J. Am. Chem. Soc. 1982, 104, 7549-7555

Organometallic Electron Reservoirs. 7.[1] One-Step Multiple Formation of C–C Bonds in CpFe$^+$(arene) Sandwiches and Unusual C$_6$Et$_6$ Geometry in the X-ray Crystal Structure of CpFe$^+$(η^6-C$_6$Et$_6$)PF$_6^-$

Jean-René Hamon,[†] Jean-Yves Saillard,[‡] Albert Le Beuze,[‡] Michael J. McGlinchey,[†,§] and Didier Astruc*[†]

Contributions from the Laboratoire de Chimie des Organométalliques, ERA CNRS No. 477, and the Laboratoire de Chimie du Solide et Inorganique Moléculaire, LA CNRS No. 254, Université de Rennes, 35042 Rennes Cedex, France. *Received June 6, 1982*

Abstract: So that Fe^I electron reservoirs in which bulky ligands encapsulate the central metal might be obtained, the steric limit for the syntheses of CpFe$^+$(arene) sandwiches was examined with the reaction system: CpFe$^+$(η^6-C$_6$H$_n$Me$_{6-n}$)PF$_6^-$ + base (t-BuOK) + alkylating reagent (RX). RCpFe$^+$(C$_6$Me$_6$)PF$_6^-$ (R = H, **1$^+$**; R = Me, **3$^+$**) reacts with excess t-BuOK and CH$_3$I in THF to give 80–90% yields of canary-yellow RCpFe$^+$(C$_6$Et$_6$)PF$_6^-$ (R = H, **2$^+$**; R = Me, **4$^+$**). **2$^+$** is orthorhombic and crystallizes in space group *Pcab* (Z = 8) with a = 13.438 (1) Å; b = 24.261 (4) Å, c = 14.617 (2) Å (current residual R index on F_o of 0.045 (R_w = 0.048)). **2$^+$** has near C_s symmetry. A new conformation of C$_6$Et$_6$ results from the bulk and the mismatch of the C$_5$ and C$_6$ sandwich rings, forcing three arene carbons to be eclipsed or nearly eclipsed by Cp carbons; the ethyl groups borne by these three carbons are directed away from the metal, and only two ethyls point toward the metal with unusually large C–CH$_2$–CH$_3$ angles (118.6°). Similar peralkylations of **1$^+$** proceed with C$_6$H$_5$CH$_2$X (X = Br or Cl), giving high yields of CpFe$^+$(C$_6$(CH$_2$)$_2$C$_6$H$_5$)$_6$PF$_6^-$ (**5$^+$**), the photolysis of which provides the free arene (58% overall yield from C$_6$Me$_6$). In CpFe$^+$(η^6-mesitylene)PF$_6^-$ (**9$^+$**), this reaction leads to the replacement of all the methyl hydrogens to give CpFe$^+$(1,3,5-C$_6$H$_3$(CMe$_3$)$_3$)PF$_6^-$ (**10$^+$**). The Na/Hg reduction of **10$^+$** gives the only thermally stable complex **10** of the d^7 Fe^I series in which the arene ligand bears less than six alkyl groups. In the intermediate case of CpFe$^+$(η^6-durene)PF$_6^-$ (**15$^+$**), the reaction with excess t-BuOK + CH$_3$I gives CpFe$^+$(η^6-1,2,4,5-C$_6$H$_2$(i-Pr)$_4$)PF$_6^-$ (**16$^+$**), resulting in the replacement of two out of three hydrogens on each methyl, as in CpFe$^+$(o-xylene)PF$_6^-$ (**13$^+$**), giving CpFe$^+$(η^6-o-C$_6$H$_4$(i-Pr)$_2$)PF$_6^-$ (**14$^+$**). Cp permethylation does not perturb the permethylation of mesitylene in C$_5$Me$_5$Fe$^+$(mesitylene)PF$_6^-$ (**11$^+$**) which essentially gives C$_5$Me$_4$EtFe$^+$(1,3,5-C$_6$H$_3$(t-Bu)$_3$)PF$_6^-$ (**12$^+$**); on the contrary, this perturbation is more dramatic in C$_5$Me$_5$Fe$^+$(C$_6$Me$_6$)PF$_6^-$ (**16$^+$**), giving a complicated mixture of C$_5$Me$_{5-x}$Et$_x$Fe$^+$(C$_6$Me$_{6-y}$)PF$_6^-$ $(1 < \bar{x}, \bar{y} < 3)$ even under forcing conditions. The organic reaction of t-BuOK with CH$_3$I limits the extent of peralkylation in **1$^+$** (but not in **9$^+$**) and in other CpFe$^+$(arene) complexes when a certain degree of steric bulk is reached, as indicated by further deprotonation and methylation of **2$^+$**, giving CpFe$^+$(C$_6$Et$_5$$i$-Pr)PF$_6^-$ (**19$^+$**). The Cp methyls are not alkylated in C$_5$Me$_5$Fe$^+$C$_6$H$_6$PF$_6^-$ (**17$^+$**) (contrary to **6$^+$** and **11$^+$**) by excess t-BuOK and CH$_3$I.

The very negative value of the reduction potential of the CpFe$^+$(arene)/CpFe^I(arene) system[2] has stimulated studies aimed at stabilizing such systems and using the "electron reservoir" properties of the reduced forms.[3] The recent discovery that the Fe(I) series is stabilized when the arene ligand bears six alkyls[4] was followed by the finding that the totally reversible Fe^{II}/Fe^I system is a redox catalyst for the reduction of NO$_3^-$ to NH$_3$ on an Hg cathode in water[4,5] and that electron transfer to O$_2$ leads to activation of C–H bonds via the superoxide radical anion.[6] In an electron-transfer reaction to a substrate by a CpFe^{I}arene complex, however, it is generally found that the radical anion of the substrate directly or indirectly reacts with the Fe(I) complex to give addition to either of the sandwich rings (eq 1)[7] or leads to deprotonation.[6] We wished to sterically protect the sandwich

$$2\mathrm{CpFe^I(C_6H_6)} + \mathrm{RX} \rightarrow \mathrm{CpFe^{II}(\eta^5\text{-}C_6H_6R)} + \mathrm{CpFe^+(C_6H_6)X^-} \quad (1)$$

rings and therefore investigated the synthetic limits of CpFe$^+$(arene) sandwiches with peralkylated rings. One esoteric but nevertheless powerful way to reach this steric limit was to peralkylate CpFe$^+$(arene) salts in which the ligands bore several methyl groups. We know that the reactions of bases with CpFe$^+$(C$_6$Me$_6$) (**1$^+$**) give thermally stable CpFe^{II}(η^5-C$_6$Me$_5$CH$_2$)[6] which reacts under mild conditions with a great variety of substrates of the RX type (R = C, Si, P, halogen, metal; X = halogen) to give nucleophilic substitution of the halogen.[8,9]

$$\mathrm{CpFe^+(\eta^6\text{-}C_6Me_6)} \xrightarrow{\text{base}} \mathrm{CpFe(\eta^5\text{-}C_6Me_5CH_2)} \xrightarrow{\text{RX}} \mathrm{CpFe^+(\eta^6\text{-}C_6Me_5CH_2R)X^-} \quad (2)$$

It was of obvious interest to examine how peralkylation could occur and to what extent when one uses an excess of base and of alkylating reagent. The deprotonated CpFe$^+$(arene) complexes are not stable when the arene bears less than six methyls,[6] but

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[†] Laboratoire de Chimie des Organométalliques, D.A. is C.N.R.S. Fellowship Recipient 1978–1982. J.R.H. was D.G.R.S.T. predoctoral Fellow 1979–1981 and is C.N.R.S. Fellow since 1981.

[‡] Laboratoire de Chimie du Solide et Inorganique Moléculaire.

[§] On sabbatical leave from McMaster University, Hamilton, Ontario, Canada, 1979.

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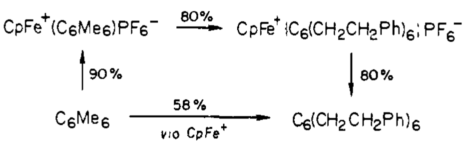
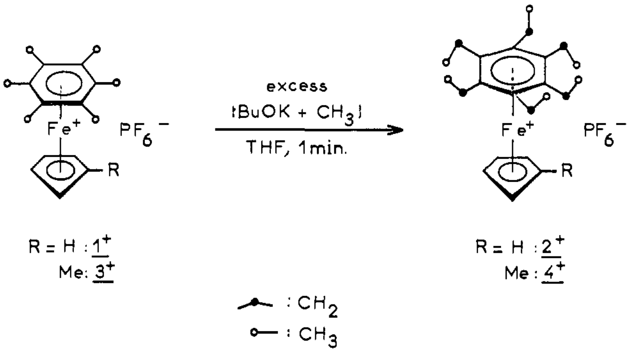
Scheme I



it was hoped that alkylation would proceed faster than decomposition or polymerization.

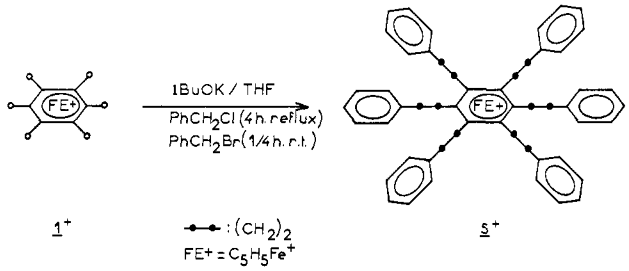
Results

Peralkylation of $CpFe^+(C_6Me_6)PF_6^-$ (1^+). The readily accessible complex $CpFe^+(\eta^6\text{-}C_6Me_6)PF_6^-$[10] was treated with excess *t*-BuOK and excess alkylating agent; addition of a THF solution of excess CH_3I to a mixture of 1^+ and *t*-BuOK gave the red color of the deprotonated complexes, and a gentle spontaneous reflux occurred during a minute whereupon the color turned beige and $CpFe^+(C_6Et_6)PF_6^-$ (2^+)[4,11] could be extracted in quantitative crude yield. The reaction should not be done in an ice bath because incomplete alkylation is found even after prolonged periods of time. The same reactions proceed with $CH_3CpFe^+(C_6Me_6)PF_6^-$ (3^+) giving $CH_3CpFe^+(C_6Et_6)PF_6^-$ (4^+) (eq 3).



(3)

Analogous reactions proceed with $C_6H_5CH_2X$ (X = Cl, Br) in 15 min at 20 °C with X = Br and 4 h at reflux with X = Cl to reach completion under the same conditions, giving 5^+, the photolysis of which gives the free ligand (58% overall yield from C_6Me_6, eq 4 and Scheme I.

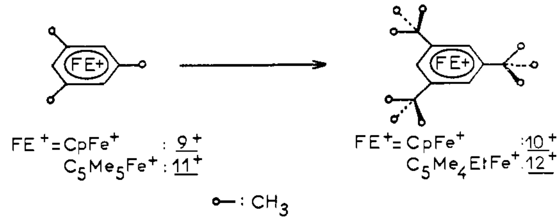


(4)

Attempts to Peralkylate $C_5Me_5Fe^+(C_6Me_6)PF_6^-$ (6^+). In order to reach a more complete encapsulation, we have attempted the peralkylation of the fully methylated complex $C_5Me_5Fe^+(C_6Me_6)PF_6^-$ (6^+)[4,11] with the hope of obtaining an alkylated sandwich $C_5Et_5Fe^+(C_6Et_6)PF_6^-$ or $C_5Me_5Fe^+(C_6Et_6)PF_6^-$. However, complicated mixtures arise from the peralklyation reactions. Under mild conditions (20 °C), the C_6Me_6 ligand is only partially alkylated (ca. 50%) and the C_5Me_5 ligand is also subject to this transformation to the extent of ca. 30%. Under more drastic conditions, it is not possible to totally alkylate the arene methyls even at reflux; the ^1H NMR spectrum of the crude reaction mixture indicates that 65% of these are alkylated after 2 weeks at reflux in DME while 55% of the Cp methyls are similarly alkylated. The $\{^1H\}^{13}C$ NMR spectrum shows the formation of a large number of cationic sandwiches. As of now the reaction is neither total nor specific and cannot be used for any synthetic purpose.

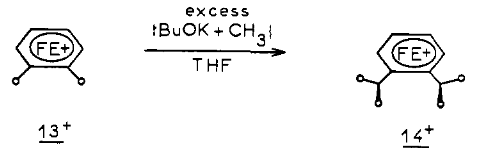
$$\underset{6^+}{C_5Me_5Fe^+(C_6Me_6)PF_6^-} \rightarrow \underset{1 < \bar{x},\, \bar{y} < 3}{C_5Me_{5-x}Et_xFe^+(C_6Me_{6-y}Et_y)PF_6^-} \quad (5)$$

Peralkylation of the $CpFe^+$(arene) Complexes with Less Than Six Arene Methyls. $CpFe^+(C_6H_5CH_3)PF_6^-$ (7^+)[12] reacts with excess CH_3I and *t*-BuOK in THF. A mild reflux occurs and $CpFe^+(C_6H_5t\text{-}Bu)PF_6^-$ (8^+) can be extracted in 22.5% yield of microcrystals. Similarly $CpFe^+$(mesitylene)PF_6^- (9^+)[12] gives, after 3 min of a spontaneous mild reflux, a 70% yield of powdered $CpFe^+(1,3,5\text{-}C_6H_3(t\text{-}Bu)_3)PF_6^-$ (10^+, 63% of microcrystals after recrystallization from ethanol). Permethylation of Cp does not inhibit the permethylation of the mesitylene ligand, and a mixture of complexes $C_5Me_{5-z}Et_zFe^+(1,3,5\text{-}C_6H_3(t\text{-}Bu)_3)PF_6^-$ is obtained upon permethylation of $C_5Me_5Fe^+$(mesitylene)PF_6^- (11^+). The ^1H and $\{^1H\}^{13}C$ NMR spectra of the reaction mixture indicate that $C_5Me_4EtFe^+(1,3,5\text{-}C_6H_3(t\text{-}Bu)_3)PF_6^-$ (12^+) is the major reaction product (50–60%).

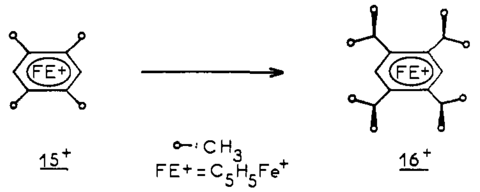


(6)

The intermediate situation between mesitylene and C_6Me_6 was also studied. In durene and *o*-xylene, each methyl has only one vicinal methyl while it has two in C_6Me_6 and none in mesitylene. The permethylation of $CpFe^+$(*o*-xylene)PF_6^- (13^+)[10] gives a 35% yield of $CpFe^+(o\text{-}C_6H_4(i\text{-}Pr)_2)PF_6^-$ (14^+) and that of $CpFe^+$(durene)PF_6^- (15^+)[10] gives $CpFe^+(1,2,4,5\text{-}C_6H_2(i\text{-}Pr)_4)PF_6^-$ (16^+) in 60% yield of recrystallized products.



(7)



(8)

Steric Stabilization of a d^7 Fe(I) Complex with Less Than Six Arene Substituents. It is known that the Na/Hg reductions of $CpFe^+$(arene) cations only give thermally stable $CpFe^I$(arene) complexes when the arene ring bears six alkyl groups.[4,11] Dimerization to $Cp_2Fe^{II}{}_2(\eta^5\text{-}C_6H_nMe_{6-n})_2$ exclusively occurs through an unsubstituted arene carbon and is thus sterically inhibited in the case of a C_6R_6 ligand (R = CH_3 or C_2H_5). For example, $CpFe^I(C_6HMe_5)$ rapidly dimerizes in the solid state at −10 °C.[11] We now find that an exception to this trend is the thermal stability observed for $CpFe^I(1,3,5\text{-}C_6H_3(t\text{-}Bu)_3)$ (**10**) in solution as well

$$\underset{10^+}{CpFe^+(1,3,5\text{-}C_6H_3(t\text{-}Bu)_3)} \xrightarrow[\text{THF, 20 °C, 0.5 h}]{\text{Na/Hg}} \underset{(\mathbf{10})}{CpFe^I(1,3,5\text{-}C_6H_3(t\text{-}Bu)_3)} \quad (9)$$

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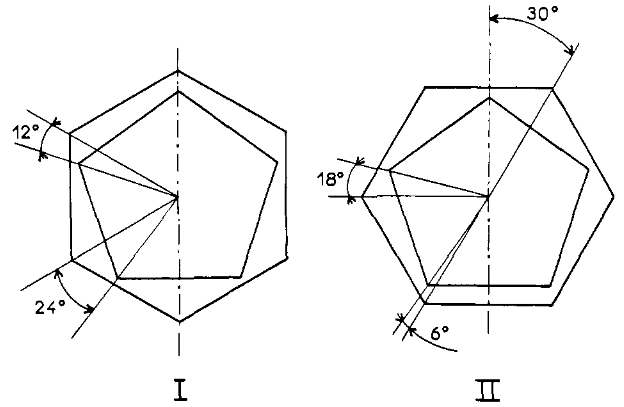
Scheme II



as in the solid state at 20 °C. This green Fe(I) complex can thus be synthesized, extracted, and handled at room temperature (in the absence of air). Its Mössbauer spectra confirm that it belongs to the d^7 CpFe^I(arene) series already studied.[11] Physical properties and an interesting reactivity pattern, especially with O$_2$, will be described later.[13]

Attempts to Permethylate C$_5$Me$_5$ in the Absence of Arene Alkyls. The acidity of the C$_5$Me$_5$ hydrogens is weaker that that of arene methyls, but the peralkylation of the fully methylated complex **6$^+$** also partially occurs on the C$_5$Me$_5$ ring (eq 5), indicating that the acidity of the C$_5$Me$_5$ hydrogens might somehow be used for alkylation. Thus we attempted to alkylate C$_5$Me$_5$Fe$^+$(C$_6$H$_6$)PF$_6^-$ (**17$^+$**),[11] but reaction with excess *t*-BuOK and CH$_3$I does not give any result in this case and the complex is recovered completely unchanged after workup of the reaction. A mild reflux of THF was noted, however, during a few minutes, which corresponds to the reaction of CH$_3$I with *t*-BuOK, giving *t*-BuOCH$_3$ and KI.

Deprotonation and Alkylation of CpFe$^+$(C$_6$Et$_6$)PF$_6^-$. Although the reaction of excess *t*-BuOK and CH$_3$I with **1$^+$** gives **2$^+$**, we know that further deprotonation to CpFe^{II}(C$_6$Et$_5$CHMe) (**18**) is possible starting from **2** and O$_2$.[9] We have treated **2$^+$** with 1 mol of *t*-BuOK in THF and obtained **18** in 75% crude yield after extraction with pentane (eq 10). Subsequent reaction with 1 mol

$$\underset{\mathbf{2^+}}{\mathrm{CpFe^+(\eta^6\text{-}C_6Et_6)PF_6^-}}\ \xrightarrow[\mathrm{THF}]{t\text{-BuOK}}\ \underset{\mathbf{18}}{\mathrm{CpFe(\eta^5\text{-}C_6Et_5CHMe)}} \qquad (10)$$

of CH$_3$I in THF proceeds at reflux in 2 h and gives CpFe$^+$(C$_6$Et$_5$*i*-Pr)PF$_6^-$ (**19$^+$**) in 70% yield after metathesis with HPF$_6$ in water and recrystallization from ethanol (eq 11). As

$$\underset{\mathbf{18}}{\mathrm{CpFe(\eta^5\text{-}C_6Et_5CHMe)}}\ \xrightarrow[\substack{\mathrm{THF}\\ \text{(reflux, 2 h)}}]{\mathrm{CH_3I}}\ \underset{\mathbf{19^+}}{\mathrm{CpFe^+(\eta^6\text{-}C_6Et_5}i\text{-}\mathrm{Pr)}} \qquad (11)$$

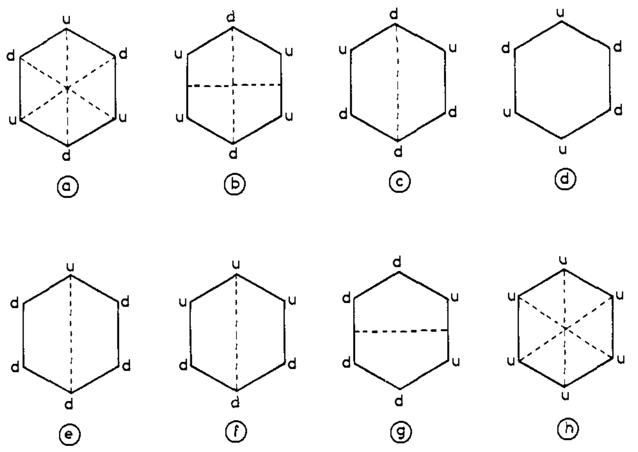
for **16$^+$**, the ^{1}H NMR spectrum of **19$^+$** indicates the presence of two magnetically nonequivalent methyls for the isopropyl group. δ_{Cp} is shifted 0.15 ppm upfield as compared to δ_{Cp} in **2$^+$**.

Conformational Problem in a Mixed C$_5$–C$_6$ Sandwich and in CpFe$^+$(C$_6$Et$_6$)

Symmetry and Ring Conformations in C$_5$–C$_6$ Sandwiches. There are two possible conformations for a mixed C$_5$–C$_6$ sandwich such as C$_5$H$_5$Fe$^+$(C$_6$H$_6$) (Scheme II), which maintain C_s symmetry.

The symmetry plane of the sandwich results in the coincidence of a σ_v plane of the D_{5h} Cp ring with a σ_v plane of the D_{6h} benzene ring for conformation I or with a σ_d plane of benzene for conformation II. The only molecular structure for a CpM(arene) sandwich known to date is that of the d^7 19-electron complex CpFe^I(C$_6$Me$_6$) which has conformation II. It is probable that, as for ferrocene,[14] the conformation of C$_5$H$_5$Fe$^+$(C$_6$H$_6$) results from electronic effects and that the interconversion energy I $\rightleftharpoons$ II is low. The situation is different, however, for CpFe$^+$(C$_6$Et$_6$) in which steric effects may predominate. The most stable conformation is that in which steric interactions Et–Et and Et–Cp as a whole are minimized.

Scheme III



Ethyl Conformations in C$_6$Et$_6$. Stable conformations of C$_6$Et$_6$ are those in which the C ring–CH$_2$–CH$_3$ planes are perpendicular to the C$_6$ ring plane. The energies of these eight possible "up–down" conformers (Scheme III) have been calculated by Mislow et al.[15] using the EFF–EHMO method.[16] Examination of these results leads to a classification of these eight conformers in four groups of increasing energy.

The first group contains only conformation a which has been shown to be that of C$_6$Et$_6$ in the solid state. Conformations b, c, and d are close in energy (group II), as are e, f, and g (group III). The last group is the least stable conformer h. This classification into four groups is not surprising insofar as it corresponds to the number of up–down alternations between neighboring ethyls about the ring. In the most stable conformation a, the up–down alternation is perfect, which minimizes the steric repulsion between vicinal ethyls. In the second group there are only four such alternations, only two in group III, and none in the least stable conformation h (group IV).

Conformations of η^6 Metal Complexes of C$_6$Et$_6$. Four X-ray crystal structures of complexes of the type C$_6$Et$_6$M(CO)$_2$L are known (M = Cr, L = CO,[15] CS,[17] and PPh$_3$;[15] M = Mo, L = CO;[15] Figure 2). For L = CO or CS, the conformation a is found as in the free ligand (M = Cr or Mo, Figure 2a), but with the bulky ligand L = PPh$_3$, the six ethyls are pushed away from the metal moiety and the (extreme) conformation h is adopted (Figure 2b).[19]

Let us examine the steric and symmetry constraints of the C$_6$Et$_6$ conformations a–h in the mixed sandwich structures with conformations I for **2$^+$**. Conformation a would imply large steric

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[19] In the X-ray crystal structure study of C$_6$Et$_6$Cr(CO)$_2$PPh$_3$,[15] some disorder was found and one-third of the molecules adopt a conformation in which only five ethyls are "up" and one is "down" (see also ref 15c). It may be that intermolecular (packing) forces play an important part by forcing specific ethyl conformations, especially in arene ML$_2$L′ type complexes in which L′ is large. See: Saillard, J. Y.; Lissillour, R.; Grandjean, D. *J. Organomet. Chem.* **1981**, *210*, 365–376.

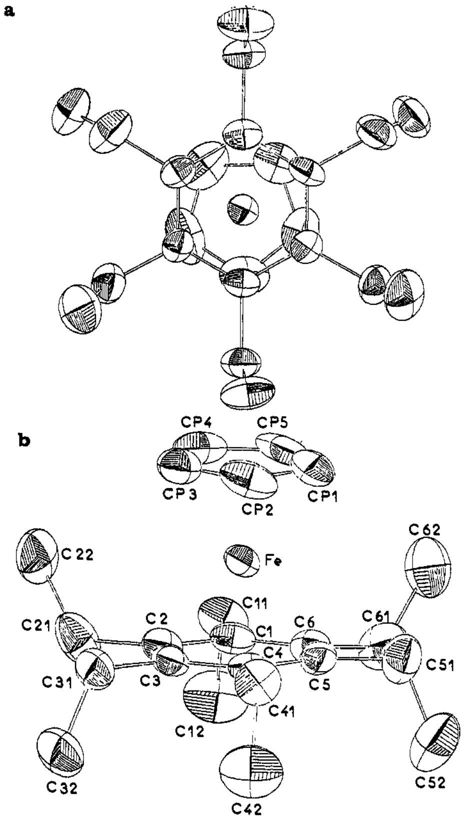

Figure 1. ORTEP drawing of the molecular structure of $CpFe^+C_6Et_6PF_6^-$ (**2**). All non-hydrogen atoms are represented by thermal vibration ellipsoids to encompass 50% of the electron density. (a) Projection on the cyclopentadienyl ring. (b) Perspective view.

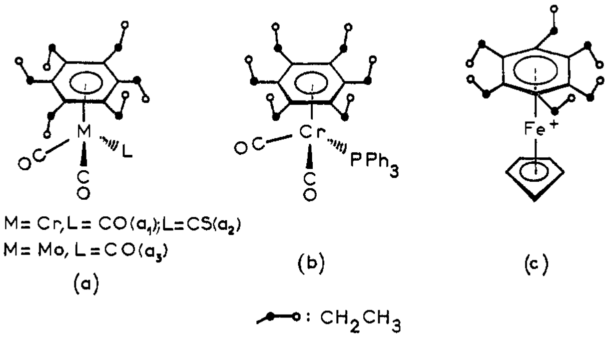

Figure 2.

constraints because one or two ethyls would be close to Cp carbons. In the second group, conformation c (less stable than a) gives, with I, the minimum global interactions, having no eclipsed Cp ring carbon close to ethyls in the "up" position ("up" refers to a distal ethyl directed away from the metal, while "down", of course, is proximal). Analogous considerations lead us to associate conformations b or g of C_6Et_6 with a type II geometry. These three selected arrangements I/c, II/b, and II/g have two "down" ethyls respectively staggered by 24°, 18°, and 30° with respect to the closest Cp carbons. As conformation g belongs to the third highest group in energy, conformation I/c (Figure 2c) is the most favored as a compromise in minimizing the Et–Et and Et–Cp repulsions.

Description of the Structure of 2^+

Prior to this study no X-ray crystal structure had been reported for a sandwich complex of C_6Et_6 nor for a $CpFe^+$(arene) cation. The only structure known to be at variance with the classical conformation of perfectly alternating "up and down" ethyls for a complex of C_6Et_6 (conformation a) is that of $C_6Et_6Cr(CO)_2(PPh_3)$[15,19] (Figure 2b) in which all the ethyls are distal (h). We

Table I. Selected Bond Distances (Å) and Bond Angles (deg)

Fe–Cp1	2.061 (7)	C6–C1–C2	120.4 (5)
Fe–Cp2	2.040 (6)	C1–C2–C3	119.7 (5)
Fe–Cp3	2.044 (6)	C2–C3–C4	119.4 (5)
Fe–Cp4	2.066 (6)	C3–C4–C5	120.2 (5)
Fe–Cp5	2.058 (6)	C4–C5–C6	120.3 (5)
Fe–C1	2.120 (5)	C5–C6–C1	119.9 (5)
Fe–C2	2.124 (5)	Cp5–Cp1–Cp2	108.5 (7)
Fe–C3	2.111 (5)	Cp1–Cp2–Cp3	107.8 (7)
Fe–C4	2.096 (5)	Cp2–Cp3–Cp4	109.2 (7)
Fe–C5	2.070 (5)	Cp3–Cp4–Cp5	107.2 (7)
Fe–C6	2.130 (5)	Cp4–Cp5–Cp1	107.3 (7)
C1–C2	1.421 (7)	C6–C1–C11	120.9 (5)
C2–C3	1.445 (7)	C2–C1–C11	118.7 (5)
C3–C4	1.432 (7)	C1–C2–C21	121.1 (5)
C4–C5	1.420 (7)	C3–C2–C21	119.2 (5)
C5–C6	1.421 (7)	C2–C3–C31	119.3 (5)
C6–C1	1.428 (7)	C4–C3–C31	121.4 (5)
C1–C11	1.533 (7)	C3–C4–C41	119.9 (5)
C2–C21	1.531 (8)	C5–C4–C41	119.9 (5)
C3–C31	1.509 (8)	C4–C5–C51	120.7 (5)
C4–C41	1.538 (7)	C6–C5–C51	118.9 (5)
C5–C51	1.525 (8)	C5–C6–C61	120.9 (6)
C6–C61	1.504 (8)	C1–C6–C61	119.2 (5)
C11–C21	1.531 (10)	C1–C11–C12	110.5 (6)
C21–C22	1.514 (11)	C2–C21–C22	118.0 (6)
C31–C32	1.501 (9)	C3–C31–C32	113.4 (6)
C41–C42	1.525 (10)	C4–C41–C42	111.1 (6)
C51–C52	1.501 (10)	C5–C51–C52	113.6 (6)
C61–C62	1.518 (11)	C6–C61–C62	119.2 (6)
Cp1–Cp2	1.364 (10)	F1–P–F2	90.3 (2)
Cp2–Cp3	1.379 (9)	F1–P–F3	89.0 (2)
Cp3–Cp4	1.383 (8)	F1–P–F4	91.0 (2)
Cp4–Cp5	1.389 (10)	F1–P–F5	89.8 (2)
Cp5–Cp1	1.405 (10)	F2–P–F3	89.1 (3)
P–F1	1.584 (4)	F2–P–F4	91.3 (3)
P–F2	1.567 (4)	F2–P–F6	90.1 (2)
P–F3	1.582 (4)	F3–P–F5	89.3 (3)
P–F4	1.549 (4)	F3–P–F6	90.0 (2)
P–F5	1.568 (4)	F4–P–F5	90.4 (3)
P–F6	1.597 (3)	F4–P–F6	90.0 (2)
		F5–P–F6	89.8 (2)

note, however, that the structure of hexaethylborazinechromium tricarbonyl has been reported[18] to adopt the conformation found in Figure 2c, presumably attributable to the puckering of the borazole skeleton.

The conclusions drawn from the (qualitative) symmetry and steric considerations above suggest a new arrangement for a complex of C_6Et_6 and, gratifyingly, are verified by the room-temperature X-ray crystal structure of 2^+ showing the I/c conformation (Figure 1). Selected bond lengths and bond angles are summarized in Table I. Least-squares plane equations, some dihedral angles, and deviations of non-hydrogen atoms of the Cp and benzene mean planes are reported in Table II. The C_{ring}–CH_2–CH_3 mean angle of the "up" (distal) ethyls (112.1°) is not significantly different from the corresponding angle in a_1, a_2, a_3 (Figure 2, respectively 111.9°, 112.1°, and 112.2° for the $Cr(CO)_3$, $Cr(CO)_2CS$, and $Mo(CO)_3$ complexes of C_6Et_6). In contrast, the C_{ring}–CH_2–CH_3 mean angle of the "down" (proximal) ethyl is larger in 2^+ (118.6°) than in a_1, a_2, and a_3 (Figure 2, 115.4° and 115.7°). The large value of this angle, close to that of an sp^2 carbon, reveals that steric constraints are larger in 2^+ than in a (Figure 2). Other features are attributable to these steric constraints between the Cp ring and the two proximal ethyls. The comparison of the Fe–C(arene) distances shows that the CpFe moiety is shifted slightly toward C4. The mean planes of the two rings are not strictly parallel (dihedral angle 4°), these planes being closer to each other at the C1, C2, C6/Cp1, Cp2 side than at the C3, C4, C5/Cp3, Cp4, Cp5 side, as a result of the presence of two ethyls "down" on the latter side. The dihedral angles beween the C_{ring}–CH_2–CH_3 planes and the least-squares plane of the six C_{ring} differ slightly from the ideal value of 90°. The larger difference observed concerns the C3, C4, and C5 ring carbons and may be interpreted in terms of mutual steric constraints between the three vicinal "up" (distal) ethyls. In contrast, the dihedral

Table II. Weighted Least-Squares Planes[a]

plane no.[a]	A	B	C	D	atoms involved
1	0.4782	−0.6985	−0.5324	−2.6723	Cp1, Cp2, Cp3, Cp4, Cp5
2	0.4449	−0.6741	−0.5897	0.4664	C1, C2, C3, C4, C5, C6
3	0.8030	0.5955	−0.0224	5.5482	C1, C11, C12
4	0.1180	0.6525	−0.7486	2.3815	C2, C21, C22
5	−0.6668	0.0748	−0.7414	−2.9965	C3, C31, C32
6	−0.7691	−0.6384	−0.0301	−5.5092	C4, C41, C42
7	0.0383	0.7725	−0.6339	2.3350	C5, C51, C52
8	−0.6953	0.0795	−0.7143	−3.1376	C6, C61, C62

Dihedral Angles between Planes (Deg)

planes	angle	planes	angle	planes	angle
1 and 2	4.0	2 and 4	86.9	2 and 6	83.9
2 and 3	91.8	2 and 5	84.8	2 and 7	97.5
				2 and 8	86.7

Deviations of Atoms from Least-Squares Planes (Å)

atom	plane 1	atom	plane 2	atom	plane 2
Cp1	−0.012 (7)	C1	−0.009 (6)	C11	−0.072 (6)
Cp2	0.009 (7)	C2	−0.005 (6)	C21	0.000 (7)
Cp3	−0.004 (6)	C3	0.003 (6)	C31	0.008 (6)
Cp4	−0.003 (7)	C4	0.012 (5)	C41	−0.010 (6)
Cp5	0.008 (7)	C5	−0.026 (6)	C51	−0.131 (7)
C1	3.322 (6)	C6	0.026 (6)	C61	0.152 (7)
C2	3.292 (6)	Cp1	−3.200 (7)	C12	1.338 (8)
C3	3.200 (6)	Cp2	−3.140 (7)	C22	−1.332 (7)
C4	3.145 (5)	Cp3	−3.226 (6)	C32	1.381 (8)
C5	3.142 (6)	Cp4	−3.310 (7)	C42	1.397 (8)
C6	3.292 (6)	Cp5	−3.278 (7)	C52	1.188 (8)
Fe	1.683 (1)	Fe	−1.551 (1)	C62	−1.104 (8)

[a] Equation of the planes is of the form $Ax + By + Cz - D = 0$, where x, y, and z are orthogonalized coordinates.

angle of the nonconstrained C1–C11–C12 ethyl is close to 90°. The geometrical deviations from the ideal C_s symmetry may be regarded as the result of crystal packing forces which are larger in an ionic crystal such as that of **2**$^+$ than in molecular solids. The 11 shorter F···H interionic distances are included in the 2.56–2.8-Å range and involve five H atoms from the ethyls. The Fe–Cp distance (1.68 Å) falls in the range of similar bonds of d^6 Fe(II) complexes such as ferrocene[14] and CpFe(η^5-$C_6Me_5CH_2$).[8] No Fe–arene distance has been recorded in a Fe(II) complex prior to this study. We note that the Fe–$C_6Me_5CH_2$ distance (1.54 Å) is not different from the Fe–arene distance found in **2**$^+$ (1.55 Å). A very slight lengthening by 0.02 Å (Fe–Cp) and 0.01 Å (Fe–arene) observed in **2**$^+$ by comparison with the other Fe(II) complexes[8] might be attributed to the steric bulk of the two "down" ethyls. On the other hand, the comparison of the Fe–ring distances in **2**$^+$ and in the d^7 19-electron complex CpFe^I(C_6Me_6)[4] is of interest because the ligands have the same electronic properties and mode of coordination in both complexes. Thus the difference in Fe–ring distances are exclusively due to the presence of one extra electron in the Fe^I complex (in a doubly degenerate antibonding e$^*_1$ orbital). Whereas the Fe–arene distance is only longer by 0.03 Å in the Fe(I) complex (1.58 Å) than in **2**$^+$ (1.55 Å), the Cp–Fe distance is 0.10 Å longer (cf. 1.78 Å in the Fe^I complex). This indicates that the antibonding e$^*_1$ orbital has more Cp than arene character, as suggested by the molecular orbital diagram (e$^*_1$ is closer to e$_1$ (Cp) than to the lower e$_1$ (arene)). This finding is most useful for the structure–reactivity relationship of paramagnetic complexes.[11]

Discussion of the Peralkylations

The peralkylation of CpFe$^+$(arene) sandwiches using *t*-BuOK and RX works best with **1**$^+$ bearing the C_6Me_6 ligand because the deprotonated complex is thermally stable above 100 °C. Thus this reaction can be applied to a great variety of reagents, RX, even those reacting slowly. Not only iodides but also chlorides and bromides react to give peralkylation. Only one H on each methyl is replaced by R for various RX systems. The dependence of the reaction on R and X concerns only the rates. A simple steric rule arises from the reactions of CpFe$^+$ complexes of poly(methyl)benzene with excess *t*-BuOK and CH_3I, correlating the number of hydrogen(s) replaced on each methyl with the number of viscinal methyl(s) on the benzene ring: only one H is replaced on a methyl having two vicinal methyls, two H are replaced on a methyl having only one and all the three on a methyl having none. One can evaluate the role of steric factors in these reactions by considering the steric constraints in **2**$^+$. Much important information in this respect derives from the structural data, viz, the interdependence of the conformation of the Cp ring and the position, up or down, of the methyl groups of the ethyls, the unusually large angle about the methylene carbons in the two ethyls pointing toward the CpFe moiety, and to a lesser extent, the twist of the CH_2–CH_3 bonds away from the plane perpendicular to the arene ring plane for the three adjacent ethyls. A comparison of the crystal structures of $C_6Et_6Cr(CO)_2L$ (L = CO and CS), $C_6Et_6Mo(CO)_3$, and **2**$^+$ shows that the steric constraints imposed by the Cp are larger than those of the $M(CO)_2CS$ moieties (X = O or S). Steric considerations must be extended to the dynamic state; i.e., the constraints limiting the syntheses are "stereoentropic". This is exemplified by the dealkylation observed during the synthesis of **2**$^+$ by the classical exchange reaction between ferrocene and C_6Et_6 above 80 °C. This low-temperature limit considerably decreases the yield, and subsequently, the peralkylation of **1**$^+$ is a more convenient route to **2**$^+$. Still more dramatic "stereoentropic" constraints are found for the synthesis of the pentamethyl Cp analogue from $C_5Me_5Fe(CO)_2Br$ and C_6Et_6, a reaction always leading to dealkylation even at low temperature and which will be discussed in more detail later.[20] The dynamic behavior of the ethyls in **2**$^+$ involves a very facile interconversion of the proximal and distal methyls, and this rotation is not slow even at 400 MHz and −110 °C on the NMR time scale.[21] Consistently the permethylation reaction is very sensitive to Cp substituents: the presence of five methyls on Cp dramatically perturbs the permethylations although it is still possible to transform the C_6Me_6 ligand into a C_6Et_6 one by permethylation when only one methyl is present on Cp. Along this line, it may be noted that the metal vapor synthesis of Cr(C_6Et_6)$_2$ failed and gave a product unstable above −60 °C.[21]

An important point that need be considered for the understanding of the peralkylation reactions is the reaction between *t*-BuOK and RX. Although this side reaction by no means reduces the yields of the peralkylations of **1**$^+$, it becomes predominant at a certain stage of steric bulk or when the acidity of the potential alkylation site is lower (i.e., C_5Me_5). The competition is striking, judging from the failure to permethylate $C_5Me_5Fe^+(C_6H_6)PF_6^-$ despite the "partial permethylation" of C_5Me_5 in $C_5Me_5Fe^+(C_6Me_6)PF_6^-$ (indicating that intermediate (η^4-fulvene)Fe^0(arene) can be reached and alkylated). In the simple case of the permethylation of **1**$^+$ giving CpFe$^+$(C_6Et_6)PF_6^-, one may first address the question as to whether this structure represents the maximum steric or "stereoentropic" constraint that can be reached or, if not, why further deprotonation and alkylation do not occur. The reactions finish when the red color of the deprotonated CpFe(η^5-benzyl) species disappears to give the beige color of the cation **2**$^+$. Thus **2**$^+$ is not further deprotonated under the reaction conditions. We know, however, that O_2 reacts with the d^7 19-electron complex CpFe^I(C_6Et_6) to give the H atom abstraction product CpFe^{II}(C_6Et_5CHMe),[9] a reaction which in fact consists of the deprotonation of **2**$^+$ by $O_2^{\cdot -}$ subsequent to electron transfer; furthermore, we have checked that *t*-BuOK does indeed deprotonate **2**$^+$ to give **18**. Thus this apparently feasible deprotonation does not proceed under the permethylation conditions because it is disfavored with respect to the organic side reactions. Indeed deprotonation of a methylene group from **2**$^+$ is slow. Now the question of the maximum bulk bearable by the hexasubstituted arene ligand in CpFe$^+$(C_6R_6) is still open. We

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(20) Hamon, J.-R.; Astruc, D., work in progress.

(21) McGlinchey, M. J.; Sayer, B. G.; Hamon, J.-R.; Astruc, D., unpublished results.

have partially answered this point insofar as we have obtained $CpFe^+(C_6Et_5\textit{i}\text{-Pr})PF_6^-$ by the (slow) reaction of **18** with CH_3I in refluxing THF.

In the permethylation of $CpFe^+(C_6H_{6-n}Me_n)$ sandwiches ($n < 6$), the relief of steric bulk about each methyl destabilizes the deprotonated species, the polymerizations of which decrease the permethylation yields. Simultaneously, however, the benzylic deprotonations are faster on ethyls and isopropyls, so that the limitation of permethylation by the organic reaction is nullified in the case of a mesitylene ligand (even if the Cp is permethylated) and in mono- or dimethylarenes in which the methyls are not vicinal. The acidity of benzylic protons has been known to be enhanced by the $Cr(CO)_3$ group since the work by Trahanovsky and Card[22] and alkylation of monoalkyl arenes via activation by this moiety was performed later.[23] In the case of the isolobal $CpFe^+$ group, activation is even stronger due to the cationic charge. Davies, Green, and Mingos have shown that more cationic charge is delocalized onto the even ligand than onto the odd one in mixed cationic sandwiches such as $CpFe^+$(arene).[24] Indeed, it has been known for a long time that $CpNH_2Fe^+(C_6H_6)$ is more basic than its isomer $CpFe^+(C_6H_5NH_2)$,[25] and consistent with this, $CpFe^+(C_6H_5CO_2H)$ is more acidic than $CpCO_2HFe^+(C_6H_6)$.[26] Nucleophilic substitution of halide is faster in $CpFe^+(C_6H_5X)$ than in $CpXFe^+(C_6H_6)$,[27] and nucleophilic addition on $CpFe^+(C_6H_6)$ proceeds on the benzene ligand.[28] In the light of these numerous features, it is clear that deprotonation of alkyl $CpFe^+$(arene) sandwiches would be much more difficult on the Cp alkyl than on an arene alkyl, and this is indeed so. The facile deprotonation of $CpFe^+$(alkylbenzene) sandwiches has already been reported,[6,8,9,29] that of **1**$^+$ giving a d^6 Fe(II) complex stabilized by a structure isoelectronic to that of ferrocene as shown by its X-ray crystal structure indicating a η^5-benzyl coordination of the deprotonated arene ligand.[8] In spite of this stabilization, the nucleophilic properties of the deprotonated species are rich and their investigation led to bond formation with many elements. Thus the balance between the deprotonation of $CpFe^+$(arene) and the nucleophilic properties of their deprotonated species renders the $CpFe^+$ activating group extremely useful in arene synthesis via benzylic activation. It is reasonable to assume that the peralkylations performed in the present study could be extended to polyfunctionalizations in the light of the synthesis already reported by using reactions of $CpFe(\eta^5\text{-}C_6Me_5CH_2)$ with a variety of electrophiles.[9] If so, the pattern of a large family of new polydentate organometallic ligands could soon be at hand. We intend to pursue further studies along this line.

Concluding Remarks

The peralkylation of the poly(methyl)arene ligand by the reaction of excess *t*-BuOK and RX in $CpFe^+$(arene) sandwiches is a clean and spectacular process of potential synthetic interest. Bulky $CpFe^+$(arene) sandwiches with hexalkylarene ligands have been obtained easily by this route. The resolution of the X-ray crystal structure of $CpFe^+(C_6Et_6)PF_6^-$ indicates that the symmetry and the bulk impose several drastic constraints, the knowledge of which is of further use to understand "stereoentropic" factors governing the synthetic limit of bulky peralkylated sandwiches such as those involving the C_5Me_5 ligand.

An additional aspect of this chemistry is the possibility of obtaining new aromatic compounds following benzylic activation by $CpFe^+$ and subsequent photolytic decomplexation. Perfunctionalization should be an important challenge subsequent to this study, with potential applications to the specific complexation of some metal ions.

Important to us is the finding of an easy route to bulky $CpFe^+$(arene) complexes which are helpful in electron-transfer studies of the d^7 Fe(I) forms. For example, the synthesis of $CpFe^I(C_6Et_6)$ allowed an examination of its reaction with O_2; the slow rate of the step following ET to O_2 (deprotonation) permitted the characterization of the intermediate $CpFe^+(C_6Et_6)O_2^{-}\cdot$.[9] The reaction of O_2 with the thermally stable complex $CpFe^I(1,3,5\text{-}C_6H_3(\textit{t}\text{-Bu})_3)$ which lacks benzylic hydrogens is also of mechanistic interest.[13] In a general way, the present approach should provide us with specific and universal neutral ET reagents, especially useful in inert solvents and in ethers.

Experimental Section

General Data. Reagent grade tetrahydrofuran was predried on Na foil and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade pentane was degassed with nitrogen before use. All other chemicals were used as received. All manipulations were done by Schlenk techniques or in glovebags. ^1H NMR spectra were obtained with a Varian EM 360 (60 MHz) spectrometer and the ^{13}C NMR spectra were recorded at 20.115 MHz in the pulsed Fourier transform mode with a Bruker WP 80 spectrometer. All chemical shifts are reported in parts per million (δ) with reference to tetramethylsilane (Me_4Si) and were measured relative to (Me_4Si). Mass spectra were recorded by Dr. P. Guénot at the Center of Physical Measurements for Chemistry of Rennes using a Varian MAT 311 spectrophotometer. Elemental analyses were performed by the CNRS Center for Microanalyses at Lyon-Villeurbanne.

(1) General Peralkylation Procedure. Synthesis of $CpFe^+(C_6Et_6)PF_6^-$ (2$^+$). To a 250-mL three-necked flask equipped with a reflux condenser and containing 4.28 g (10 mmol) of **1**$^+$ and 22.4 g (200 mmol) of *t*-BuOK is added by cannula a solution of 28.4 g (200 mmol) of CH_3I in 150 mL of THF. A mild reflux occurs during 1 min and the color of the solution turns from red to beige: the solution is stirred 15 min and THF is removed in vacuo; the creamy solid is washed with 100 mL of distilled water, filtered, and dried over $MgSO_4$ in acetone. After concentration, addition of excess ether provides 4.86 g (95%) of yellow powder identified and found pure by ^1H NMR.[11] Recrystallization from hot ethanol gives 4.61 g (90%) of canary-yellow microcrystals.

(2) Synthesis of $CH_3CpFe^+(C_6Et_6)PF_6^-$ (4$^+$) from $CH_3CpFe^+(C_6Me_6)PF_6^-$ (3$^+$). Procedure 1 applied to **3**$^+$ gives a 86% yield of **4**$^+$ as yellow plates after recrystallization from hot ethanol: ^1H NMR (CD_3COCD_3) δ 4.80 (m, $C_5\textit{H}_4CH_3$, 4 H), 3.17 (q, CH_2, 12 H), 1.93 (s, $C_5H_4C\textit{H}_3$, 3 H), 1.43 (t, CH_3, 18 H); ^{13}C NMR (CD_3CN) δ 78.3, 78.0, 77.8 ($\textit{C}_5H_4CH_3$), 105.3 ($\textit{C}_6Et_6$), 23.7 (CH_2), 16.3 (CH_3), 12.0 ($C_5H_4\textit{C}H_3$); mass spectrum for **4** (M^+) calcd 381.240, found 381.242. Anal. Calcd for $C_{24}H_{37}FePF_6$: C, 54.76; H, 7.08; Fe, 10.61. Found: C, 54.54; H, 7.15; Fe, 10.90.

(3) Synthesis of $CpFe^+C_6(CH_2CH_2Ph)_6PF_6^-$ (5$^+$) from 1$^+$. The reaction of procedure 1 takes 15 min using $C_6H_5CH_2Br$ at room temperature (4 h in refluxing THF with $C_6H_5CH_2Cl$) and gives an 80% yield of **5**$^+$ as yellow plates after recrystallization from ethanol: ^1H NMR (CD_3COCD_3) δ 7.46 (s, C_6H_5, 30 H), 5.26 (s, Cp, 5 H), 3.50 [m, $(CH_2)_2$, 24 H]; ^{13}C NMR (CD_3CN) δ 77.8 (Cp), 99.8 (C_6 ring), 25.3 and 24.7-$(CH_2)_2$, 137.1, 135.1, 130.0, 129.4 (C_6H_5). Anal. Calcd for $C_{59}H_{59}FePF_6$: C, 73.13; H, 6.13; Fe, 5.76. Found: C, 72.85; H, 6.20; Fe, 6.00.

(4) Synthesis of $C_6[(CH_2)_2C_6H_5]_6$. **5**$^+$ (1.42 g, 1.47 mmol) is photolyzed in 250 mL of CH_3CN with UV irradiation 240 nm for 3 min. After the solvent is removed in vacuo, the black residue is stirred for 1 h in concentrated H_2SO_4 to oxidize ferrocene formed during the photolysis. The organic compound is extracted from the aqueous layer with ether and dried over $MgSO_4$; recrystallization from hexane gives 0.912 g (1.29 mmol) of $C_6(CH_2)_2C_6H_5$: mp 115 °C; ^1H NMR ($CDCl_3$) δ 7.43 (s, C_6H_5, 30 H), 3.03 (b, $(CH_2)_2$, 24 H); ^{13}C NMR ($CDCl_3$) δ 38.0 and 36.8 $(CH_2)_2$, 142.4, 133.2, 128.3, 126.3, (C_6H_5), 136.5 (C_6 ring). Anal. Calcd for $C_{54}H_{54}$: C, 92.25; H, 7.74. Found: C, 92.30; H, 7.70.

(5) Synthesis of $CpFe^+(1,3,5\text{-}C_6H_3(\textit{t}\text{-Bu})_3)PF_6^-$ (10$^+$) from 9$^+$. The reaction as in 1 gives, after recrystallization from ethanol, 63% yield of yellow microcrystals of **10**$^+$: ^1H NMR (CD_3COCD_3) δ 6.48 (s, C_6H_3, 3 H), 5.25 (s, Cp, 5 H), 1.55 (s, *t*-Bu, 27 H); ^{13}C NMR (CD_3CN) δ 76.3 (Cp), 117.1 (C quaternary), 79.7 (C_6H_3), 35.6 [$\textit{C}(CH_3)_3$], 30.8 [$C(\textit{C}$-

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Table **III**. Positional Parameters of Non-Hydrogen Atoms

atom	x	y	z
Fe	0.31580 (6)	0.15353 (3)	0.05358 (5)
P	0.3776 (1)	0.12838 (8)	0.4350 (1)
F1	0.3044 (3)	0.0972 (2)	0.3676 (3)
F2	0.2996 (3)	0.3770 (2)	0.0142 (3)
F3	0.3274 (4)	0.1847 (2)	0.4061 (3)
F4	0.4271 (4)	0.4268 (2)	0.9628 (4)
F5	0.4544 (3)	0.1354 (2)	0.3551 (3)
F6	0.4510 (3)	0.1608 (2)	0.5020 (3)
C1	0.4058 (4)	0.0826 (2)	0.0717 (4)
C2	0.4631 (4)	0.1251 (3)	0.0304 (4)
C3	0.4255 (4)	0.1530 (2)	−0.0497 (4)
C4	0.3309 (4)	0.1374 (2)	−0.0866 (3)
C5	0.2735 (4)	0.0958 (2)	−0.0431 (4)
C6	0.3124 (5)	0.0666 (2)	0.0332 (3)
C11	0.4453 (5)	0.0550 (3)	0.1587 (4)
C12	0.5109 (6)	0.0055 (3)	0.1345 (5)
C21	0.5648 (5)	0.1416 (3)	0.0690 (4)
C22	0.5687 (5)	0.1884 (3)	0.1374 (5)
C31	0.4870 (5)	0.1981 (3)	−0.0930 (4)
C32	0.5631 (5)	0.1769 (3)	−0.1595 (5)
C41	0.2898 (5)	0.1677 (3)	−0.1706 (4)
C42	0.3296 (7)	0.1431 (3)	−0.2592 (4)
C51	0.1691 (5)	0.0819 (3)	−0.0770 (4)
C52	0.1679 (6)	0.0427 (3)	−0.1564 (5)
C61	0.2580 (6)	0.0180 (3)	0.0730 (5)
C62	0.1790 (6)	0.0277 (3)	0.1455 (5)
Cp1	0.1788 (5)	0.1834 (3)	0.0933 (5)
Cp2	0.2305 (5)	0.2230 (3)	0.0471 (4)
Cp3	0.3162 (5)	0.2339 (2)	0.0957 (5)
Cp4	0.3196 (5)	0.2001 (3)	0.1718 (4)
Cp5	0.2343 (5)	0.1678 (3)	0.1705 (5)

$H_3)_3$]. Anal. Calcd for $C_{23}H_{35}FePF_6$: C, 53.92; H, 6.88; Fe, 10.90. Found: C, 53.94; H, 6.68; Fe, 11.24.

Na/Hg reduction of **10**$^+$ in DME (30 min, 20 °C) gives **10** as already reported for other Fe(I) complexes.[11] **10**: Mössbauer parameters (293 K); IS 0.84 mm s^{-1}; QS 0.50 mm s^{-1}; Mass spectrum (M^+) calcd 367.206, found 367.208.

The known complex $CpFe^+(C_6H_5CMe_3)PF_6^-$ (**8**$^+$)[30] is similarly synthesized from **7**$^+$ in 22.5% yield.

(6) Synthesis of $C_5Me_5Fe^+$(mesitylene)PF_6^- (11$^+$). $C_5Me_5Fe^+(C_6H_3Me_3)PF_6^-$ is obtained by ligand exchange between $C_5Me_5Fe\ (CO)_2Br$ and mesitylene according to a standard published method.[11] A 48% yield of yellow plates is obtained after recrystallization from hot ethanol: ^1H NMR (CD_3COCD_3) δ 5.67 (s, C_6H_3, 3 H), 2.37 (s, $C_6(CH_3)_3$, 9 H), 1.90 [s, $C_5(CH_3)_5$, 15 H]; ^{13}C NMR (CD_3CN) δ 102.9 [$\mathit{C}_6(CH_3)_3$], 90.0 (C_6H_3), 88.5 [$\mathit{C}_5(CH_3)_5$], 18.5 [$C_6(\mathit{C}H_3)_3$], 9.5 [$C_5(\mathit{C}H_3)_5$]. Anal. Calcd for $C_{19}H_{27}FePF_6$: C, 50.02; H, 5.96; Fe, 12.24. Found: C, 50.12; H, 6.00; Fe, 12.26.

(7) Permethylation of $C_5Me_5Fe^+$(mesitylene)PF_6^-. Procedure 1, applied to 1.37 g of **11**$^+$ (3 mmol), provides 0.673 g of orange powder. The ^1H and $\{^1H\}^{13}C$ NMR spectra indicate that the major reaction product is $C_5Me_4EtFe^+(C_6H_3(t\text{-}Bu)_3)PF_6^-$ (**12**$^+$, 50–60%); ^1H NMR (CD_3COCD_3) δ 6.00 (s, C_6H_3), 2.80 (q, CH_2), 1.90 [s, $C_5(\mathit{CH}_3)_4Et$], 1.50 (s, *t*-Bu), 1.13 (t, CH_3); ^{13}C NMR (CD_3CN) δ 119.7 [$\mathit{C}_6(t\text{-}Bu)_3$], 95.3 ($\mathit{C}_6H_3$), 77.5, 76.9, 76.7 ($\mathit{C}_5Me_4Et$), 36.9 [$\mathit{C}(CH_3)_3$], 31.3 [$C(\mathit{C}H_3)_3$], 20.7 ($CH_2$), 15.9 ($CH_3$), 9.7 and 9.6 [$C(\mathit{C}H_3)_4Et$]. Peaks due to $C_5Me_{5-z}Et_zFe^+(1,3,5\text{-}C_6H_3(t\text{-}Bu)_3)$ with $z = 2$ and 3 (two isomers each) indicate the presence of 5–10% of each of these four cations.

(8) Synthesis of $CpFe^+(1,2\text{-}C_6H_4(i\text{-}Pr)_2)PF_6^-$ (14$^+$) from 13$^+$. 14$^+$ is obtained in 28% yield according to procedure 1 after recrystallization from ethanol: ^1H NMR (CD_3COCD_3) δ 6.44 and 6.36 (s, C_6H_4, 4 H), 5.16 (s, Cp, 5 H), 3.52 (m, $C\mathit{H}(CH_3)_2$, 2 H), 1.56, 1.66 and 1.18, 1.28 [dd, $CH(C\mathit{H}_3)_2$, 12 H]; ^{13}C NMR (CD_3CN) δ 82.3, 81.5 (C_6H_4), 102.7 [$C_6(i\text{-}Pr)_2$], 78.1 (Cp), 40.2 [$\mathit{C}H(CH_3)_2$], 25.6 and 24.9 [$CH(\mathit{C}H_3)_2$]. Anal. Calcd for $C_{17}H_{17}FePF_6$: C, 48.37; H, 4.06; Fe, 13.23. Found: C, 48.52; H, 4.05; Fe, 13.31.

(9) Synthesis of $CpFe^+(1,2,4,5\text{-}C_6H_2(i\text{-}Pr_4))PF_6^-$ (16$^+$) from 15$^+$. As in 1, **16**$^+$ is obtained in 63% yield after recrystallization from acetone: ^1H NMR (CD_3COCD_3) δ 6.23 (s, C_6H_2, 2 H), 5.14 (s, Cp, 5 H), 3.52 [m, $C\mathit{H}(CH_3)_2$, 4 H], 1.60, 1.71 and 1.20, 1.31 [dd, $CH(C\mathit{H}_3)_2$, 12 H]; ^{13}C NMR (CD_3CN) δ 100.5 [$C_6(i\text{-}Pr)_4$], 80.2 (C_6H_2), 78.5 (Cp), 42.1 [$\mathit{C}H(CH_3)_2$], 27.5, 26.8 [$CH(\mathit{C}H_3)_2$]. Anal. Calcd for $C_{23}H_{35}FePF_6$: C, 53.92; H, 6.88; Fe, 10.90. Found: C, 54.08; H, 6.75; Fe, 11.22.

(10) Preparation of $CpFe^+(C_6(C_2H_5)_5CH(CH_3)_2)PF_6^-$ (19$^+$) from 2$^+$. (a) Deprotonation of 2$^+$ by *t*-BuOK. To 1.024 g (2 mmol) of **2**$^+$ and 0.224 g (2 mmol) of *t*-BuOK is added 50 mL of THF. The reaction mixture immediately turns red. After stirring 30 min, the solvent is removed in vacuo and the red complex **18** is extracted with 2 × 20 mL of pentane and filtered; the solvent is evaporated to dryness and 550 mg (75% crude yield) of the oily complex **18** are obtained (and identified as previously[11]).

(b) Reaction of 18 with CH_3I. To a THF solution of 550 mg (1.5 mmol) of **18** is added 0.09 mL (1.5 mmol) of CH_3I in 10 mL of THF by cannula. The solution is allowed to stir for 2 h at reflux. The color turns from red to yellow. The solvent is removed in vacuo; metathesis with aqueous HPF_6 followed by addition of ether to an acetone solution gives 580 mg (73.5%) of **19**$^+$. Recrystallization from hot ethanol provides 552 mg (70%) of yellow microcrystals: ^1H NMR (CD_3COCD_3) δ 4.97 (s, Cp, 5 H), 3.58 [m, $C\mathit{H}(CH_3)_2$, $J_{H-H} = 7$ Hz, 1 H], 3.16 (m, CH_2, 10 H), 1.83 [d, $CH(C\mathit{H}_3)_2$, $J_{HH} = 7$ Hz, 3 H], 1.36 (t, CH_3, 18 H); ^{13}C NMR (CD_3CN) δ 112.4 [$\mathit{C}\text{-}CH(CH_3)_2$], 105.8, 105.5, 14.5 ($C_6$ ring), 78.2 (Cp), 29.4 [$\mathit{C}H(CH_3)_2$], 24.7, 24.2, 23.9 (CH_2), 16.4 (CH_3). Anal. Calcd for $C_{24}H_{37}FePF_6$: C, 54.76; H, 7.08; Fe, 10.61. Found: C, 54.82; H, 7.16; Fe, 10.50.

(11) X-ray Crystallography. Yellow crystals of **2**$^+$ were grown by slow evaporation of an ethanol solution at 20 °C. A suitable biprismatic crystal was mounted on a Nonius CAD 4 diffractometer using graphite-monochromated Mo $K\alpha_1$ radiation. Unit cell dimensions, determined for 25 reflections at moderate 2θ angles, indicate an orthorhombic unit cell of dimensions $a = 13.438$ (1) Å, $b = 24.261$ (4) Å, $c = 14.617$ (2) Å. The observed volume is consistent with that expected for $Z = 8$, using a density of 1.43 g cm^{-3}. Observed systematic absences are consistent with the nonconventional space group *Pcab*. A total of 2340 independent reflections were collected under the following experimental conditions $1° < \theta < 28°$; scan type $\omega/2\theta$; scan angle (deg) $S = 1.00 + 0.35 \tan\theta$; detector aperture D (mm) $= 2.0 + 0.5 \tan\theta$. A total of 1774 unique reflections having $I > 3\sigma(I)$ were considered observed. The data were corrected from L and P factors and used in the structure determination. Anomalous dispersion effects were included in calculation of F_c. Non-hydrogen atoms were located through the Patterson method and difference Fourier syntheses: isotropic least-squares index residual value at this stage was $R = 0.101$. Then most hydrogen atoms were located from a difference Fourier syntheses, and the remnant hydrogens could be located in calculated positions. An isotropic fixed B value of 4.0 Å^2 was assigned to them. Full anisotropic (except for H atoms) least-squares refinement led to a current residual R index on F_o of 0.045 ($R_w = 0.048$) with an ESD of an observation of unit weight of 1.54. Positional parameters of non-hydrogen atoms are reported in Table III.

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Registry No. 1$^+$, 53702-66-2; **2**$^+$, 71713-63-8; **3**$^+$, 32799-21-6; **4**$^+$, 83528-69-2; **5**$^+$, 83528-71-6; **6**$^+$, 71713-57-0; **7**$^+$, 33435-42-6; **8**$^+$, 34978-89-7; **9**$^+$, 32757-45-2; **10**, 83528-72-7; **10**$^+$, 83528-74-9; **11**$^+$, 83528-76-1; **12**$^+$, 83528-78-3; **13**$^+$, 34978-35-3; **14**$^+$, 83528-80-7; **15**$^+$, 83542-60-3; **16**$^+$, 83528-82-9; **17**$^+$, 76747-93-8; **18**, 80080-16-6; **19**$^+$, 83528-84-1; CH_3I, 74-88-4; *t*-BuOH, 865-47-4; $C_6H_5CH_2Cl$, 100-44-7; $C_6H_5CH_2Br$, 100-39-0.

Supplementary Material Available: A listing of atomic and thermal parameters with standard deviations for **2**$^+$ and of interatomic distances and angles (7 pages). Ordering information is given on any current masthead page.

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