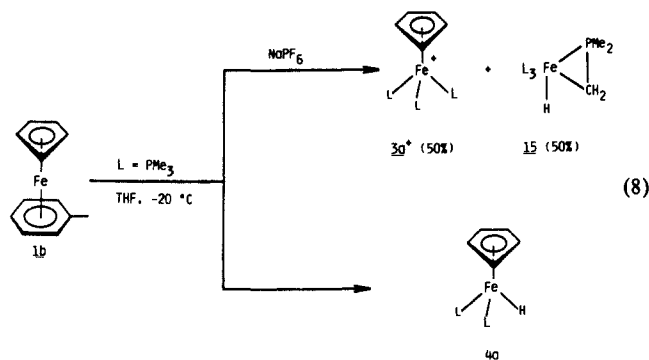
(27) (a) Julliard, M.; Chanon, M. *Chem. Rev.* **1983**, *83*, 425. (b) Kavarinos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.

(24) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87.
 (25) For CO₂ reduction, see: (a) Inoue, S.; Yamazaki, N. Y. *Organic and Bioinorganic Chemistry of Carbon Dioxide*; Wiley: New York, 1982. (b) Gressin, J. C.; Michelet, D.; Nadjo, L.; Savéant, J.-M. *Nouv. J. Chim.* **1979**, *545*. (c) Hawecker, J.; Lehn, J.-M.; Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1984**, 328. (d) Beley, M.; Colin, J. P.; Rupper, R.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1984**, 1315. (e) Ruiz, J.; Guerschais, V.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 812. (f) Ishida, H.; Tanaka, H.; Tanka, K.; Tanaka, T. *J. Chem. Soc., Chem. Commun.* **1987**, 131. (g) Dubois, D.-L.; Miedaner, A. *J. Am. Chem. Soc.* **1987**, *109*, 113.

species ArH_2^{\cdot} . Aromatics with E° values of $\text{ArH}/\text{ArH}^{\cdot-}$ more negative than -2 V vs SCE do not react. The fact that aromatics with thermodynamic potentials as negative as -1.76 V can be quantitatively and rapidly reduced to their radical anion indicates that the reducing species is extremely electron-rich and that its redox couple has an E° value close to -2 V. This is indeed the range found for the system $\text{FeCp}(\text{PMe}_3)_3^{+/0}$. Since PMe_3 is a strong donor, the redox potential of the system $\text{FeCp}(\text{PMe}_3)_2^{+/0}$ must be much less negative than that of $\text{FeCp}(\text{PMe}_3)_3^{+/0}$. Thus, a significant conclusion of these ET reactions is that the 19e species $\text{FeCp}(\text{PMe}_3)_3$ forms and is responsible for ET and not the 17e species $\text{FeCp}(\text{PMe}_3)_2$. This question has been a matter of recent debate^{26a-c} in other series, and 17e species have been shown to be oxidizable.^{26r} Obviously, in the present case, $\text{FeCp}(\text{PPh}_3)_2$ would be a good candidate for the study of this property since $\text{FeCp}(\text{PPh}_3)_3$ cannot be formed.

5. Disproportionation²⁸ Induced by Na^+ Salts.²⁹ Evidence That 17e and 19e Species $\text{Fe}^{\text{I}}\text{CpL}_n$ Rapidly Interconvert. It was shown in section 1 that the reactions of $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$ with various P donors in THF always end up with a radical reaction of the 17e species $\text{Fe}^{\text{I}}\text{CpP}_2$. In this section, we now describe the same reactions in the presence of a salt (typically Na^+PF_6^-). We find that the radical-type reactions observed are totally inhibited by 1 equiv of Na^+PF_6^- . The products found in the presence of 1 equiv of Na^+PF_6^- are always those resulting from the disproportionation of Fe^{I} to Fe^0 and Fe^{II} . We will detail the reactions of PMe_3 , $\text{P}(\text{OMe})_3$, and $\text{P}(\text{OPh})_3$ with $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$ complexes. The study of the influence of the donicity of both the P donor and the arene ligand will be helpful in establishing the mechanism of the salt-induced disproportionation.

Let us start with PMe_3 which is the strongest P donor used here. The compared reactions of $\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})$ in the absence and in the presence of Na^+PF_6^- (stoichiometric amount) are shown in eq 8. In the presence of 1 equiv of Na^+PF_6^- , both dipropor-



tionation products formed $3a^{30a}$ and 15^{30b} are already known. The complex FeL_4 ($\text{L} = \text{PMe}_3$) has been reported to be in equilibrium with the dominant C-H activated form 15 shown in eq 8. This

(28) For disproportionation of metal carbonyl species in the presence of donors, see: (a) Hieber, W.; Sedlmeier, J.; Abeck, W. *Chem. Ber.* **1953**, *86*, 700. (b) Hieber, W.; Beck, W.; Zeitler, G. *Angew. Chem.* **1961**, *11*, 364. (c) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 43. (d) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q.; Pitts, R. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1189. (e) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528. (f) Gard, D. R.; Brown, T. L. *Organometallics* **1982**, *1*, 1143. (g) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1982**, *104*, 2944; *Inorg. Chem.* **1984**, *23*, 527 and **1987**, *26*, 253. (h) Stiegman, A. E.; Stieglitz, M.; Tyler, D. R. *J. Am. Chem. Soc.* **1983**, *105*, 6032. (i) Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 76.

(29) For the "special" salt effect, see: (a) Winstein, S.; Clippenger, E.; Fainberg, A.; Robinson, G. C. *J. Am. Chem. Soc.* **1954**, *76*, 2597. (b) Loupy, A.; Tchoubar, B. *Effets de sel en chimie Organique et Organométallique*; Bordas: Paris, 1988. (c) Gogel, G. W.; Weber, W. P. *Phase Transfer Catalysis in Organic Synthesis*; Springer Verlag: New York, 1977. (d) Peter, K. S. *Acc. Chem. Res.* **1984**, *17*, 277. (e) Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, *41*, 2207. (f) Goodson, B.; Schuster, G. B. *Ibid.* **1986**, *27*, 3123. (g) Masnovi, J. M.; Levine, A.; Kochi, J. K. *J. Phys. Chem.* **1987**, *91*, 1878. (h) In the reactions of Fe^{I} complexes with O_2 , a strong salt effect was also studied. The presence of Na^+PF_6^- has no influence on the ET which is exergonic by 1 V but inhibits the cage chemistry following ET. Hamon, J.-R.; Astruc, D. *J. Am. Chem. Soc.* **1983**, *105*, 5951 and *Organometallics* **1988**, *7*, 1036.

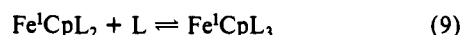
Table II. Yield of $\text{Fe}^{\text{II}}\text{CpL}_3^+$ in the Reaction of $\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ with PMe_3^a

salt	KPF ₆ + 18-crown-6 (1/1)					no salt
	NaPF ₆	NaBF ₄	n-Bu ₄ NBF ₄	KBF ₄		
yield of $\text{Fe}^{\text{II}}\text{CpL}_3^+$ %	50	35	30	26	17	0

^a Influence of various salts in stoichiometric amounts. The maximum theoretical yield is 50%. See eq 8.

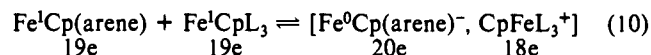
complex 15 was identified by its known, characteristic ^{31}P NMR spectrum^{30b} (Experimental Section, no. IVa).

Turning now to the mechanistic interpretation, it is clear that Na^+PF_6^- induces an ET which is not observed in its absence. Note that the cation $\text{Fe}^{\text{II}}\text{CpL}_3^+$ ($\text{L} = \text{PMe}_3$) is formed when the reaction of $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$ with PMe_3 is carried out in the presence of the mono-electronic acceptors CO_2 or aromatics of section 3. The species susceptible to being involved in the redox process of disproportionation are $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$, $\text{Fe}^{\text{I}}\text{CpL}_2$, and $\text{Fe}^{\text{I}}\text{CpL}_3$, the latter two being in fast equilibrium as shown in section 3.

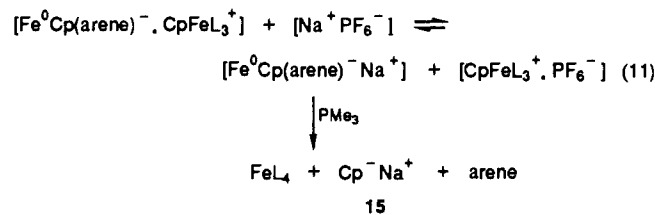


The 19e species FeCpL_3 is by far the strongest reducing species, thus it is the most likely candidate to reduce Fe^{I} to Fe^0 . More precisely, the thermodynamic potential of the redox system $\text{Fe}^{\text{I}}\text{CpL}_3/\text{Fe}^{\text{II}}\text{CpL}_3^+$ can be estimated to be close to -2.05 V vs SCE on the basis of the cyclic voltammogram of $\text{Fe}^{\text{II}}\text{CpL}_3^+$. The thermodynamic potential of $\text{CpFe}(\text{toluene})^{0/-}$ is known to be -2 V vs SCE.^{30c,d,31a} The potential of the systems $\text{Fe}^{\text{I}}\text{CpL}_2^{0/+}$ are unknown, but $\text{Fe}^{\text{I}}\text{CpL}_2$ is a much weaker reducing agent than FeCpL_3 because the latter bears one more strong donor (PMe_3).

Thus ET from $\text{Fe}^{\text{I}}\text{CpL}_3$ to $\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})$ is approximately isoergonic, whereas ET from $\text{Fe}^{\text{I}}\text{CpL}_2$ to $\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})$ would be strongly endergonic. Let us now discuss the nature of the acceptor in this disproportionation. The two candidates are $\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})$ and $\text{Fe}^{\text{I}}\text{CpL}_2$. Given the fact that PMe_3 ligands are much stronger donors than the toluene ligand, $\text{Fe}^{\text{I}}\text{CpL}_2$ cannot be reduced to Fe^0CpL_2 at -2 V vs SCE, the redox potential of $\text{CpFe}(\text{toluene})^{0/-}$. We will see later that phosphites, on the contrary, are weaker donors and that consequently reduction of $\text{Fe}^{\text{I}}\text{Cp}[\text{P}(\text{OR})_3]_2$ to the 18e anion can occur at least for $\text{R} = \text{Ph}$. These arguments lead us to propose that $\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})$ is the acceptor in the disproportionation.

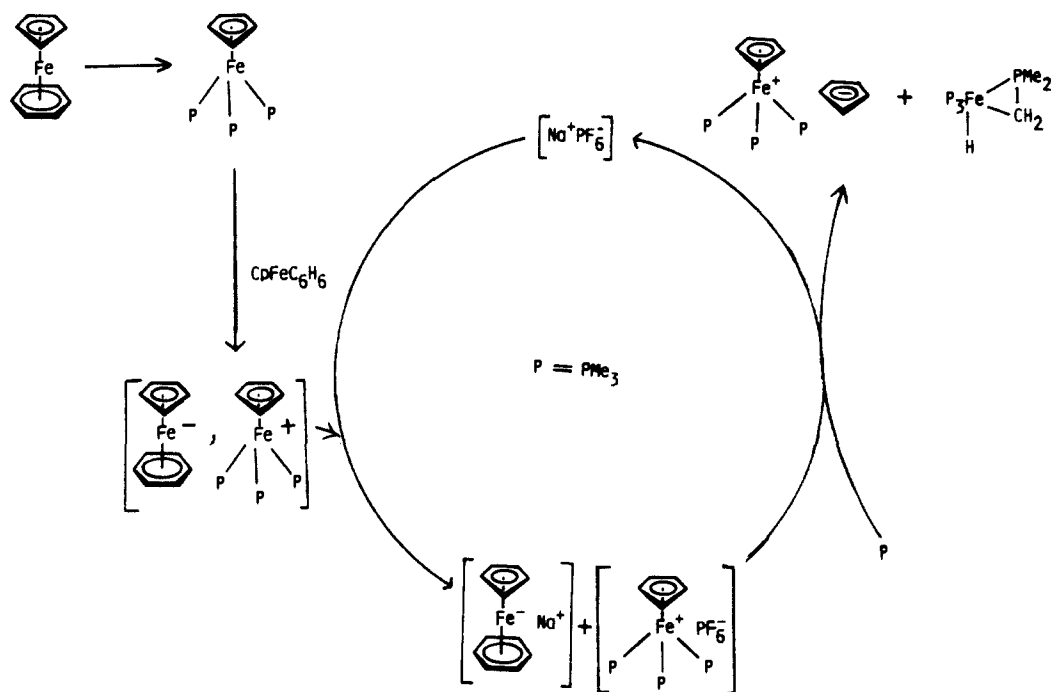


Why is this ET process observed only in the presence of Na^+PF_6^- ? As discussed above, this ET is about isoergonic; thus in the absence of Na^+PF_6^- , the radical reaction of the 17e species $\text{Fe}^{\text{I}}\text{CpL}_2$ (in fast equilibrium with $\text{Fe}^{\text{I}}\text{CpL}_3$) is faster than the decomposition of the 20e anion $[\text{Fe}^0\text{Cp}(\text{arene})]^-$. The latter must be slowed down because of the kinetic stabilization of the large organometallic ion pair by the large counter-cation. On the contrary, when Na^+PF_6^- is present, fast ion pair exchange leads to the extremely unstable ion pair containing Na^+ in which the 20e anion rapidly loses both ligands.



(30) (a) Treichel, P. M.; Shubkin, R. L.; Reichard, D. *Inorg. Chem.* **1966**, *5*, 1177. (b) Rathke, J. W.; Muettterties, E. L. *J. Am. Chem. Soc.* **1975**, *97*, 3272. Karsch, H.-H.; Klein, H.-F.; Schmidbauer, H. *Angew. Chem.* **1975**, *87*, 630; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 637. (c) El Murr, N. *J. Chem. Soc., Chem. Commun.* **1981**, 219 and 251. (d) Desbois, M.-H.; Astruc, D.; Guillin, J.; Mariot, J.-P.; Varret, F. *J. Am. Chem. Soc.* **1985**, *107*, 5280.

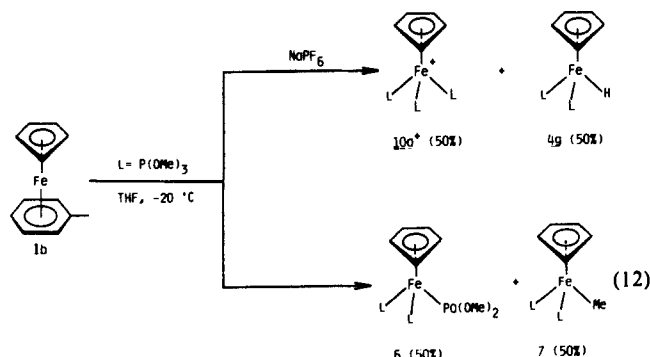
Scheme IV



In order to confirm this "special salt effect",²⁹ relevant to the pioneering work by Winstein,^{29a} we have conducted reactions in the presence of other salts (Table II). When the size of the cation is increased, the salt effect becomes weaker. A similar weakening of the salt effect is observed if one switches from Na⁺PF₆⁻ to Na⁺BF₄⁻ because the electrostatic attraction is stronger in the latter; thus the above equilibrium is not so much shifted to the right (thermodynamic factor). Note that the most efficient salt is Na⁺PF₆⁻, the quantitative salt effect being observed only in the presence of the latter (stoichiometric amount).

We thus addressed the question of whether a catalytic amount of Na⁺PF₆⁻ would be sufficient to induce a quantitative disproportionation. Since [Fe^{II}CpL₃]⁺PF₆⁻ precipitates from THF, it was necessary to add acetonitrile to the reaction medium in order to keep it homogeneous. In the absence of NaPF₆, the reaction of Fe^ICp(toluene) with PMe₃ in THF/MeCN, 1/1 gives only the radical product FeCpL₂(H), as in THF. In the presence of 0.1 equiv of Na⁺PF₆⁻, the disproportionation is still quantitative, and FeCpL₃⁺ is isolated in 50% yield as with 1 equiv of Na⁺PF₆⁻. The ions of Na⁺PF₆⁻ remain in solution and can act catalytically with a turnover number of 10. Thus we propose Scheme IV as the operating catalytic mechanism.

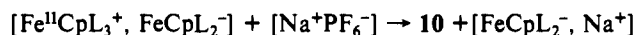
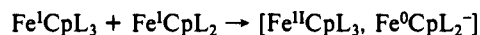
We have varied the nature of the P donor and of the arene ligand in order to investigate whether the salt effect would drive an endergonic ET (eq 10). The reaction of Fe^ICp(toluene) with P(OMe)₃ is shown in eq 12. In the presence of 1 equiv of Na⁺PF₆⁻



in THF, the known complex 3b⁺^{30a} and the new hydride 4g are formed in 50% yield each. Both were characterized inter alia by elemental analysis and ¹H and ³¹P NMR (see the hydride triplet in ¹H NMR for 4g, Table I).

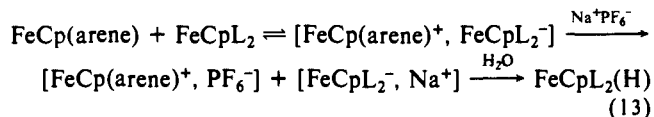
When this reaction was carried out in the presence of 5 equiv of D₂O, it proceeded to give FeCpL₂(D) as the major product. This suggests that a protic source leads to the hydride 4g. Note that 4g is not formed in the reaction carried out in the absence of salt; thus 4g does not result from a radical pathway. We believe that 4g is formed by protonation of the disproportionation product Fe⁰CpL₂⁻. The other disproportionation product, 10, is FeCpL₃⁺ as with PMe₃. The reduction potential of 10 is found at -1.73 V vs SCE without chemical reversibility; thus the estimation of the thermodynamic potential is worse than with PMe₃, but the difference of donicity between PMe₃ and P(OMe)₃ should lead to a difference of E^o somewhat larger than that found for the difference of E_p values (0.3 V). The reducing agent should be Fe^ICpL₃ again since it is (as with L = PMe₃) the most electron-rich species in the medium and since it is less bulky around iron than with L = P(OMe)₃. The oxidant can be either Fe^ICp(arene) or FeCpL₂. The latter is much less electron-rich than with L = PMe₃ (the redox potential of FeCpL₂^{0/-} is unknown). In the first case, the mechanism would be as with PMe₃, eq 10 being now endergonic by ca. 0.2 V. In the second case, the mechanism follows:

Scheme V



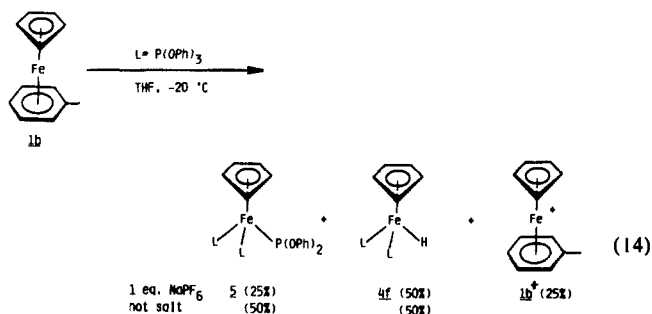
The available data do not allow us to decide between these two possibilities. However the second mechanism becomes more and more probable as the number of methyl substituents increases on the arene ligand because the endergonicity of eq 14 also increases. We have also performed the same reaction with [Fe^ICp(mesitylene)]. This complex is even more difficult to reduce by 0.2 V, so that the endergonicity of the ET of eq 10 is around 0.4 V. A similar disproportionation is indeed obtained. Finally, we have attempted to conduct this reaction with [Fe^ICp(C₆Me₆)] which is reduced at E^o = -2.5 V vs SCE. This would give an endergonicity of around 0.7 V for eq 10, but 10 is not found in this case. The Arbusov products arising from the radical pathway are not obtained either. The cation [FeCp(C₆Me₆)]⁺ is reproducibly isolated in 45% yield from this reaction along with 4g in 30% yield. The isolation of [Fe^{II}Cp(C₆Me₆)]⁺ in such a yield shows that half of [Fe^ICp(C₆Me₆)] is oxidized. This indicates

that the 17e species FeCpL_2 is reduced to FeCpL_2^- since the P donor is weak enough, whereas the complex $[\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)]$ is more electron-rich ($E^\circ \text{FeCp}(\text{C}_6\text{Me}_6)^{0/+} = -1.55 \text{ V vs SCE}$).^{7,9} Thus the ET proceeds in the opposite direction in this salt-induced disproportionation, which leads us to propose the mechanistic scheme of eq 13.



In order to confirm this mechanistic dichotomy, we carried out the reaction of $\text{FeCp}(\text{toluene})$ with $\text{P}(\text{OPh})_3$ which is a poor donor. We were able to reduce reversibly $\text{FeCp}[\text{P}(\text{OPh})_3]_3^+$ on Pt ($E_{1/2} = -1.2 \text{ V vs SCE}$ ($i_a/i_c = 0.6 \text{ V at } -35^\circ\text{C}$, scan rate = 1 V s^{-1}) which provided a good estimation of the thermodynamic potential of $\text{FeCp}[\text{P}(\text{OPh})_3]_3^{+/0}$. The endergonicity is about the same (0.7 V) as in the preceding case for eq 10, and indeed the ET of eq 10 does not occur.

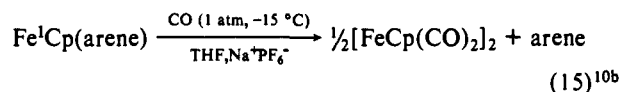
The products obtained in the absence and in the presence of 1 equiv of Na^+PF_6^- are shown in eq 14.



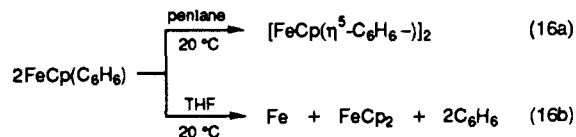
This is the only studied reaction with a P donor where the salt effect is not quantitative with 1 equiv of Na^+PF_6^- . Indeed 25% of the complex $\text{FeCpL}_2\text{P}(\text{OPh})_2$ resulting from the radical pathway is obtained. The two other reaction products, **4f** and the long known complex **1b**^{+,31b,c} arise from the disproportionation according to the ET of eq 13. The hydride **4f** was characterized *inter alia* by the molecular peak in the mass spectrum and by the characteristic high field hydride triplet in $^1\text{H NMR}$ (see Table I). The formation of **4f** from the reduction of FeCpL_2 by **1b** (eq 13) is favorable as above. In summary, the proposed dichotomy is represented in Scheme VI. It is in accord with the values of the redox potentials of the systems $\text{FeCp}(\text{arene})^{+/0/-}$ and $\text{CpFeL}_3^{+/0}$ estimated or known and with the influence of the donicity of L on the unknown redox potentials of $\text{FeCpL}_2^{0/-}$. In all cases, the salt effect induces ET because of the kinetic instability of the reactive ion pair formed between the large organometallic anion and the small (hard) Na^+ counter-cation.³²

We have also carried out the reaction of $\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{H}_6)$ with CO^{33} in the absence and in the presence of 1 equiv of Na^+PF_6^- and have found no salt effect. The reaction occurs at -20°C to give $[\text{FeCp}(\text{CO})_2]_2$ as already reported by Nesmeyanov.^{10b} This is consistent with our mechanism (eq 10) since $\text{FeCp}(\text{CO})_3$ is not electron-rich. On the other hand, eq 10 is not observed either although $\text{FeCp}(\text{CO})_2^*$ is probably electron poor enough to be reducible by $[\text{Fe}^{\text{I}}\text{Cp}(\text{toluene})]$. This means that the competing

dimerization of $\text{FeCp}(\text{CO})_2^*$ is very fast. In particular, it is faster than the radical-type reactions of the other much bulkier 17e species FeCpL_2^* in which L is a P donor.



6. Decomposition of $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$ Revisited: Disproportionation Catalyzed by Na^+ . Nesmeyanov's group reported that $\text{FeCp}(\text{C}_6\text{H}_6)$ slowly dimerizes in pentane (24 h, 20°C) and that it disproportionates to metallic iron, benzene, and ferrocene in THF ($0-20^\circ\text{C}$).¹⁰



We have reinvestigated the behavior of $\text{FeCp}(\text{C}_6\text{H}_6)$ in THF in the absence of a P donor. We find that, in THF, $\text{FeCp}(\text{C}_6\text{H}_6)$ cleanly dimerizes at 20°C as in pentane (eq 16a). Monitoring this reaction by variation of the visible absorption of **1a** shows two isosbestic points at 460 and 570 nm. Note that this is again a radical-type reaction of **1a**. If the same reaction is carried out in the presence of 0.07 equiv of Na^+PF_6^- under identical conditions, only 5% of the dimer is found, and 95% of **1a** gives equal amounts of metallic iron and ferrocene, the disproportionation products. None of these disproportionation products were found in the rigorous absence of Na^+PF_6^- . We conclude that, again, Na^+PF_6^- acts as a catalyst for the disproportionation of **1a** and that the report of Nesmeyanov (eq 16b) overlooked the presence and dramatic role of the Na^+ salt in the disproportionation. It is probable that the Russian authors have used THF solutions of $\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{H}_6)$ which contained Na^+BF_4^- coming from the Na/Hg reduction of the precursor $\text{FeCp}(\text{C}_6\text{H}_6)^+\text{BF}_4^-$. By analogy with the reactions carried out in the presence of P donors and aware of the fact that THF is a weak ligand for Fe^{I} and Fe^{II} , we propose that THF plays a comparable role to that of PMe_3 and that $\text{FeCp}(\text{THF})_3$ reduces **1a**. Since THF is not a π acceptor,³⁴ $\text{FeCp}(\text{THF})_3$ is very electron-rich and the ET to **1a** is exergonic. Note that THF reacts much more slowly than PMe_3 or $\text{P}(\text{OMe})_3$ (the chemistry described here with THF occurs slowly between 0 and 20°C). However, the salt-induced disproportionation (0°C) is still faster than the dimerization, which allows the catalytic activity of Na^+ . The main difference between the salt-induced ET with THF above and that recorded in the presence of PMe_3 appears to be the reaction of Cp^-Na^+ with $[\text{FeCp}(\text{THF})_3]^+$, giving ferrocene by the facile substitution of the weak THF ligands. This ligand displacement providing neutral disproportionation products leaves Na^+PF_6^- in solution for catalytic use so that CH_3CN need not be added. Thus, we propose the mechanistic Scheme VII, close to Scheme IV.

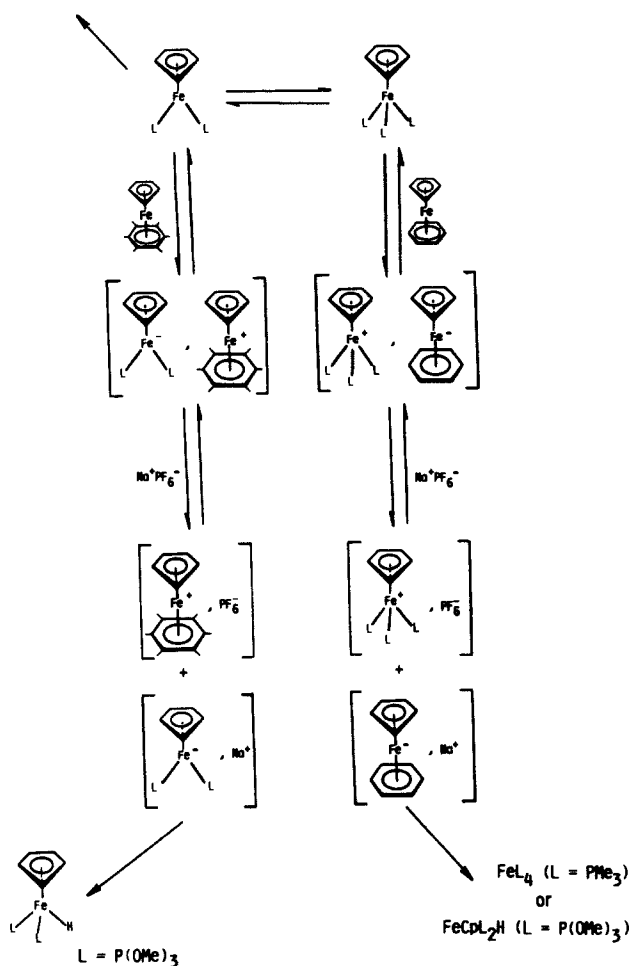
7. Electrocatalytic Ligand Exchange of the Arene by P Donors in $[\text{Fe}^{\text{II}}\text{Cp}(\text{arene})]^+$. Comparison with the Photolytic Process. On the basis of electrochemical studies,^{11a,b} we have achieved electrocatalytic arene displacement reactions in $[\text{Fe}^{\text{II}}\text{Cp}(\text{arene})]^+$ by using $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$ complexes as ET catalysts. Thus, we found that $\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ catalyzes arene exchange by P donors in $[\text{Fe}^{\text{II}}\text{Cp}(\text{C}_6\text{H}_5\text{Me})]^+\text{PF}_6^-$ in THF suspension as well as in acetonitrile solution. The yields are quantitative when the amount of Fe^{I} catalyst is as low as 1% but become insignificant when it is 0.1%. Thus, coulombic efficiencies are about 100, and the side radical reactions described in the preceding sections compete at the lower concentration limit of the electrocatalyst. With $\text{L} = \text{P}(\text{OMe})_3$ or PMe_3 , the complexes $[\text{Fe}^{\text{II}}\text{CpL}_3]^+$ are formed in THF as well as in acetonitrile. In acetonitrile, with a stoichiometric amount of $\text{L}_2 = \text{dppm}$ or dppe , the reaction gives $[\text{Fe}^{\text{II}}\text{Cp}(\text{L}_2)(\text{NCMe})]^+\text{PF}_6^-$. This procedure is very clean and is so far the

(31) (a) The 20e species $\text{Fe}^0\text{Cp}(\text{arene})^-$ have only been observed by cyclic voltammetry.²⁴ Their protonation gives the 18e complexes $\text{FeCp}(\text{cyclohexadienyl})$: Gubin, S. P. *Pure Appl. Chem.* **1970**, *23*, 463. (b) Coffield, T. H.; Sandel, V.; Closon, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 5825. (c) Nesmeyanov, A. N.; Vol'kenau, N. A.; Bolesova, I. N. *Tetrahedron Lett.* **1963**, 1765.

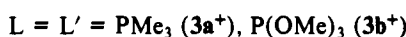
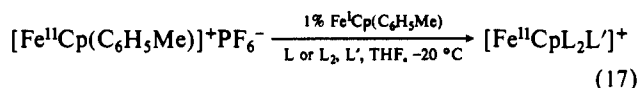
(32) For the stabilization of organometallic anions by large counter-cations, see: Darensbourg, D. J.; Kudarecki, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129.

(33) This reaction was previously reported by Nesmeyanov's group.^{10b} We found that it also works with $\text{Fe}^{\text{I}}\text{Cp}(\text{C}_6\text{Me}_6)^{+/0}$ at 20°C in THF under 1 atm of CO (this work) and with $\text{Fe}^{\text{I}}\text{C}_3\text{Me}_5(\text{arene})$, arene = C_6Me_6 or $\text{C}_6\text{Et}_5\text{H}$ at 100°C to give $[\text{Fe}(\text{C}_3\text{Me}_5)_2(\text{CO})_2]_2$ and the free arene (Hamon, J.-R.; Astruc, D. Submitted for publication).

(34) The influence of the stereoelectronic properties of L have already been shown in the photolytic disproportionation of metal carbonyl dimers in the presence of L.^{26(a),26b-1}

Scheme VI
radical reaction

best one to synthesize the complexes $[FeCpL_3]^+$ or $[FeCp(L_2)(NCMe)]^+$. It can be carried out on a large scale.



Although the electrocatalytic nature of the exchange has already been demonstrated in the electrochemical experiments,^{11a,b} a few points deserve to be mentioned.

(i) In the homogeneous experiments in acetonitrile, the most stable 19e species $Fe^I Cp(PR_3)_3$ must rapidly form and reduce $[Fe^{II}Cp(C_6H_5Me)]^+$ in a cross ET step. The 19e species containing the MeCN ligand do not reduce the cations. If it were the case, 18e cation(s) bearing MeCN ligand(s) would be found since the exchange of acetonitrile by PR_3 in these complexes does not occur under the reaction conditions. On the other hand, if the stoichiometry of the P donor is only two, the third coordination site is occupied by acetonitrile, and the complexes $[FeCpL_2(NCMe)]^+PF_6^-$ are found ($L_2 = dpmm, dppe$).

(ii) The mechanism of ligand exchange in the chemical step of the propagation cycle is proposed in section 2.

(iii) From (i), the ET step of the propagation cycle involves the two redox couples $[FeCp(C_6H_5Me)]^{+/0}$ and $[FeCp(PR_3)]^{+/0}$ which have E° values vs SCE of -1.25 V^{7,35} and, respectively, close

to -1.73 V ($R = OMe$) and -2.05 V ($R = Me$). Thus the exergonicity of this reaction (Scheme VIII) is close to 0.48 V for $R = OMe$ and 0.80 V for $R = Me$.

(iv) With $L = P(OPh)_3$, the electrocatalytic ligand exchange does not occur no matter what the amount of added Fe^I catalyst is, although the expected reaction product $[FeCp[P(OPh)_3]_3]^+$ is known.³⁶ The reason for the lack of electrocatalytic exchange in this case is the endergonicity of the cross ET step.^{8h,36c} Indeed triphenyl phosphite ligands are less electron-donating than all the P donors mentioned above, and three of them are less electron-donating than the arene ligand. E° for $FeCp[P(OPh)_3]_3^{+/-}$ is only -1.2 V vs SCE.

(v) The same reaction using visible light instead of the electrocatalyst gives the same products if the photolysis is carried out in CH_2Cl_2 .³⁷ In MeCN, the same compounds $[Fe^{II}CpL_2(NCMe)]^+$ are obtained by both the photolytic and electrocatalytic reactions when the stoichiometry of L is two. However, the major difference between these two techniques appears when the stoichiometry of the P donor used is three or more and the reaction is carried out in MeCN. Under these conditions, the electrocatalytic reaction gives $[Fe^{II}CpL_3]^+$, whereas the photolytic reaction gives $[Fe^{II}CpL_2(NCMe)]^+$, $L = P(Me)_3$ or $P(OMe)_3$. Control experiments show that $[Fe^{II}CpL_3]^+$ is not photolyzed to $[Fe^{II}CpL_2(NCMe)]^+$ under these conditions. These observations imply that the two mechanisms are different. We propose the following.

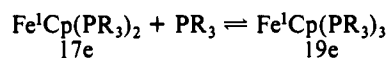
The electrocatalytic reaction is under *thermodynamic control* since the 17e and 19e species are in rapid equilibrium (no kinetic constraint) leading to the more stable 19e intermediate $Fe^I CpL_3$ (as compared to $Fe^I CpL_{3-n}(NCMe)_n$).

The photolytic reaction is under *kinetic control* because loss of the arene from the photoexcited state subsequently involves even-electron species $[Fe^{II}CpL_m(NCMe)_n]^+$ ($14e$ to $18e$ species with $1 \leq n + m \leq 3$); the 18e species ($n + m = 3$) rapidly forms, and acetonitrile ligand(s) may be rapidly exchanged by L except the last one, whose replacement is negligible (even with $P(Me)_3$) on the time scale of the experiment (1 h).

Concluding Remarks

The new series of inorganic radicals $Fe^I Cp(PR_3)_n$ is conveniently generated from the 19e sandwich complexes $Fe^I Cp(arene)$ and PR_3 at low temperature or by mono-electronic reduction of the 18e cations $[Fe^{II}Cp(PR_3)_3]^+$.

Rapid equilibrium between the 17e and 19e forms ($n = 2$ and 3) is shown to occur in the course of these reactions with $L = P(Me)_3$ and $P(OMe)_3$.



In this way, the reactivity of the 17e form or that of the 19e one is observed depending on the reaction conditions.

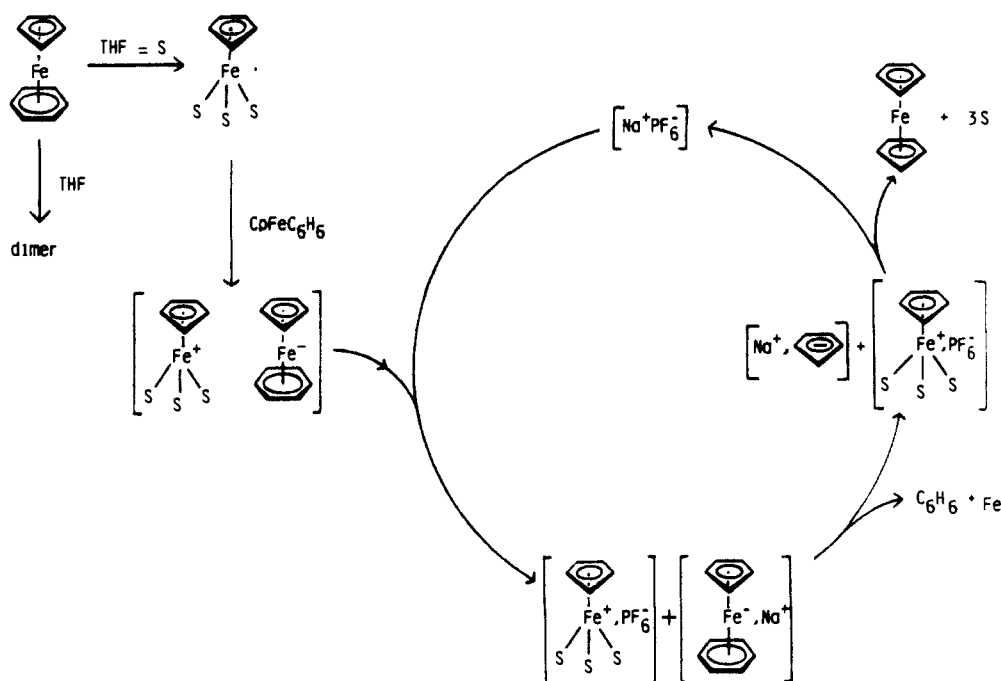
In the absence of reducible substrate, the radical reactivity of the 17e form $Fe^I CpL_2$ is observed. In particular a new series of hydride complexes $FeCpL_2(H)$ is easily synthesized by H-atom abstraction from the medium. With Hg, a trinuclear complex $Fe-Hg-Fe$ is formed. The radical Arbusov reaction is observed with $P(OMe)_3$. On the other hand, the radical cleavage of a P-O bond is observed with $P(OPh)_3$. The ESR characterization of the 17e radical $FeCp(PPh_3)_2$ shows a triplet for the coupling with the two phosphorus atoms.

A variety of reducible substrates S can trap the 19e species $Fe^I CpL_3$ by single ET and formation of the salt $(Fe^I CpL_3)^+S^-$, showing the very electron-rich character of these new 19e species: CO_2 , aromatics, $Fe^I Cp(arene)$, and of course $[Fe^{II}Cp(arene)]^+$ are reduced. The reversible reduction of an aromatic gives the possibility of checking the thermodynamic potential of the redox

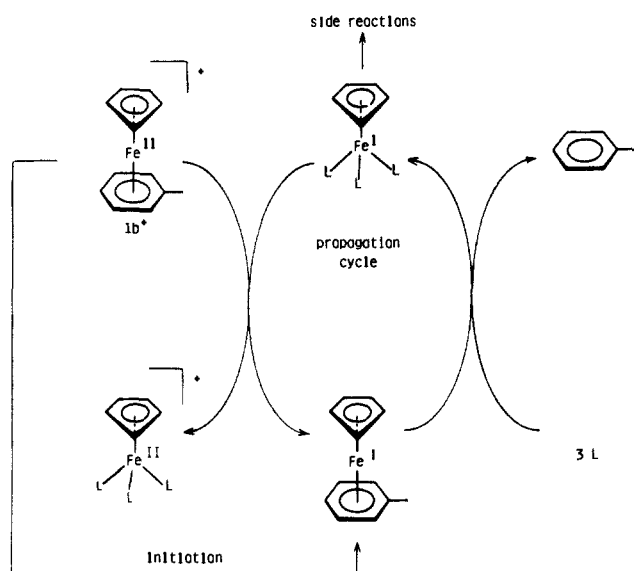
(35) For a discussion concerning the influence of the substituents on the reduction potential of $FeCp(arene)^+$, see: Lacoste, M.; Rabaa, H.; Astruc, D.; Le Beuze, A.; Saillard, J.-Y.; Précigoux, G.; Courseille, C.; Ardoin, N.; Bowyer, W. *Organometallics* 1989, 8, 2233.

(36) (a) Green, M. L. H.; Whiteley, R. N. *J. Chem. Soc. A* 1971, 1943. (b) Gill, T. P.; Mann, K. R. *Inorg. Chem.* 1983, 22, 1986. (c) As previously stated,^{8h} electrocatalytic ligand exchange reactions with an endergonic cross ET are rare. For an example, see ref 26s.

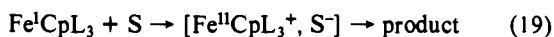
Scheme VII



Scheme VIII



system $\text{Fe}^{\text{I}}\text{CpL}_3^{0/+}$ (-2 V for $\text{L} = \text{PMe}_3$). However the ET step can be endergonic with substrates which are irreversibly reduced because, in these cases, the follow-up chemistry drives the reaction (CO_2 and eventually $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$).



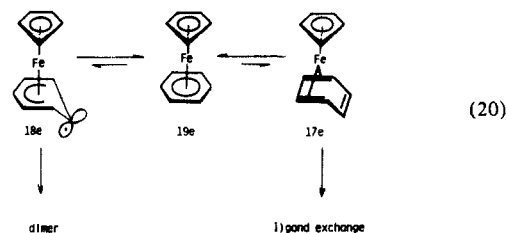
A fine tuning of the competition between the radical reaction of the 17e species $\text{Fe}^{\text{I}}\text{CpL}_2$ and the ET chemistry of the 19e species $\text{Fe}^{\text{I}}\text{CpL}_3$ can be obtained inter alia by the choice of the ions of an added salt. In particular with Na^+PF_6^- , the ET reaction is quantitative, and this salt can even be used catalytically.

When the stereoelectronic properties of the 19e species $\text{Fe}^{\text{I}}\text{CpL}_3$ are not appropriate for this ET (L too electron-poor in the case of $\text{P}(\text{O}Ph)_3$), the 17e species $\text{Fe}^{\text{I}}\text{CpL}_2$, which is thus also electron-poor, can be reduced to the 18e anion $\text{Fe}^0\text{CpL}_2^-$. Alternatively, with $\text{L} = \text{CO}$, dimerization of this 17e species is faster than ET. This also confirms that the only types of reactivity of the 19e species $\text{Fe}^{\text{I}}\text{CpL}_3$ are (i) ET and (ii) loss of a ligand L leading to the 17e species $\text{Fe}^{\text{I}}\text{CpL}_2$.

Since the kinetics of the exchange of the arene by P donors in $\text{Fe}^{\text{I}}\text{Cp}(\text{arene})$ shows that the mechanism is associative, we propose

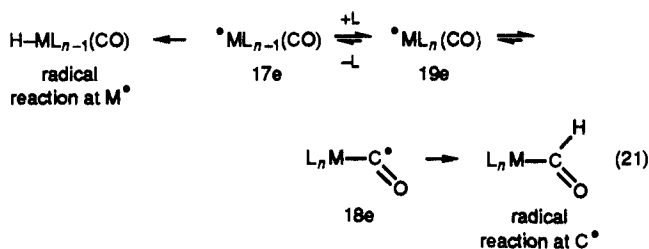
a fast preequilibrium with a 17e species $\text{Fe}^{\text{I}}\text{Cp}(\eta^4\text{-arene})$. This idea fits the fact that 17e and 19e species have close energies because the former lacks one electron in a bonding orbital, whereas the latter bears one electron (in excess) in an antibonding orbital. When two-electron ligands L are available in the medium, the interconversion $17e + \text{L} \rightleftharpoons 19e$ must be fast when the steric factors are compatible. The steric and electronic factors must indeed control the kinetics and thermodynamics of this equilibrium. In the Fe^{I} sandwich, the 19e state is preferred (proximity of the decoordinated double bond and loss of aromaticity in the 17e form). In $\text{Fe}^{\text{I}}\text{CpL}_n$, the 19e form is not sterically accessible when L is too large (PPh_3), and the bulk of L thus disfavors the 19e form. The ET trapping experiment sometimes gives a picture of the equilibrium between two 19e species: this is the case with $\text{Fe}^{\text{I}}\text{Cp}(\text{PMe}_3)_3$ in the presence of CO . The total incorporation of CO in the isolated 18e cation shows that PMe_3 and CO rapidly exchange and that $\text{Fe}^{\text{I}}\text{Cp}(\text{PMe}_3)_2(\text{CO})$ is more stable than $\text{Fe}^{\text{I}}\text{Cp}(\text{PMe}_3)_3$.

In conclusion, we think it is very important to note that the fast $17e + \text{L} \rightleftharpoons 19e$ interconversion in solution leads to a unifying view of transition-metal organometallic radicals. The structure of these radicals must not be directly attributed to a given type of solution reactivity³⁸ for kinetic reasons which are now obvious. For instance, in the absence of a reducible substrate, 19e complexes lose a 2e ligand which leads to the radical reaction of 17e species. Similarly 19e complexes are also in equilibrium with steady-state amounts of their 18e form in which the extra electron is localized on a ligand atom. This is illustrated by the dimerization of $\text{Fe}^{\text{I}}\text{Cp}(\eta^6\text{-C}_6\text{H}_6)$.



- (37) (a) Gill, T. P.; Mann, K. R. *Inorg. Chem.* **1980**, *19*, 3007. (b) Catheline, D.; Astruc, D. *J. Organomet. Chem.* **1982**, *226*, C52. (c) Román, E.; Astruc, D. *Bol. Soc. Chil. Quím.* **1986**, *31*, 129. (d) Ruiz, J.; Román, E.; Astruc, D. *J. Organomet. Chem.* **1987**, *322*, C13. (e) Ruiz, J.; Garland, M. T.; Román, E.; Astruc, D. Submitted to *J. Organomet. Chem.*
 (38) Bhaña, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

One can easily speculate that similar equilibria should describe the structure-reactivity relationship of all 19e radicals in solution (17e \rightleftharpoons 19e \rightleftharpoons 18e), for example³⁹



Experimental Section

General Data. All manipulations of oxygen- or water-sensitive materials were carried out under a recirculating atmosphere of nitrogen in a vacuum atmosphere HE-63-P Dry-Lab with attached HE-493 Dry-Train or under argon, by using standard Schlenk or vacuum line techniques. Infrared spectra, IR, were recorded on a Perkin-Elmer 1420 grating spectrometer (Nujol or KBr disks). NMR spectra were recorded on a Bruker AM-300 WB spectrometer. All chemical shifts (δ) are reported in ppm relative to SiMe₄ (¹H and ¹³C) and 85% H₃PO₄ external (³¹P). Mass spectroscopy analyses (MS) were conducted on a Varian Mat 311 spectrometer. (NMR and MS were done at the "Centre de Mesures Physiques de Rennes.") Microanalyses were performed by the Centre of Microanalyses of the CNRS at Lyon-Villeurbanne. ESR spectra were recorded by using a Bruker ER 200 tX band spectrometer. Cyclic voltammetry (CV) data were recorded with a PAR 273 potentiostat galvanostat. Halfwave potentials $E_{1/2}$ with ferrocene as internal reference, were recorded with reference to SCE in DMF (*n*-Bu₄N⁺BF₄⁻, 0.1 M). Toluene, tetrahydrofuran (THF), diethyl ether, and pentane were purified before use by distillation from sodium/benzophenone ketyl under argon. Acetonitrile was stirred under argon overnight on phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. PMe₃ was vacuum transferred before use. All other chemicals were used as received. All the cations [FeCp(C₆H₅-Me_n)]⁺PF₆⁻ (or BF₄⁻) were synthesized as described previously.^{31c,40} Kinetic methods: all reactions were carried out under pseudo-first-order conditions with the concentration of the incoming ligands at least 12 times greater than that of Fe^ICp(arene), by observing the change in optical density at 680–710 nm. All the reactions were carried out under an atmosphere of argon. Reactions were carried out in a 1.00-cm quartz cell modified for work with air-sensitive compounds, in the thermostated cell compartment of a Varian Cary 219 spectrophotometer. Plots of ln(A_t - A_∞) vs time were linear for more than 3 half-lives, and k_{obs} was determined from the slope of this line by least-squares analysis.

I. Syntheses of Fe^ICp(C₆H₅-Me_n), 1. General Method. All these syntheses were carried out, as previously described,^{12c,40a} at temperatures not higher than -20 °C, except for Fe^ICp(C₆H₅Me), 1d.^{12c,40a} A 3-mmol sample of [FeCp(C₆H₅-Me_n)]⁺PF₆⁻^{31c,40} in 10 mL of THF was stirred on 20 g of sodium amalgam (1%). The reduction was achieved in 30 min.

(a) The dark-green solution was transferred into another Schlenk tube to remove the sodium amalgam. This readily led to a THF solution of type "a" containing the Fe^I species and NaPF₆.

(b) THF was then removed in vacuo, and the residue was extracted with cold pentane (2 × 25 mL), leading to a solution of type "b" containing the Fe^I complex without NaPF₆.

II. Reactivity of Fe^ICp(C₆H₅), 1a, in THF. (a) In the Presence of NaPF₆ (7% vs Fe^ICp(C₆H₅)). A solution of "b" of Fe^ICp(C₆H₅) (3 mmol) was evaporated in vacuo. Cold THF (60 mL) and NaPF₆ (0.035 g, 0.2 mmol) were added. The resulting solution was slowly warmed to room temperature, stirred overnight, and gave a metallic iron precipitate (0.077 g, 1.4 mmol) and ferrocene (0.233 g, 1.33 mmol after recrystallization). The same result was obtained by using a solution of type "a". This result corresponds to that obtained by Nesmeyanov et al.^{10c} on the decomposition of Fe^ICp(C₆H₅) (apparently these authors had not removed NaPF₆ or NaBF₄).

(b) **Without NaPF₆.** After evaporation of a solution of "b" of Fe^ICp(C₆H₅) (3 mmol) 60 mL of cold THF was added. Stirring overnight followed by evaporation of the solvent gave 0.56 g (93% yield) of an orange complex characterized as [FeCp(η⁵-C₆H₅)₂] by comparison

with an authentic sample. This dimerization was reported to occur in pentane.^{10b}

III. Reaction between Fe^ICp(C₆H₅), 1a, with CO. (a) In the Presence of NaPF₆. A solution "a" of Fe^ICp(C₆H₅) (3 mmol) in 60 mL of THF was left under 1 atm of CO. After stirring overnight and slowly warming up to room temperature, the solvent was evaporated in vacuo, and the residue was extracted with toluene (2 × 20 mL). Filtration, concentration of the solvent, and addition of cold pentane gave a red powder of [FeCp(CO)₂]₂ (0.372 g, 70% yield), characterized by comparison of its ¹H NMR (C₆D₆, δ) 4.1 (Cp) and infrared (1780, 1945, 1990 cm⁻¹) spectra with those of an authentic sample.

(b) **Without NaPF₆.** A solution "b" of Fe^ICp(C₆H₅) was concentrated to dryness. After addition of 60 mL of THF, the mixture was stirred overnight under 1 atm of CO. Workup as in IIIa gave [FeCp(CO)₂]₂⁴¹ (0.451 g, 85% yield).

IV. Reaction between Fe^ICp(C₆H₅Me), 1b, and PMe₃. (a) In the Presence of NaPF₆. A solution of PMe₃ (1.141 g, 15 mmol) in THF (50 mL) and a solution "a" of Fe^ICp(C₆H₅Me) (3 mmol) were stirred at -30 °C for 3 h. The reaction mixture was then slowly warmed to room temperature; the orange solution was concentrated in vacuo. The residue was extracted with pentane (2 × 20 mL). The yellow pentane solution

was evaporated and gave 0.378 g (35% yield) of [Fe(PMe₃)₃-(PMe₂CH₂)H] characterized by comparison of its ³¹P NMR spectrum with that of an authentic sample^{30b} (C₆D₆ δ -38.1 (m, 1 P), -30.7 (m, 1 P), -24.1 (m, 1 P), +17.4 (m, 1 P)). The pentane insoluble residue was found to be pure [FeCp(PMe₃)₃]⁺PF₆⁻, 3a⁺ (0.713 g, 48% yield), by comparison of its ¹H NMR spectrum with that of an authentic sample.^{13a}

(b) **Without NaPF₆.** A solution of PMe₃ (1.141 g, 15 mmol) in 50 mL of THF was stirred with a solution "b" of Fe^ICp(C₆H₅Me) (3 mmol) at -30 °C. The green solution was slowly warmed to room temperature after 3 h. The solvent was removed in vacuo. The oily residue was extracted and crystallized from cold pentane. Two recrystallizations afforded orange crystals of the known complex^{13a} FeCp(PMe₃)₂H, 4a (0.206 g, 25% yield): ¹H NMR (C₆D₆, δ) 4.06 (t, 5 H, Cp), 1.12 (t, 18 H, PMe₃), -16.2 (t, 1 H, ²H_{P-H} = 76.6 Hz, FeH); ¹³C NMR (C₆D₆, δ) 73.57 (s, Cp), 26.10 (t, PMe₃); ³¹P NMR (C₆D₆, δ) 33.5; mass spectrum, *m/z* calcd 274.0703, found 274.0704.

(c) **In the Presence of KPF₆.** A 3-mmol sample of [FeCp(C₆H₅Me)]⁺PF₆⁻ was stirred on a potassium mirror in 60 mL of THF at -30 °C. After 30 min the solution was filtrated, PMe₃ (1.141 g, 15 mmol) was added, workup proceeded as above in IVa, giving [FeCp(PMe₃)₃]⁺PF₆⁻, 3a⁺ (0.534 g, 36% yield).

(d) **In the Presence of K⁺18-crown-6PF₆⁻.** The same method as in IVc was used, but, before addition of PMe₃, 1 equiv of K⁺18-crown-6PF₆⁻ was added. This yielded 0.252 g (17% yield) of [FeCp(PMe₃)₃]⁺PF₆⁻, 3a⁺.

(e) **In the Presence of NaBF₄.** A 3-mmol sample of [FeCp(C₆H₅Me)]⁺BF₄⁻ was stirred on sodium amalgam (1%) in 60 mL of THF. After filtration, the solution was worked up as in IVa giving [FeCp(PMe₃)₃]⁺BF₄⁻, 3a⁺ (0.458 g, 35% yield).

(f) **In the Presence of KBF₄.** A 3-mmol sample of [FeCp(C₆H₅Me)]⁺BF₄⁻ was worked up as in IVc yielding 340 g (26% yield) of [FeCp(PMe₃)₃]⁺BF₄⁻, 3a⁺.

(g) **In the Presence of *n*-Bu₄N⁺BF₄⁻.** The same workup as in IVe was used, but, before addition of PMe₃, 1 equiv of *n*-Bu₄N⁺BF₄⁻ was added. This gave [FeCp(PMe₃)₃]⁺BF₄⁻, 3a⁺ (0.392 g, 30% yield).

(h) **In the Presence of 10% of NaPF₆.** After evaporation of a solution "b" of [Fe^ICp(C₆H₅Me)] (3 mmol), 50 mg (0.3 mmol) of NaPF₆ was added. Then, after addition of 50 mL of THF/acetonitrile (1/1) mixture, the workup proceeded as in IVb. Overnight stirring gave the color change of the solution from green to orange. After metathesis with NaPF₆, the solvent was removed in vacuo. Recrystallization of the residue from acetone/ether gave [FeCp(PMe₃)₃]⁺PF₆⁻, 3a⁺ (0.667 g, 45% yield).

(i) **In the Presence of CO₂ and NaPF₆.** A solution of PMe₃ (0.380 g, 5 mmol) in 20 mL of THF was stirred under 1 atm of CO₂ at -30 °C with a solution of "a" of Fe^ICp(C₆H₅Me) (1 mmol). The green solution turned yellow-orange in 1 h. Concentration in vacuo and addition of diethyl ether caused the precipitation of 0.420 g of [FeCp(PMe₃)₃]⁺PF₆⁻, 3a⁺, and [FeCp(PMe₃)₂(CO)]⁺PF₆⁻, 11⁺, in the ratio of 2/1 which were found to be pure by ¹H, ³¹P NMR, and IR spectra by comparison with those of authentic samples.

(j) **In the Presence of Perylene and NaPF₆.** A solution of PMe₃ (0.380 g, 5 mmol) and perylene (0.252 g, 1 mmol) in 25 mL of THF were stirred with a solution "a" of Fe^ICp(C₆H₅Me) (1 mmol) at -20 °C. In 30 min, small microcrystalline aggregates precipitated. These aggregates slowly

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turned yellow-orange. Evaporation of the solvent in vacuo and recrystallization with an acetone/ether mixture gave 0.410 g (83% yield) of $[\text{FeCp}(\text{PMe}_3)_3]^+\text{PF}_6^-$, **3a**⁺.

(k) **In the Presence of Perylene and without NaPF₆.** A solution "b" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ (1 mmol) was stirred with a solution of PMe_3 (0.380 g, 5 mmol) and perylene (0.252 g, 1 mmol) in 25 mL of THF at -20°C for 30 min. The solution afforded a red-brown microcrystalline aggregate. After concentration of the solution and filtration, 0.524 g (72% yield) of the salt $[\text{FeCp}(\text{C}_6\text{H}_5\text{Me})]^+[\text{perylene}]^-$ was isolated: ESR (solid-state sample, 10 K) $g = 2.019$. Acidic hydrolysis (HPF_6) gave, after recrystallization with an acetone/ether mixture, 0.316 g (64% yield) of $[\text{FeCp}(\text{PMe}_3)_3]^+\text{PF}_6^-$, **3a**⁺.

(l) **In the Presence of *p*-Dicyanobenzene and without NaPF₆.** The same method as in IVk was used and gave the blue-brown ionic pair (0.387 g, 81% yield): ESR (solid-state sample, 10 K) $g = 2.076$. Acidic hydrolysis with HPF_6 and recrystallization with an acetone/ether mixture gave 0.366 g (74% yield) of $[\text{FeCp}(\text{PMe}_3)_3]^+\text{PF}_6^-$, **3a**⁺.

(m) **In the Presence of *p*-(Cyanomethyl)benzoate and without NaPF₆.** The same method as in IVk was used and gave 0.445 g (87% yield) of brown plates of $[\text{FeCp}(\text{PMe}_3)_3]^+[\text{CN}-\text{C}_6\text{H}_4-\text{COOMe}]^-$: ESR (solid state sample, 10 K) $g = 2.033$. Acidic hydrolysis with HPF_6 and recrystallization with an acetone/ether mixture gave 0.390 g (79% yield) of $[\text{FeCp}(\text{PMe}_3)_3]^+\text{PF}_6^-$, **3a**⁺.

V. **Reaction between $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})_n$ and $\text{P}(\text{OMe})_3$.** (1) $n = 1$, $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$, **1b**. (a) **In the Presence of NaPF₆.** A solution of $\text{P}(\text{OMe})_3$ (1.861 g, 15 mmol) in 50 mL of THF and a solution "a" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ (3 mmol) were stirred at -30°C overnight. The solution was then slowly warmed to room temperature. Removal of the solvent in vacuo gave an oily and yellow powder which was extracted with pentane (2×20 mL). The yellow solution was then transferred into another Schlenk tube and evaporated in vacuo. The sublimation of the residue gave a yellow oil of $\text{FeCp}[\text{P}(\text{OMe})_3]_2(\text{H})$, **4g** (0.310 g, 28% yield): $^1\text{H NMR}$ (C_6D_6 , δ) 4.65 (s, 5 H, Cp), 3.65 (t, 18 H, $\text{P}(\text{OMe})_3$), -14.63 (t, 1 H, $^2J_{\text{P-H}} = 82.5$ Hz); $^{13}\text{C NMR}$ (C_6D_6 , δ) 76.85 (Cp), 51.55 ($\text{P}(\text{OMe})_3$); $^{31}\text{P NMR}$ (C_6D_6 , δ) 1.9; mass spectrum, m/z calcd 370.0397, found 370.0377. The pentane insoluble solid was crystallized with acetone/ether mixtures yielding 0.765 g (40% yield) of $[\text{FeCp}[\text{P}(\text{OMe})_3]_3]^+$, **10a**⁺, shown to be pure by its $^1\text{H NMR}$ spectrum.^{42a}

(b) **In the Presence of NaPF₆ and 5 equiv of D₂O.** The same workup as in Va yielded 2/3 of $\text{FeCp}[\text{P}(\text{OMe})_3]_2\text{D}$ and 1/3 of $\text{FeCp}[\text{P}(\text{OMe})_3]_3\text{H}$. Mass spectrum of $\text{FeCp}[\text{P}(\text{OMe})_3]_2\text{D}$, m/z calcd 371.0460, found 371.0460.

(c) **Without NaPF₆.** A solution of $\text{P}(\text{OMe})_3$ (1.861 g, 15 mmol) was added to a solution "b" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ (3 mmol) at -30°C . Overnight stirring resulted in an orange, homogeneous solution. After evaporation in vacuo of the solvent, extraction with pentane (2×20 mL), and filtration, the pentane was removed in vacuo giving $[\text{FeCp}[\text{P}(\text{OMe})_3]_2[\text{P}(\text{O})(\text{OMe})_2]]$, **6**, and $[\text{FeCp}[\text{P}(\text{OMe})_3]_2(\text{Me})]$, **7**. The mixture was sublimed (40 $^\circ\text{C}$, 1 mmHg) yielding 0.346 g of an orange oil of $[\text{FeCp}[\text{P}(\text{OMe})_3]_2\text{Me}]$, **7** (30% yield): $^1\text{H NMR}$ (C_6D_6 , δ) 4.48 (s, 5 H, Cp), 3.73 (t, 18 H, $\text{P}(\text{OMe})_3$), 0.20 (t, 3 H, $^3J_{\text{P-H}} = 5.3$ Hz, CH_3); $^{13}\text{C NMR}$ (C_6D_6 , δ) 80.6 (Cp), 51.5 ($\text{P}(\text{OMe})_3$), -11.5 (t, $^2J_{\text{P-C}} = 37$ Hz, Me); $^{31}\text{P NMR}$ (C_6D_6 , δ) 11.42; λ_{max} (THF) = 372 ($\epsilon = 768$ L mol⁻¹ cm⁻¹); mass spectrum, m/z calcd 384.055, found 384.058. The residue was dissolved in pentane; filtration and cold concentration gave $[\text{FeCp}[\text{P}(\text{OMe})_3]_2[\text{P}(\text{O})(\text{OMe})_2]]$, **6** (0.359 g, 25% yield): $^1\text{H NMR}$ (C_6D_6 , δ) 4.81 (br s, 5 H, Cp), 3.99 (d, 6 H, $\text{P}(\text{O})(\text{OMe})_2$), 3.82 (t, 18 H, $\text{P}(\text{OMe})_3$); $^{13}\text{C NMR}$ (C_6D_6 , δ) 81.3 (Cp), 52.9 ($\text{P}(\text{O})(\text{OMe})_2$), 50.25 ($\text{P}(\text{OMe})_3$); $^{31}\text{P NMR}$ (C_6D_6 , δ) 71.19 (2 P), 17.28 (1 P); λ_{max} (THF) = 364 nm ($\epsilon = 827$ L mol⁻¹ cm⁻¹); mass spectrum, m/z calcd 478.138, found 478.037.

(2) $n = 3$, $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})_3$, **1c**. **In the Presence of NaPF₆.** A solution "a" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})_3$, **1c**, was worked up as in VIa giving $[\text{FeCp}[\text{P}(\text{OMe})_3]_2(\text{H})]$, **4g**, and $[\text{FeCp}[\text{P}(\text{OMe})_3]_3]^+\text{PF}_6^-$, **10a**⁺, found to be pure by $^1\text{H NMR}$.

(3) $n = 6$, $\text{Fe}^1\text{Cp}(\text{C}_6\text{Me}_6)$, **1d**. **In the Presence of NaPF₆.** A solution "a" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{Me}_6)$ (3 mmol) and $\text{P}(\text{OMe})_3$ (1.861 g, 15 mmol) in 50 mL of THF was stirred and heated at 60°C for 3 h. The green solution progressively became yellow. Workup as in VIa gave 45% of $[\text{FeCp}[\text{P}(\text{OMe})_3]_3]^+\text{PF}_6^-$, **1d**⁺, and 30% of $[\text{FeCp}[\text{P}(\text{OMe})_3]_2(\text{H})]$, **4g**.

VI. **Reaction between $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ and $\text{P}(\text{OPh})_3$.** (a) **In the Presence of NaPF₆.** A THF solution (50 mL) of $\text{P}(\text{OPh})_3$ (2.792 g, 9 mmol) was stirred with a solution "a" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ (3 mmol) overnight at -20°C . The medium was then slowly warmed to room temperature. After evaporation of the solvent in vacuo, the residue was extracted with pentane (2×20 mL). The pentane insoluble residue

yielded 25% of $[\text{FeCp}(\text{C}_6\text{H}_5\text{Me})]^+\text{PF}_6^-$ found to be pure by $^1\text{H NMR}$. The yellow pentane solution was concentrated yielding $[\text{FeCp}[\text{P}(\text{OPh})_3]_2[\text{P}(\text{OPh})_2]]$, **5**, and $\text{FeCp}[\text{P}(\text{OPh})_3]_2(\text{H})$, **4f**, in the ratio 1/2.

Two methods of separation were used.

(i) The pentane solution of $\text{FeCp}[\text{P}(\text{OPh})_3]_2(\text{H})$, **4f**, and $\text{FeCp}[\text{P}(\text{OPh})_3]_2[\text{P}(\text{OPh})_2]$, **5**, was filtered through a pentane-wetted alumina column. The alumina was then washed with a toluene-pentane mixture (1/1), and a yellow solution was obtained. Evaporation of the solvent gave 0.512 g (23% yield) of $\text{FeCp}[\text{P}(\text{OPh})_3]_2(\text{H})$, **4f**, found to be pure by $^1\text{H NMR}$: $^1\text{H NMR}$ (C_6D_6 , δ) 7.37, 6.94 (m, 30 H, $\text{P}(\text{OPh})_3$), 3.98 (s, 5 H, Cp), -13.88 (t, 1 H, $^2J_{\text{P-H}} = 87.7$ Hz); $^{13}\text{C NMR}$ (C_6D_6 , δ) 129, 128, 122 (m, $\text{P}(\text{OPh})_3$), 77.57 (Cp); $^{31}\text{P NMR}$ (C_6D_6 , δ) 178.914; λ_{max} (THF) 359 nm ($\epsilon = 1260$ L mol⁻¹ cm⁻¹); mass spectrum, m/z calcd 742.133, found 742.134.

(ii) The pentane solution of $\text{FeCp}[\text{P}(\text{OPh})_3]_2(\text{H})$, **4f**, and $\text{FeCp}[\text{P}(\text{OPh})_3]_2[\text{P}(\text{OPh})_2]$, **5**, was concentrated and cooled down to -40°C . Three recrystallizations gave a yellow powder (which decomposed on alumina) of $\text{FeCp}[\text{P}(\text{OPh})_3]_2[\text{P}(\text{OPh})_2]$, **5**: $^1\text{H NMR}$ (C_6D_6 , δ) 7.42, 7.01 (m, 40 H, $\text{P}(\text{OPh})_3$), 4.61 (s, 5 H, Cp); $^{13}\text{C NMR}$ (C_6D_6 , δ) 130, 128, 122 ($\text{P}(\text{OPh})_3$), 81 (Cp); $^{31}\text{P NMR}$ (C_6D_6 , δ) 162.96 (d, 2 P) 124.43 (t, 3 P, $J_{\text{P-P}} = 150$ Hz); λ_{max} (THF) 3.65 ($\epsilon = 920$ L mol⁻¹ cm⁻¹). Anal. Calcd for $\text{C}_{53}\text{H}_{45}\text{FeP}_3\text{O}_8$: C, 66.40; H, 4.73; P, 9.70; Fe, 5.82. Found: C, 66.78; H, 4.68; P, 9.78; Fe, 5.70.

(b) **Without NaPF₆.** A solution "b" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ (3 mmol) and a THF solution (50 mL) of $\text{P}(\text{OPh})_3$ (9 mmol) were worked up as in VIa. The complexes $\text{FeCp}[\text{P}(\text{OPh})_3]_2(\text{H})$, **4f**, and $\text{FeCp}[\text{P}(\text{OPh})_3]_2[\text{P}(\text{OPh})_2]$, **5**, were shown by $^1\text{H NMR}$ to be formed in equal proportion. After separation 0.802 g (36% yield) of **4f** and 0.570 g (20% yield) of **5** were obtained.

VII. **Reactions of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ with PPh_3 , PPh_2H , PPh_2D , dppe , and dppm without NaPF₆.** (a) **With PPh_3 .** To a solution "a" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ (3 mmol), 3.361 g (9 mmol) of PPh_3 were added. The solution was stirred at -30°C overnight and then slowly warmed to room temperature. After evaporation in vacuo of the orange solution, the precipitate was extracted with pentane (2×25 mL). Concentration in vacuo, addition of a pentane/THF (10 mL/2 mL) mixture, and standing at -40°C for 24 h afforded 1.164 g (60% yield) of $[\text{FeCp}(\text{PPh}_3)_2\text{H}]$, **4b**, as yellow crystals: $^1\text{H NMR}$ (C_6D_6 , δ) 7.61, 7.17, 6.94 (m, 30 H, PPh_3), 3.98 (s, 5 H, Cp), -13.25 (t, 1 H, $^2J_{\text{P-H}} = 71.35$ Hz); $^{13}\text{C NMR}$ (C_6D_6 , δ) 141, 134, 124 (PPh_3), 78 (Cp); $^{31}\text{P NMR}$ (C_6D_6 , δ) 88.79. Anal. Calcd for $\text{C}_{41}\text{H}_{36}\text{FeP}_2$: C, 76.17; H, 5.61. Found: C, 76.48; H, 5.64.

(b) **With PPh_2H and PPh_2D .** A solution "b" of $\text{Fe}^1\text{Cp}(\text{C}_6\text{H}_5\text{Me})$ (1.5 mmol) and a THF solution (50 mL) of PPh_2H (0.838 g, 4.5 mmol) were stirred overnight at -30°C . After evaporation of the solvent in vacuo, the residue was extracted with pentane (3×25 mL). Extraction with THF of the pentane insoluble residue was followed by filtration. Concentration and standing 24 h at -40°C gave black purple plates of $\text{FeCp}(\text{PPh}_2\text{H})_2(\text{PPh}_2)$, **8** (0.214 g, 21% yield): $^1\text{H NMR}$ (C_6D_6 , δ) 7.54, 7.30, 7.07, 6.93 (m, 30 H, PPh_2H , PPh_2), 5.9 (dm, 2 H, $^1J_{\text{P-H}} = 341$ Hz), 4.2 (s, 5 H, Cp); $^{13}\text{C NMR}$ (C_6D_6 , δ) 134, 128 (Ph), 79 (Cp); $^{31}\text{P NMR}$ (C_6D_6 , δ) 65.21 (2 P, PPh_2H), 1.1 (1 P, PPh_2). Anal. Calcd for $\text{C}_{41}\text{H}_{37}\text{P}_3\text{Fe}$: C, 72.58; H, 5.50; P, 13.69; Fe, 8.23. Found: C, 72.13; H, 5.55; P, 13.69; Fe, 8.01. The dark yellow pentane solution was filtered through pentane-wetted alumina column. The alumina was washed with oxygen-free toluene/pentane mixture (1/3), which afforded a yellow solution. Removal of the solvent from the toluene/pentane solution yielded a yellow oil of $\text{FeCp}(\text{PPh}_2\text{H})_2(\text{H})$ (0.120 g, 23% yield): $^1\text{H NMR}$ (C_6D_6 , δ) 7.50, 7.16, 7.01 (m, 20 H, PPh_2H), 6.41 (d, 2 H, $^1J_{\text{P-H}} = 285$ Hz), 4.17 (s, 5 H, Cp), -14.81 (t, 1 H, $^2J_{\text{P-H}} = 72.5$ Hz); $^{13}\text{C NMR}$ (C_6D_6 , δ) 132.91, 132.73, 128.36, 127.72 (m, Ph); 76.02 (Cp); $^{31}\text{P NMR}$ (C_6D_6 , δ) 71.486 (2 P); mass spectrum $M-2$, m/z calcd 492.0859, found 492.0849; $\text{Ph}_2\text{P}-\text{PPh}_2$ at 370; with PPh_2D , mass spectrum $M' = M + 3$; $M' - 4$, m/z calcd 493.0921 found 493.0893.

(c) **With dppe .** The same workup as above gave $\text{FeCp}(\text{dppe})\text{H}$ as a yellow powder (0.447 g, 56% yield), which was found to be pure by its ^1H , ^{13}C , and ^{31}P NMR spectra: $^1\text{H NMR}$ (C_6D_6 , δ) 7.82, 7.45, 7.13, 7.01 (m, 20 H, Ph), 4.19 (s, 5 H, Cp), 1.97, 1.75 (m, 4 H, CH_2), -16.06 (t, 1 H, FeH, $^2J_{\text{P-H}} = 71.41$ Hz); $^{13}\text{C NMR}$ (C_6D_6 , δ) 133, 128, 127 (m, Ph), 75.70 (Cp), 31 (CH); $^{31}\text{P NMR}$ (C_6D_6 , δ) 112.42^b. The same reaction carried out in CH_2Cl_2 under identical conditions and followed by workup and recrystallization from pentane yielded 30% of the known black purple complex $\text{FeCp}(\text{dppe})\text{Cl}$. The $^1\text{H NMR}$ spectrum is identical with that of an authentic sample.^{14c}

(d) **With dppm .** Again the same workup as in VIIIa gave the yellow orange powder (0.420 g, 55% yield): $^1\text{H NMR}$ (C_6D_6 , δ) 7.73, 7.52, 7.12, 7.04 (m, 20 H, Ph), 4.4 (s, 5 H, Cp), 4.15 (m, 1 H, CH_2), 3.18 (sextet, 1 H, CH_2 , $^1J_{\text{H-H}} = 13.80$ Hz, $^2J_{\text{P-H}} = 11.50$ Hz), -12.0 (t, d, 1 H, Fe-H, $^2J_{\text{P-H}} = 66.36$ Hz, $^4J_{\text{H-H}} = 5.30$ Hz); $^{13}\text{C NMR}$ (C_6D_6 , δ) 143, 141, 132, 128 (m, Ph), 72.77 (s, Cp), 50.30 (CH_2); $^{31}\text{P NMR}$ (C_6D_6 , δ) 47.90. The X-ray crystal structure has been resolved.^{13d}

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VIII. Reduction of the Cationic Complexes [FeCpL₂L']⁺ (L = L' = PMe₃, P(OMe)₃, PPh₃; L₂ = dppm, L' = MeCN, PMe₃, P(OMe)₃).

(a) [FeCp(PMe₃)₃]⁺PF₆⁻, 3a⁺ with Na/Hg. A 1-mmol sample of the complex was stirred on 10 g of sodium amalgam (1%) in 15 mL of THF for 1 h. After evaporation of the solvent in vacuo, the residue was extracted with pentane (3 × 20 mL). Concentration of the solution and recrystallization at -40 °C for 12 h, afforded 0.261 g (35% yield) of brown crystals of [FeCp(PMe₃)₂]₂Hg, 9: ¹H NMR (C₆D₆, δ) 4.64 (s, 10 H, Cp), 1.32 (t, 36 H, PMe₃); ¹³C NMR (C₆D₆, δ) 72.00 (Cp), 25.97 (m, Me); ³¹P NMR (C₆D₆, δ) 15.66. This complex was reported by Green et al.^{13a}

(b) [FeCp(PMe₃)₃]⁺PF₆⁻, 3a⁺ with Na under CO. This complex (0.495 g, 1 mmol) was stirred in THF (20 mL) under 1 atm of CO on sodium mirror for 2 h. Concentration to dryness gave a residue which was then extracted with ether. After filtration and evaporation of the solvent, a red powder (0.100 g, 56% yield) of [FeCp(CO)₂]₂ precipitated (characterized by comparison of its ¹H NMR and infrared spectra with those of authentic samples).⁴¹

(c) [FeCp(PMe₃)₃]⁺PF₆⁻, 3a⁺ with Na. This complex (0.495 g, 1 mmol) was stirred in THF (20 mL) on sodium mirror for 2 h. Evaporation to dryness gave a residue which was then extracted with pentane (2 × 20 mL). Workup as in IVb gave 0.090 g (33% yield) of FeCp(PMe₃)₂(H), 4a.^{13a}

(d) [FeCpP(OMe)₃]₃⁺PF₆⁻, 10a⁺. This complex (0.638 g, 1 mmol) was stirred in THF (20 mL) on sodium amalgam (1%) at 20 °C for 2 h. Evaporation of the solvent in vacuo and extraction with pentane (2 × 20 mL) gave an orange solution which was evaporated to dryness. The orange oil obtained (0.220 g, 58% yield) was characterized by its ¹H NMR as a mixture of 4g and 7 in equal proportion.

(e) [FeCp(dppm)(NCMe)]⁺PF₆⁻, 12⁺. This complex (0.346 g, 0.50 mmol) in THF (20 mL) and a solution "b" of Fe^ICp(C₆Me₆) (0.142 g, 0.50 mmol) were stirred at -80 °C for 1 h. The green solution turned red-brown with formation of a yellow precipitate of [FeCp(C₆Me₆)]⁺PF₆⁻. THF was removed in vacuo after filtration. The crude product obtained was identified as FeCp(dppm)H, 4e, and purified as in VIIc, yielding 0.136 g (54%) as an orange-yellow powder.

IX. Electrocatalytic Substitution of the Toluene Ligand in [FeCp(C₆H₅Me)]⁺PF₆⁻ by P Donors, Initiated by Fe^ICp(C₆H₅Me). (a) A THF solution (100 mL) of PMe₃ (1.825 g, 24 mmol) and [FeCp(C₆H₅Me)]⁺PF₆⁻ (1.074 g, 3 mmol) was stirred at -30 °C in the presence of a solution "a" of Fe^ICp(C₆H₅Me) (0.0107 g, 0.030 mmol) for 30 min and then slowly warmed to room temperature. Evaporation of the solvent gave a yellow-brown solid. Recrystallization from acetone/ether gave a yellow-brown powder (1.350 g, 91% yield) of [FeCp(PMe₃)₃]⁺PF₆⁻, characterized as in IVa.

(b) The same workup as above with 1% Fe^ICp(C₆H₅Me), 1b, was used for P(OMe)₃ (3 g, 24 mmol) and [FeCp(C₆H₅Me)]⁺PF₆⁻, giving 1.836 g (96% yield) of a yellow powder of 10⁺PF₆⁻ characterized as in Va.

(c) P(OMe)₃ (3 g, 24 mmol) and [FeCp(C₆H₅Me)]⁺PF₆⁻ (1.074 g, 3 mmol) were stirred in a THF/acetonitrile mixture (1/1) at -30 °C, in the presence of 1% of Fe^I complex. The same procedure as in Xa gave 1.818 g (95% yield) of 6⁺ characterized as in Va.

(d) Dppe (1.594 g, 4 mmol) and [FeCp(C₆H₅Me)]⁺PF₆⁻ (1.074 g, 3 mmol) were stirred in a THF/acetonitrile mixture (9/1) in the presence of a solution "a" of Fe^ICp(C₆H₅Me) (0.15 mmol, 5%) at -30 °C for 30

min. After workup as in Xa, a red purple powder of [FeCp(dppe)(NCMe)]⁺PF₆⁻, 13⁺ (2.033 g, 96% yield), was obtained and characterized by comparison with an authentic sample.³⁶

(e) The same procedure as in Xd was used for dppm and allowed the formation of 1.848 g (89% yield) of [FeCp(dppm)(NCMe)]⁺PF₆⁻, 12⁺, as a red microcrystalline powder found to be pure by comparison with an authentic sample.^{37d}

(f) A THF solution (100 mL) of [FeCp(C₆H₅)Me]⁺PF₆⁻ (1.074 g, 3 mmol) and P(OPh)₃ (5.585 g, 18 mmol) was worked up as in Xd, and 0.980 g (92% yield) of the starting material was recovered.

X. Electrochemical Data. (DMF, 0.1 M *n*-Bu₄NBF₄, *v* = 1 V/s at -35 °C). [FeCp(PMe₃)₃]⁺PF₆⁻, Hg cathode, E_{1/2} = -2.05 V vs SCE (i_a/i_c = 0.1). [FeCp[P(OMe)₃]₃]⁺PF₆⁻, Pt cathode, E^{red} = -1.73 V vs SCE (i_a/i_c = 0). [FeCp(dppm)CH₃CN]⁺PF₆⁻, Pt cathode, E^{red} = 1.55 V vs SCE (i_a/i_c = 0). [FeCp[P(OPh)₃]₃]⁺PF₆⁻, Pt cathode, E_{1/2} = -1.2 V vs SCE (i_a/i_c = 0.6).⁴³

Acknowledgment. We are indebted to Drs. M.-H. Desbois (Bordeaux) and J.-R. Hamon (Rennes I) for invaluable experimental assistance and discussions and to N. Ardoin and J. Moncada (Bordeaux) for their kind help in the preparation of the manuscript. Thanks are also due to Drs. P. Guénot and S. Sinbandhit (Centre de Mesures Physiques, Rennes), P. Hamon (Rennes I), and L. Latié (Centre de Recherches Paul Pascal, Bordeaux) for excellent assistance in the recording of spectroscopic data, to the Laboratoire de Photochimie et Photophysique Moléculaire (Bordeaux) and Dr. J.-P. Desvergne for allowing us to use their Cary 219 spectrophotometer, to E. Marquestaut (Laboratoire de Chimie du Solide, Bordeaux I) for kindly recording the ESR spectrum of 2 (L = PPh₃), and finally to a referee for helpful comments. The financial help by the Région Aquitaine, the University of Bordeaux I and the CNRS are gratefully acknowledged.

Registry No. 1a, 51812-05-6; 1b, 69022-30-6; 1c, 51812-08-9; 1d, 70414-92-5; 1d⁺, 53702-66-2; 3a⁺BF₄⁻, 111460-63-0; 3a⁺PF₆⁻, 78192-41-3; 4a, 84283-30-7; 4b, 110118-62-2; 4c, 127421-43-6; 4d, 127248-35-5; 4e, 51509-20-7; 4f, 12150-99-1; 4g, 84283-31-8; 5, 127421-41-4; 6, 125843-68-7; 7, 72447-25-7; 8, 127421-42-5; 9, 111460-61-8; 10a⁺, 79105-28-5; 11⁺, 78192-44-6; 12⁺, 112470-77-6; 13⁺, 83172-78-5; dppe, 663-45-2; dppm, 2071-20-7; [FeCp(η⁵-C₆H₆)₂], 54967-76-9; [FeCp(CO)₂]₂, 12154-95-9; PMe, 594-09-2; [Fe(PMe₃)₃(PMe₂CH₂)H], 56586-24-4; [FeCp(C₆H₅Me)]⁺PF₆⁻, 33435-42-6; [FeCp(C₆H₅Me)]⁺BF₄⁻, 32758-59-1; [FeCp(C₆H₅Me)]⁺[perylene]⁻, 127421-37-8; [FeCp(C₆H₅Me)]⁺[NC-*p*-C₆H₄Cn]⁻, 127421-38-9; [FeCp(C₆H₅Me)]⁺[NC-*p*-C₆H₄COOMe]⁻, 127421-39-0; P(OMe)₃, 121-45-9; FeCp[P(OMe)₃]₂D, 127421-40-3; P(OPh)₃, 101-02-0; PPh₃, 603-35-0; PPh₂H, 829-85-6; PPh₂D, 18632-84-3; FeCp(dppe)Cl, 32843-51-9.

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