

Organometallic Electron Reservoirs. 5. A Novel Mode of C-H Activation Using Dioxygen via Superoxide Radical Anion in Solution and in the Solid State with $C_5R_5Fe^I C_6R'_6$. Subsequent Bond Formation with C, Si, P, Mn, Fe, Cr, Mo, and Halogens¹

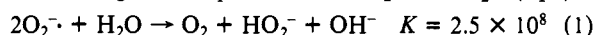
Didier Astruc,^{*2a} Jean-René Hamon,^{2a} Enrique Román,^{2a} and Pascal Michaud^{2a,b}

Contribution from the Laboratoire de Chimie des Organométalliques, Université de Rennes, 35042 Rennes Cedex, and Groupe de Physique et Chimie du Solide, Université du Maine, 72017 Le Mans Cedex, France. Received April 20, 1981

Abstract: The 19-electron complexes $CpFe^I(\eta^6-C_6Me_6)$ (**1**), $C_5Me_5Fe^I(\eta^6-C_6Me_6)$ (**26**), $(CpFe^I C_6Me_5CH_2)_2$ (**22**), and $CpFe^I C_6Et_6$ (**29**) react quickly with 1/4 mol of O_2 /mol of sandwich in pentane, THF, or DME to give 0.5 mol of H_2O and 81–96% of thermally stable d^6 $CpFe(\eta^5-C_6Me_5CH_2)$ (**2**), $C_5Me_5Fe(\eta^5-C_6Me_5CH_2)$ (**27**), $(CpFe(\eta^5-C_6Me_4CH_2CH_2))_2$ (**28**), and $CpFe(\eta^5-C_6Et_5CHMe)$ (**30**), resulting from benzylic H atom abstraction. 1H and ^{13}C NMR spectra indicate that the hexaalkylarene ligands are transformed into cyclohexadienyls with doubly bonded exocyclic methylene groups. The same reactions at $-78^\circ C$, fast with **1**, **22**, and **26**, consume 0.5 mol of O_2 and produce 0.5 mol of H_2O_2 , the cyclohexadienyl complexes **2**, **27**, and **28** in somewhat lower yields, and the hydroxides of **1**⁺, **22**⁺, and **26**⁺. *t*-BuOK (in THF) or KO_2 (in Me_2SO or with stoichiometric 18-crown-6 ether in THF) also gives **2** by reaction with **1**⁺ PF_6^- . With **26**, the aerobic reaction is regioselective on the arene whereas that of **22** is not so. The reaction between **29** and O_2 is slow at $-20^\circ C$ (5 min), and the intermediate $O_2^{\cdot-}$ could be characterized by its temperature-dependent EPR spectra. This indicates that H atom abstractions by O_2 are best explained in terms of electron transfer to O_2 due to the large difference (1 V) between the two reversible systems $CpFe(arene)/CpFe^+(arene)$ (≈ -1.8 V/SCE) and $O_2/O_2^{\cdot-}$ (-0.7 V/SCE), followed by deprotonation of the cationic sandwich by $O_2^{\cdot-}$. The aerobic reaction **1** \rightarrow **2** also proceeds in the solid state and can be monitored by Mössbauer spectroscopy on microcrystalline samples and monocrystals. In the latter case, the rhombic distortion can be used as a probe showing that aerobic oxidation proceeds on the surface rather than in the bulk. **2** reacts with H_2 (Pd/C, THF, $20^\circ C$) to give **3** by exo hydrogenation. Replacement of the 18 methyl hydrogens by 18 deuteriums occurs (90% in 2 h upon contact of **1**, **2**, or **1**⁺ OH^- with Na/Hg in DME + air + D_2O). **2** also gives nucleophilic substitution with CH_3I , $PhCOCl$, $SiMe_3Cl$, PPh_2Cl , $CpFe(CO)_2Cl$, $CpMo(CO)_3I$, $Mn(CO)_5Br$, $Fe_2(CO)_9$, $Cr(CO)_6$, and $Mo(CO)_6$ and nucleophilic addition with CO_2 , CS_2 , $CpFe(\eta^6-PhCl)$ (ortho to Cl), $CpFe^+(CO)_3$ (to Cp), and $CpFe^+(CO)_2(C_2H_4)$ (to C_2H_4). Electron transfer often occurs between **2** and organometallics, giving **1**⁺, and with TCNQ, giving **1**⁺ $TCNQ^-$. Coupling of **2** to **22**⁺ is obtained by reaction of 0.5 mol of I_2 in THF. Thus straightforward synthesis of bonds to many elements are achieved upon simple contact of **1** with air followed by reaction with these substrates in situ.

The reactions of dioxygen with transition-metal complexes have attracted the attention of chemists for several decades. Among the more fascinating aspects of dioxygen reactivity are the ability of coordination complexes to relax their spin and symmetry constraints,³ the modeling and understanding of the function of heme proteins which transport O_2 ,^{4,5} and more recently the use of the one-step four-electron reduction of O_2 to H_2O in fuel cell technology.⁶ Two driving forces are commonly known in transition-metal aerobic reactions: (i) the large electronegativity difference between early transition metals and O_2 induces the formation of bridging or nonbridging oxo compounds;⁴ (ii) complexes having a free coordination site let O_2 bind the central metal in end-on and edge-on modes and it required great efforts to render

the reaction reversible in order to mimic natural heme systems.⁵⁻⁸ Indeed the organometallic chemist routinely uses an armada of Schlenk techniques, dryboxes, and glovebags to protect his complexes from O_2 , but the cause of air sensitivity is often fuzzy.⁹ The low value of the redox potential of the reversible reduction of O_2 to $O_2^{\cdot-}$ ($E_{1/2} = -0.7$ V/SCE)¹⁰ leaves room for a great range of complexes oxidizable by O_2 from air. However, most aerobic oxidation studies are performed in aqueous medium, so that the dramatic reactivity of $O_2^{\cdot-}$ from O_2 in such systems was scarcely examined, owing to the rapid reaction of $O_2^{\cdot-}$ with H_2O (eq 1).¹¹



The toxicity of O_2 for microorganisms has been well-known since Pasteur's work on butyric vibrium last century, but it was only shown during the last decade that the toxicity of O_2 on red cells, membranes, granulocytes, and bacteria does imply the intermediate $O_2^{\cdot-}$.¹¹ Moreover if the aging of cells is known to occur

(1) For parts 1-4 see respectively ref 20, 24, 25, and 21.

(2) (a) Laboratoire de chimie des Organométalliques, Rennes, ERA CNRS No. 477. D.A. is CNRS Fellowship recipient, 1978-1982, J.-R.H. DGRST predoctoral Fellow, 1979-1981, and E. R. Ministère des Affaires Etrangères predoctoral Fellow, 1975-1979. (b) Laboratoire de Spectrométrie Mössbauer, Le Mans, ERA No. 682. P.M. is DGRST Predoctoral Fellow, 1980-1982.

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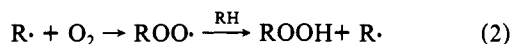
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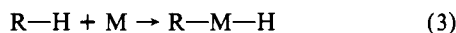
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under the action of O₂ via O₂⁻, further roles of these species remain to be cleared up.¹² Indeed the simple organometallic chemistry of O₂⁻ is unknown due to the handling difficulties¹³ (KO₂ can be efficiently used only in Me₂SO or with stoichiometric amounts of 18-crown-6 ether in THF; alternatively O₂⁻ can be generated electrochemically from O₂ in pyridine).

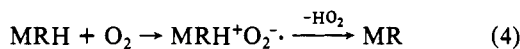
In view of the bioenergetic importance of O₂⁻,¹⁴ and of the recent discovery of its nucleophilic, basic, and redox properties, we have wished to examine the reactivity of transition-metal complexes toward O₂⁻ generated from O₂ or air, in particular with respect to C-H activation. Two synthetic modes of C-H activation are known so far.¹⁵ One involves oxidation of C-H bonds by a radical pathway (autoxidation) and is familiar to organic chemists and those dealing with main-group metal complexes¹⁶ (eq 2).



The other, developed more recently, involves the oxidative addition¹⁷ well-known to transition-metal chemists (eq 3).



The unprecedented mode of activation that we have devised implies a mono-electronic transfer from an organometallic complex to O₂ followed by the deprotonation of O₂⁻ of a ligand activated by the cationic metal moiety (eq 4).



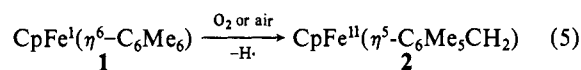
This type of C-H activation needs the organometallic complex to fulfill two conditions: (i) to have a redox potential more negative than that of O₂/O₂⁻, -0.7 V/SCE; (ii) to have a coordination sphere with not less than 18 valence electrons on the transition metal to prevent coordination by O₂.^{18,19} In a preliminary communication we described the reactions of O₂ with the 19-electron complexes CpFe^I(arene).²⁰ These include (i) the rather extraordinary abstraction of H from a methyl group in the C₆Me₆ ligand, (ii) dimerization, and (iii) electron transfer. These two latter types of aerobic reactions are only observed when the arene ligand bears less than six methyl groups, and thus, we are focusing here on the details of C-H activation by O₂ in the electron-rich sandwiches C₅R₅Fe^IC₆R'₆ (R = H or CH₃; R' = CH₃ or C₂H₅) in various solvents and in the solid state. Bond formation with a variety of elements subsequent to aerobic C-H activation is described, illustrating the multiple syntheses achievable by this process.

Preliminary accounts of this work have appeared,^{20,21} and the crystal structures of **1** and **2** indicate that H atom abstraction by

O₂ from **1** proceeds with decoordination of one arene carbon.²¹

Results

1. The Aerobic Activation of the C-H Bond of a Methyl Group in CpFe^IC₆Me₆. The 19-electron sandwiches CpFe(arene) are d⁷ Fe(I) paramagnetic complexes obtained by Na/Hg reduction²² of stable d⁶ Fe(II) cations.²³ We have shown that they are thermally stable if the arene is hexasubstituted by alkyl groups.²⁴⁻²⁶ The 19th electron is in an antibonding e*₁ orbital of high metal character, and "inter alia" the crystal structure of CpFeC₆Me₆ (**1**) has been described.²⁴ This dark green complex is extremely air sensitive. It reacts instantaneously at 20 °C in pentane with (dry) air or O₂ to give a dark red solution and a small amount (3%) of a yellow precipitate which is identified as CpFe⁺C₆Me₆OH⁻ (1⁺OH⁻). The filtered liquor gives, upon cooling to -40 °C, a 60% yield of dark red crystals of a neutral diamagnetic complex **2** (overall yield 96%). The mass spectra show that the aerobic reaction has occurred with loss of one H atom (molecular peaks: **1**, m/e 283.115; **2**, m/e 282.106). The mass spectrum of **1** also shows a peak at m/e 282.106. If the reaction is performed in an IR cell, broad bands appear at 3400 cm⁻¹ (H₂O) and at 1600 cm⁻¹ (olefin). The Mössbauer spectrum of **2** shows a temperature-independent quadrupole doublet¹³ (IS = 0.43 mm s⁻¹; QS = 1.88 mm s⁻¹) typical of the d⁶ CpFe^{II}(η⁵-cyclohexadienyl) series (the EFG is less symmetrical than those in ferrocene or even in CpFe⁺(arene); therefore QS is smaller). The ¹H and ¹³C NMR spectra (Figure 2) clearly confirm that a H atom has been abstracted from a CH₃ group. The peak of intensity of **2** at 3.60 ppm in the ¹H spectrum and the triplet obtained from the off-resonance experiment for the corresponding ¹³C resonance at 77.2 ppm show the presence of an exocyclic CH₂ group (noncoupled spectrum, J_{CH₂} = 156.5 Hz). That the ring carbon bearing this CH₂ group is not coordinated to the metal is shown by its large downfield shift (δ 145) with respect to the five other cyclohexadienyl carbons (δ 57-90). Thus the loss of H can be formulated as shown in eq 5.



This high double-bond character is also demonstrated by the ready hydrogenation of **2** using a THF solution of Pd on charcoal (eq 6) at 20 °C to give CpFe(η⁵-C₆Me₆H) (**3**)²⁷ as orange crystals after recrystallization from pentane.

The reduction is stereospecifically exo, giving the C₆ endo methyl complex as indicated by the presence of an intense band in the IR spectrum at 2750 cm⁻¹ (exo-C-H stretch).²⁸ The ¹H NMR spectrum shows the quartet of the exo-C-H at 1.05 ppm

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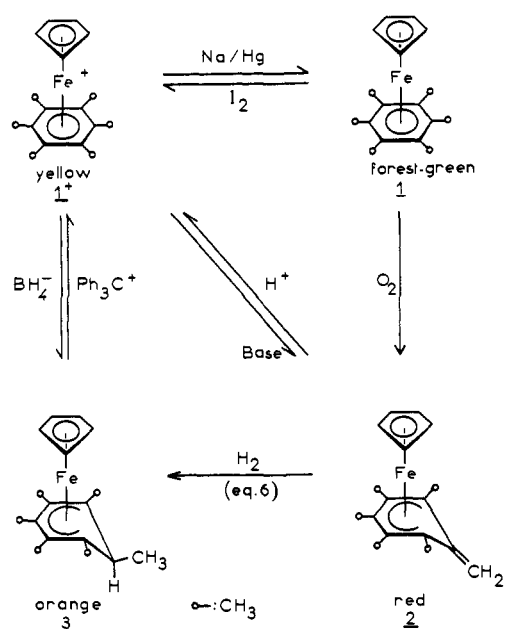
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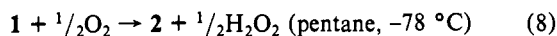
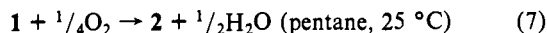
Scheme I



but no trace of the endo-C-H at 2.2 ppm,²⁷ and the ¹³C spectrum indicates the 3 is isomerically pure.

1⁺, 1, 2, and 3 are now related by the general scheme shown in Scheme I.²⁹

2. The Nature of the Reduction Products of O₂ in the Aerobic Reaction of CpFe¹C₆Me₆. The KMnO₄ titration of the reaction products after hydrolysis shown that very little H₂O₂ is formed (≈ 1%) and the quantity of O₂ needed for the reaction is 0.25 mole (the end of the reaction being characterized by color change from deep green to bright red). If the reaction is carried out at -78 °C, 0.5 mol of O₂ is needed for completion of the reaction (in 1 min) and the KMnO₄ titration shows the formation of 0.5 mol of H₂O₂. Thus the reactions are summarized as shown in eq 7 and 8. These reactions also proceed with the same stoichiometries in ether, THF, DME, and toluene.



3. Aerobic Oxidation of CpFe¹C₆Me₆ to 2 in the Solid State. Aerobic transformation of CpFe(η⁶-C₆Me₆) in the solid state can be suitably characterized by Mössbauer spectroscopy which shows that (a) aerobic oxidation proceeds with loss of one H atom for CpFe(η⁶-C₆(CH₃)₆), (b) the rhombic distortion is observed at 77 K, demonstrating specific surface oxidation, and (c) oxidation of a single crystal at its surface gives a polycrystalline material.

The ⁵⁷Fe quadrupole splitting (QS) value of the oxidation product, 1.88 mm s⁻¹, compares well for identification with those of pure isolated samples of 2.

Parts 1 and 3 of Figure 1 show the spectra of CpFe(η⁶-C₆Me₆) at 298 K before and after exposure to air. The new doublet appearing in part 3 presents features (smaller isomer shift, IS, much larger QS) typical of an Fe(II) species.³⁰ The two possible reaction products are 2 and 1⁺. From the QS value (1.91 ± 0.02 mm s⁻¹) one concludes the presence of 2 in the aerobically oxidized sample of 1.

In the spectrum of 1 at 77 K (Figure 1(5)), surprisingly two sets of doublets are observed. We believe they are due to two crystallographic sites possessing greatly different asymmetry of

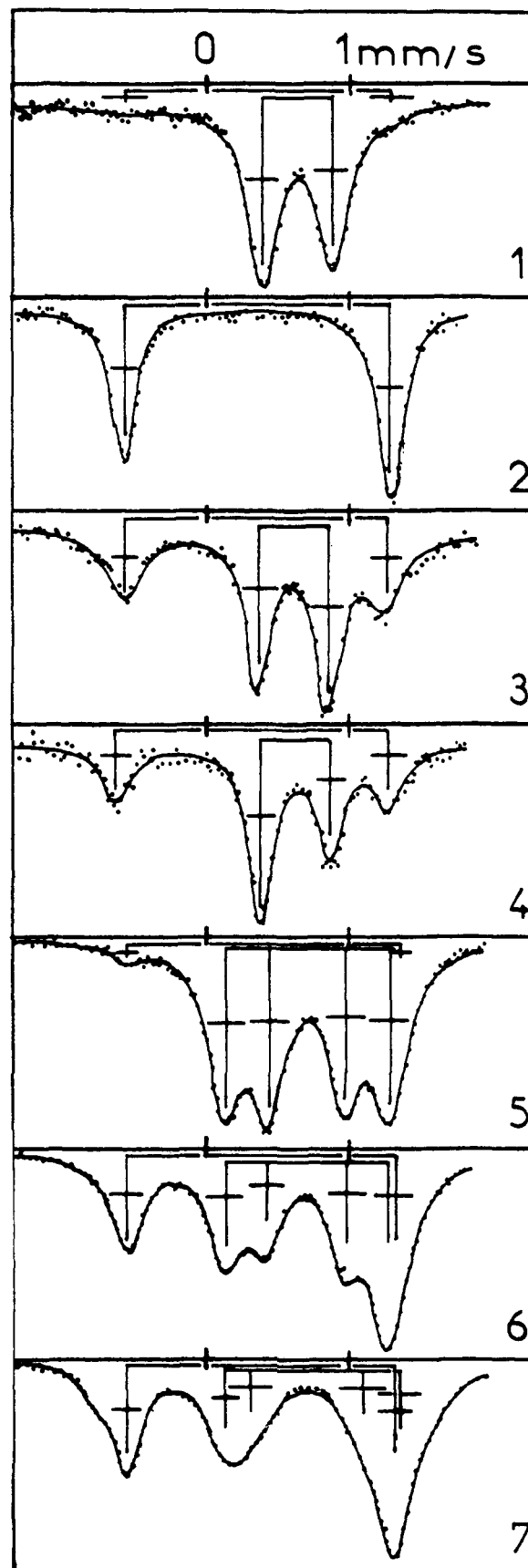


Figure 1. Mössbauer spectra of 1 and aerobically oxidized samples: (1) polycrystalline sample of 1 (with traces of 2) at 293 K; (2) pure polycrystalline sample of 2 at 293 K; (3) partly oxidized polycrystalline sample of 1 (38% of 2) at 293 K; (4) partly oxidized single crystal of 1 (32% of 2) at 293 K; (5) polycrystalline sample of 1 (with traces of 2) at 77 K; (6) partly oxidized polycrystalline sample of 1 at 77 K; (7) sample with cosublimed 1 and 2 (38% of 2) at 77 K.

(29) For the interconversion of 1⁺ and 3 (addition of H⁻ to 1⁺ and abstraction of H⁻ from 3) see ref 27.

(30) Mössbauer data for CpFe⁺C₆H₆^{30a} and CpFe⁺C₆Me₆^{30b} have been reported. (a) Stukan, R. A.; Vol'kenau, N. A.; Nesmeyanov, A. N.; Goll'danskii Izv. Akad. Nauk SSSR, Ser. Khim. 1966, 8, 1472-1474. (b) Morrison, W. H., Jr.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* 1975, 14, 500-506.

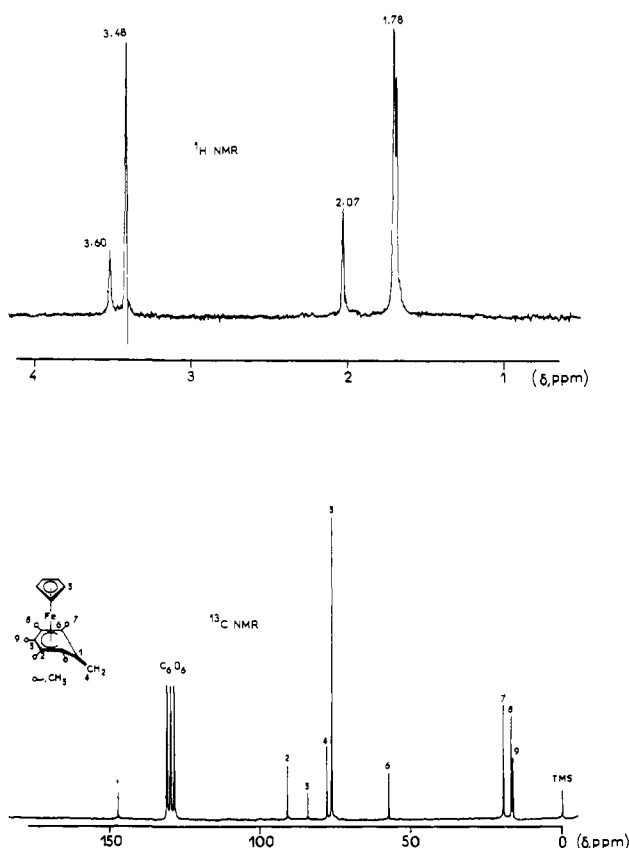


Figure 2. ^1H NMR (above) and proton-decoupled ^{13}C NMR (below) of $\text{CpFe}(\eta^5\text{-C}_6\text{Me}_5\text{CH}_2)$ in C_6D_6 (internal reference Me_4Si ; $J(\text{=CH}_2) = 156.5$ Hz).

the external potential³¹ around the sandwiches, since the species are Jahn-Teller active (singly occupied, doubly degenerate antibonding e^*_1 level³²). One site for which QS does not depend on the temperature corresponds to a fully dynamic distortion while temperature-dependent QS of the other site indicates a thermal population of the upper Kramers' doublet.

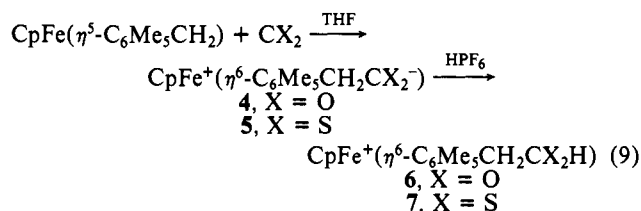
As a consequence any perturbation in the lattice is expected to have a strong effect upon the QS value. This is indeed observed in the spectra at 77 K³³ of samples obtained by cosublimation of **1** and of the oxidized complex **2**: Figure 1(7) illustrates drastic environment effects on the QS due to a random distribution of the sandwiches **1** and **2** in the material. In contrast, the 77 K spectrum (Figure 1(6)) of an oxidized sample of **1** only shows the new doublet characteristic of **1** but no perturbation in the spectrum of **1**. This indicates that oxidation of the solid $1 \rightarrow 2$ occurs, not in the bulk but exclusively at the surface.

Further information on the oxidation texture can be gained by examining a monocrystalline sample of **1**. Since the axes of the sandwiches are all parallel in the packing, the single crystal can be oriented to get the direction of γ -rays perpendicular to the EFG axis; then the doublet is no longer symmetric, Figure 1(4) (theoretical intensity ratio is 3/5; that the line of larger intensity is observed for lower energy, indicates $\text{EFG} > 0$). Indeed an asymmetrical doublet is also observed in the spectrum (Figure 1(2)) of a polycrystalline textured sample of **2**, although the packing of **2** does not present iron chains with parallel sandwiches, unlike that of **1** (considerable packing rearrangement has occurred

following H atom abstraction³⁴). After exposure to air, a symmetrical doublet due to **2** appears (Figure 1(4)) showing that oxidation provides a polycrystalline material at the surface of the single crystal.

4. Acid-Base Properties of $\text{CpFeC}_6\text{Me}_5\text{CH}_2$ (2**).** Alternatively **2** can be synthesized in 90% yield by simple deprotonation of $\text{CpFe}^+\text{C}_6\text{Me}_5\text{PF}_6^-$ (1^+PF_6^-) by *t*-BuOK in THF or DME at ambient temperature in a few seconds. Deprotonation of **2** can also be performed by KO_2 in good yield provided solubility problems are overcome for KO_2 , e.g., in Me_2SO or with a stoichiometric amount of 18-crown-6 ether in THF. **2** is hygroscopic. The red color of the acetone solution immediately turns yellow if a moderate excess of water is added. This is characteristic of the protonation reaction. The yellow organometallic hydroxide (1^+OH^-) crystallizes out with an indefinite number of water molecules (from ^1H NMR) from slow evaporation of the acetone solution. If only a stoichiometric amount of water is added, it can be clearly seen that the red color remains; e.g. the reaction is not complete. If now 1^+OH^- is isolated and left in the desiccator, the red color of the neutral complex **2** appears again and can be characterized in the solid state by the strong 1600-cm^{-1} absorption. Heating 1^+OH^- in an ethanol solution also yields **2**, the process being hastened if KOH pellets are added. These observations indicate that the basic counteranion OH^- deprotonates the cation 1^+ at a CH_3 group. Thus the protonation of **2** is reversible. This explains why only 3% of 1^+OH^- is formed in the reaction of O_2 with **1** (eq 1). Note that this amount is increased up to 8.6% upon reaction at -78°C since now H_2O_2 is formed, which is more acidic than H_2O (compare eq 7 and 8). Reaction of **2** with excess D_2O (100:1) provides 1^+OH^- with a Gaussian distribution of D (0–4, average over two runs is 1.3, from the mass spectra of **2** produced by deprotonation of 1^+ by the counteranion OH^- in 1^+OH^-). When a large excess of D_2O is added to **1** or **2** with Na/Hg in THF in a flask open to air, the 2-h reaction provides replacement of the 18 methyl hydrogens in 18 deuteriums (^1H NMR and mass spectra indicate 90% labeling).

5. Nucleophilic Properties of $\text{CpFeC}_6\text{Me}_5\text{CH}_2$. The chemistry of **2** is extremely rich. Its nucleophilic properties afford the syntheses of C–C, C–Si, C–P, and various C–metal bonds. In pentane or THF, **2** instantaneously reacts with CO_2 or CS_2 at room temperature (the reactions are also rapid at -78°C) to precipitate the yellow zwitterions $\text{CpFe}^+(\eta^6\text{-C}_6\text{Me}_5\text{CH}_2\text{CX}_2^-)$ (**4**, $\text{X} = \text{O}$; **5**, $\text{X} = \text{S}$; eq 9). These are isolated and analyzed, and reaction with aqueous acids at pH 1 affords the corresponding acid **6** and dithio acid **7**.



Nucleophilic substitution occurs very smoothly with a large variety of organic and organometallic halides. Not only CH_3I but also PhCOCl , SiMe_3Cl , and PPh_2Cl react immediately with **2** at room temperature essentially giving quantitative crude yields (Scheme II) of yellow salts of the $\text{CpFe}^+\text{C}_6\text{Me}_5\text{CH}_2\text{R}^-$ type. Metathesis with PF_6^- by dissolution in water and addition of aqueous HPF_6 affords hexafluorophosphates which are recrystallized from ethanol to give high yields of crystalline salts. Reactions with various organometallic halides also proceed in the same manner except substantial quantities of organometallic dimers may be obtained as side products depending on the nucleophilic properties of the corresponding organometallic anion and of the reaction temperature. This side reaction can give as

(31) (a) Ammeter, J. H.; Brown, J. M., Jr. *Chem. Phys. Lett.* **1974**, *27*, 380–384.

(32) (a) Ammeter, J. H. *J. Magn. Reson.* **1978**, *30*, 299–325. (b) Ammeter, J. H.; Swalen, J. D. *J. Chem. Phys.* **1972**, *57*, 678–682. (c) Ammeter, J. H.; Ostwald, N.; Bucher, R. *Helv. Chim. Acta* **1975**, *58*, 671–682. (d) Prins, R. *Mol. Phys.* **1970**, *19*, 603–620. (e) Warren, K. D. *Struct. Bonding (Berlin)* **1976**, *27*, 45–159.

(33) At room temperature, the spectrum of the cosublimed sample and that of the oxidized sample are similar since the upper Kramers' doublet is thermally populated.

(34) It is noteworthy in this respect that the lattice parameters for **1** and **2** are very close (**1**, $a = 8.368 \text{ \AA}$, $b = 14.710 \text{ \AA}$, $c = 11.845 \text{ \AA}$; **2**, $a = 8.230 \text{ \AA}$, $b = 14.599 \text{ \AA}$, $c = 11.779 \text{ \AA}$). Batail, P., personal communication. Full details of the crystal structures of **1** and **2** will be reported later. See ref 21 and 24.

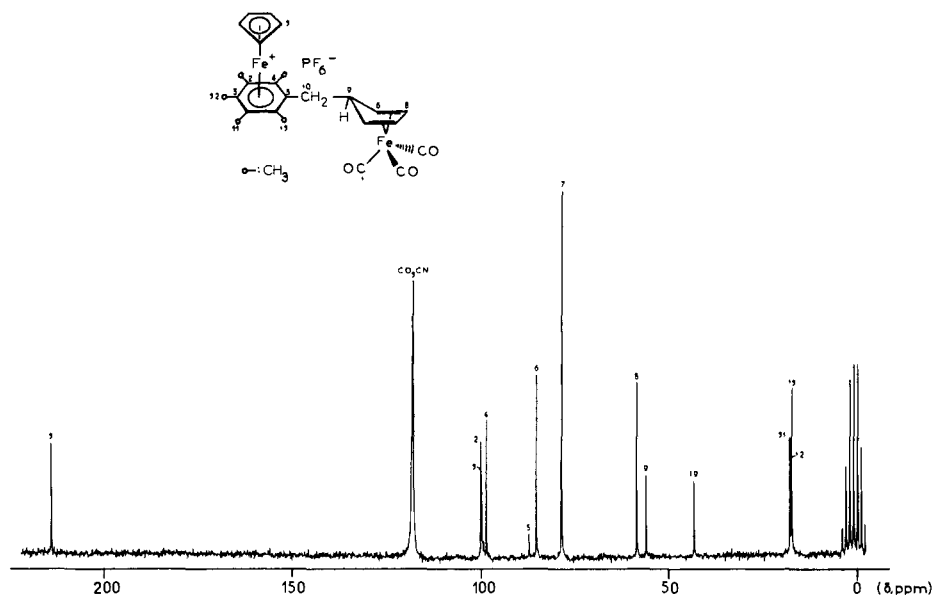


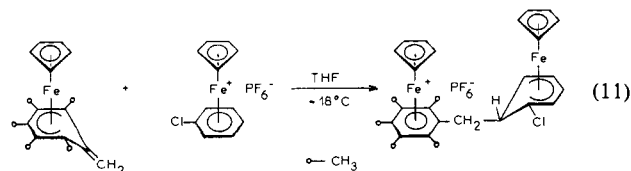
Figure 3. ^{13}C NMR spectrum of $\text{CpFe}^+(\eta^6\text{-C}_6\text{Me}_5\text{CH}_2)(\eta^4\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3\text{PF}_6^-$ in CD_3CN .

high as 80% yields of dimer at room temperature upon reaction between **2** and $\text{CpFe}(\text{CO})_2\text{Cl}$ (eq 10). Note that I^+Cl^- is formed



by the H atom abstraction from the solvent by $\mathbf{2}^+$. If, however, such a reaction is carried out at -20°C , nucleophilic substitution occurs in about 1 h with the formation of only 20% of the isolated dimer. This dimerization is also less marked in the course of the reactions between **2** and the other organometallic halides $\text{CpMo}(\text{CO})_3\text{Cl}$ and $\text{Mn}(\text{CO})_5\text{Br}$ so that only minute amounts of dimers are obtained at -20°C . The limits of the nucleophilic substitution ability of **2** are encountered during unsuccessful attempts at reactions with PhX ($\text{X} = \text{Cl}, \text{F}$). Complexation of PhX by CpFe^+ does not afford nucleophilic substitution either, but instead nucleophilic addition is obtained (vide infra). In order to inhibit nucleophilic addition onto $\text{CpFe}^+(\eta^6\text{-haloarene})$ in favor of nucleophilic substitution of the halide, we have synthesized $\text{CpFe}^+(\eta^6\text{-}p\text{-C}_6\text{Me}_4\text{Cl}_2)$, but this latter molecule does not react at all even in refluxing ethanol although $\text{CpFe}^+(\eta^6\text{-C}_6\text{H}_5\text{Cl})$ does react with NHEt_2 to give $\text{CpFe}^+(\eta^6\text{-C}_6\text{H}_5\text{NHEt}_2)$ under these conditions.³⁵

This ability of **2** to form C–C bonds by addition to hydrocarbon ligands activated by cationic organoiron moieties has encouraged us to extend the range of this reaction type. Nucleophilic addition of CH_3Li to $\text{CpFe}^+(\eta^6\text{-PhCl})$ is known to be directed onto the ortho position of the arene ligand.³⁶ The ^1H and decoupled ^{13}C spectra of the adduct resulting from reaction of eq 11 indicate

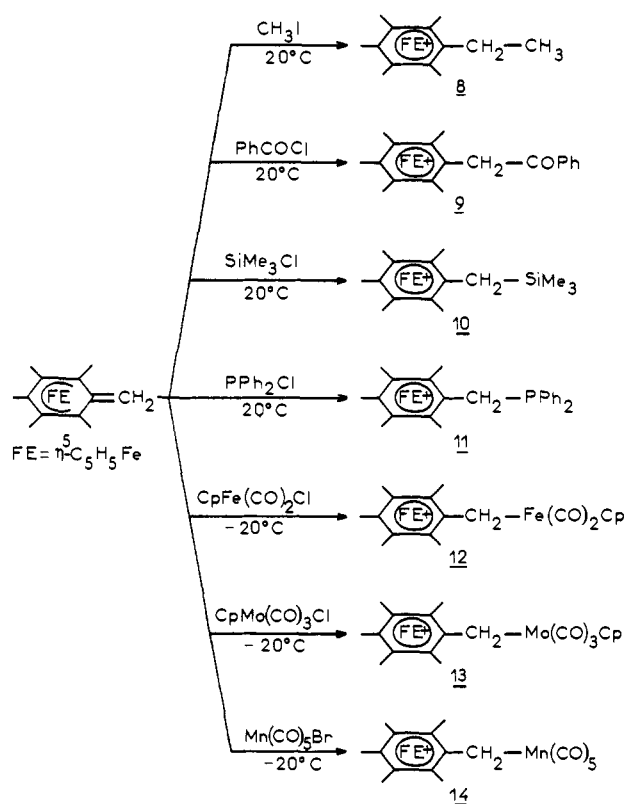


that addition is also exclusively ortho. We have also attempted to induce nucleophilic addition of **2** onto the parent cation $\text{CpFe}^+\text{C}_6\text{H}_6$. Whereas nucleophilic addition occurs immediately at -18°C on $\text{CpFe}^+(\eta^6\text{-C}_6\text{H}_5\text{Cl})$, no reaction is observed below room temperature in THF or acetone with the parent cation. Yet the slow reaction at 20°C does not give the hoped for adduct but instead decomposition is observed, only I^+PF_6^- (upon metathesis) together with ferrocene. Reactions with

(35) Althoff, G. Diplome Thesis, Rennes, 1979.

(36) Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1968**, 2261–2265.

Scheme II



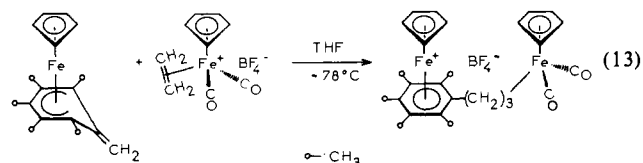
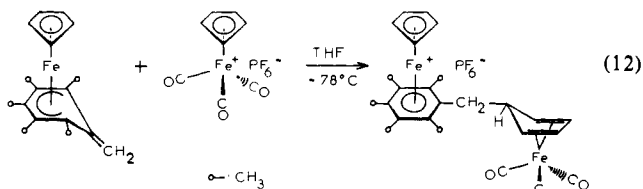
$\text{CpFe}(\text{CO})_3$ ³⁷ and $\text{CpFe}^+(\text{CO})_2(\text{C}_2\text{H}_4)$ ³⁸ are also of interest. At room temperature the electron-transfer products $[\text{CpFe}(\text{CO})_2]_2$ and I^+ are formed again, whereas reactions at -80°C specifically give nucleophilic addition onto a selected ligand^{39,40} (eq 12 and 13). The decoupled ^{13}C NMR spectrum of **17** (Figure 3) clearly

(37) Román, E.; Astruc, D. *Inorg. Chem.* **1979**, *18*, 3284–3285.

(38) Green, M. L. H.; Nagy, P. L. I. *J. Organomet. Chem.* **1963**, *1*, 58–69.

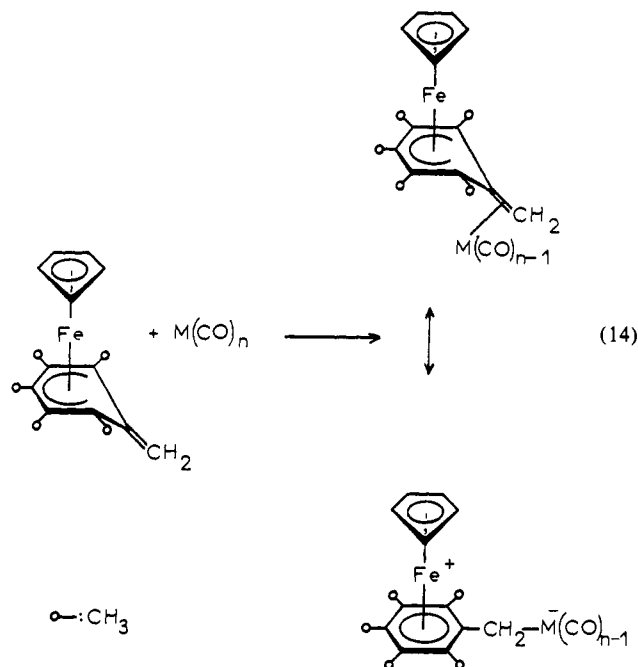
(39) For a general discussion, see: Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, 3047–3077.

(40) For nucleophilic additions onto $\text{CpFe}(\text{CO})_2(\text{C}_2\text{H}_4)^+$, see ref 39 and (a) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122–128. (b) Lennon, P. J.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Waterman, P. *J. Am. Chem. Soc.* **1980**, *102*, 7033–7038. (c) Eisentein, O.; Hoffmann, R. *Ibid.* **1980**, *102*, 6148–6149.



indicates that nucleophilic addition of **2** occurs onto the Cp ligand rather than onto CO giving the bimetallic monocationic complex in which the oxidation states of Fe are 0 and II. The quadrupole splittings in the Mössbauer spectrum of **17** are characteristic of these two oxidation states of iron as exemplified by $\text{CpFe}^+\text{C}_6\text{Me}_5\text{CH}_2\text{R}$ and $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$, respectively. In contrast **18** has two d^6 Fe(II) centers, only the sandwich one being cationic. This latter characteristic renders both **17** and **18** THF soluble whereas $\text{CpFe}^+(\text{arene})$ salts usually are not.

In earlier attempts to characterize the exocyclic double bond of **2**, we reacted it with various binary metal carbonyls with the hope that this double bond would replace one carbonyl. Indeed $\text{Fe}_2(\text{CO})_9$, $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, and $\text{Mo}(\text{CO})_6$ do react with **2** in 1 h at 80 °C in benzene (eq 14). Air-sensitive complexes are



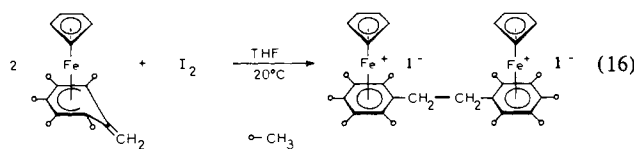
obtained, and the iron carbonyl adduct is even pyrophoric. These heterobimetallic complexes¹⁹⁻²¹ are insoluble in most solvents. They are soluble in hot acetonitrile, however, and can be extracted and recrystallized in this solvent, but this solubility can only afford recording ¹H NMR spectra and a weak ¹³C NMR spectrum of the iron carbonyl adduct, whereas the chromium and molybdenum carbonyl adducts showed insufficient solubility to obtain ¹³C NMR. However, microanalysis, Mössbauer and NMR data clearly indicate that the metal carbonyl adducts are σ -metallates attached to $\text{CpFe}^+\text{C}_6\text{Me}_5\text{CH}_2^-$ rather than π complexes of **2**. $\delta(\text{Cp})$ (¹H NMR) is intermediate between that of **2** (3.4 ppm) and that of the salts $\text{CpFe}^+\text{C}_6\text{Me}_5\text{CH}_2\text{R}$ (4.7 ppm), but in the Mössbauer spectra, the quadrupole splittings are identical with those of $\text{CpFe}^+\text{C}_6\text{Me}_5\text{CH}_2\text{R}$ salts, slightly shifted with respect to that of **2** (1.88 mm s⁻¹). It is thus best to formulate these complexes as zwitterionic metallates $\text{CpFe}^+(\eta^6\text{-C}_6\text{Me}_5\text{CH}_2\text{M}^-$

$(\text{CO})_{n-1}^-$) with some π character. The zwitterionic nature is also supported by their insolubility whereas **2** is extremely pentane soluble.

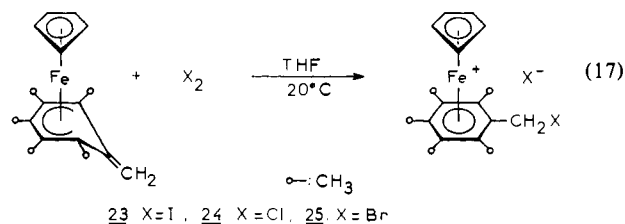
Attempts to remove one electron from **2**⁴¹ in order to couple radical cations **2**⁺ led us to react **2** with a relatively strong electron acceptor, TCNQ. The reaction proceeds immediately at room temperature in THF to give a green precipitate characterized by the characteristic optical spectrum of the anion TCNQ^- ,⁴² and the Mössbauer spectrum of **1**⁺.^{24,25} Furthermore Na/Hg reduction yields a green pentane-soluble paramagnetic complex identified as **1** by the molecular peak observed in its mass spectrum. Thus the electron-transfer reaction is formally identical with these observed with organometallic halides or cations in as much as it is followed by H atom abstraction from the solvent (eq 15).



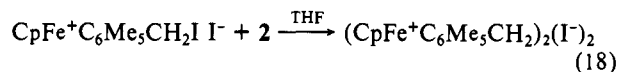
Reactions of **2** with other oxidizing agents were also performed, for example, with the halogens I₂, Cl₂, and Br₂. Successful coupling of **2** was achieved when a THF solution of I₂ was added to a THF solution of **2** (eq 16). The binuclear salts obtained are much less



soluble in acetone and acetonitrile than the monomer, and clear evidence for their structure was obtained from the ¹³C NMR spectrum of a $\text{Me}_2\text{SO}-d_6$ solution of the PF_6^- salt. The salts (I^- or PF_6^-) can be slowly reduced (Na/Hg, DME, 20 °C, overnight) to a neutral species, the mass spectrum of which shows a very weak molecular peak M^+ , m/e 564, and intense peaks also consistent with the proposed structure $(\text{M}/2)^+$, m/e 282, $(\text{C}_6\text{Me}_5\text{CH}_2)_2^+$, m/e 322, and $\text{C}_6\text{Me}_5\text{CH}_2$, m/e 161. If 1 mol of **2** in THF is added to 1 mol of I₂ in THF, the iodo complex $\text{CpFe}^+\text{C}_6\text{Me}_5\text{CH}_2\text{I}^-$ is isolated and can be metathesized to the PF_6^- salt. No further reaction occurs if excess iodine is reacted overnight. With Cl₂ and Br₂, the chloro and bromo compounds are obtained analogously. The ¹H and proton-decoupled ¹³C spectra provide good evidence for the proposed structures, the signal pattern being characteristic of the formation of one monomeric complex of $\text{CpFe}^+\text{C}_6\text{Me}_5\text{CH}_2\text{R}$ type; this was confirmed by elemental analyses (eq 17). Finally the reaction between 1 mol of the iodo complex



23 and 1 mol of **2** in THF at 20 °C yields the binuclear bicationic complex (eq 18), indicating that the coupling obtained by reacting I₂ with **2** is a double nucleophilic substitution of I^- .

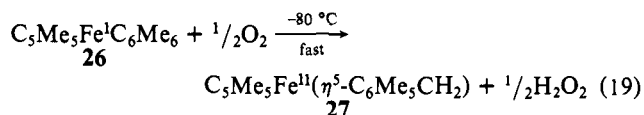


(41) For electron-transfer reactions in organometallic chemistry, see ref 9, 17c,d, and Kochi, J. K. *Acc. Chem. Res.* **1974**, *7*, 351-360.

(42) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mockel, V. E. *J. Am. Chem. Soc.* **1962**, *84*, 3374-3387.

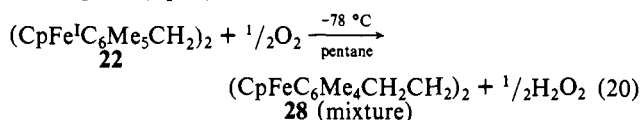
(43) The fully methylated Fe(I) sandwich **26** is also the most electron-rich neutral compound known so far, having the most negative value of half-wave potential²⁵ in this series and the lowest value of ionization potential ever recorded (from He I photoelectron spectroscopy: Green, J. C., personal communication).

6. Regiospecific H Atom Abstraction by O₂ from the 19-Electron Complexes C₅R₅Fe^IC₆R'₆ (R = H, CH₃; R' = CH₃, C₂H₅). **a.** C₅Me₅Fe^IC₆Me₆ (**26**). This dark ivory-green sandwich **26**²⁵ is the most air-sensitive complex of these series.⁴³ It reacts with 0.5 mol of O₂ at -80 °C instantaneously in pentane or THF to give 55% of yellow C₅Me₅Fe^{II}C₆Me₆ OH⁻ and a deep red solution. After subsequent workup with pentane, a dark red complex crystallizes easily from this solvent, being less soluble than its analogue **2**. The mass spectrum shows a molecular peak at *m/e* 352, indicating that this new complex **27** is formed from **26** by loss of one H atom (40% yield of crystals). **27** is diamagnetic, and its ¹H and ¹³C NMR spectra show a singlet for C₅Me₅ and a pattern characteristic of the C₆Me₅CH₂ moiety, the arene signals being even more separated than those in **2**. This indicates that the H atom has been abstracted by O₂ from a methyl group of the C₆Me₆ ligand rather than from C₅Me₅. Thus the H atom abstraction is regiospecific in **26**. No side product is observed by NMR spectroscopy. The reaction characteristics (eq 19) are the



same as those of CpFeC₆Me₆ (eq 5, 7, and 8). The reaction with 0.5 mol of O₂ at -80 °C gives 0.5 mol of H₂O₂ whereas only 0.25 mol of O₂ is consumed at 20 °C, giving 0.5 mol of H₂O. Note that the decreased yield upon reaction at -80 °C (81% at 20 °C, 45% at -80 °C) is much more dramatic than that for **1** (96% at 20 °C, 91% at -80 °C). The hydroxide C₅Me₅Fe^{II}C₆Me₆ OH⁻ (**26**⁺OH⁻) is isolated in complementary yields, indicating the tendency toward protonation of **27**. **27** reacts with H₂ in the presence of Pd/C to give C₅Me₅Fe^{II}(η⁵-C₆Me₆H) (**3a**) (*t*_{1/2} = 1.5 h) via **26** (*t*_{1/2} = 0.18 h). This reaction is analogous to that of **2**.

b. (CpFe^IC₆Me₅CH₂)₂ (**22**). As mentioned in section 5, a green neutral complex is obtained by reduction of the binuclear dication **22**²⁺. Its Mössbauer spectrum at 4 K confirms that **22** belongs to the Fe(I) series, the parameter observed (quadrupole doublet, QS = 0.6 mm s⁻¹, IS = 0.74 mm s⁻¹) being typical. Specific behavior due to the binuclear "19-electron" nature will be detailed later. **22** reacts with 1 mol of O₂ at -80 °C in pentane giving a red complex as expected. Removing the pentane in vacuo gives a dark red oil which crystallizes from pentane at -90 °C. The decoupled ¹³C NMR spectrum indicates the presence of three sets of peaks corresponding to H atom abstraction from positions ortho, meta, and para, in approximately equal amounts (15 isomers including racemates); thus this reaction proceeds without selectivity at this point (eq 20).



c. CpFe(I)C₆Et₆ (**29**). This 19-electron complex is much less air sensitive than the others. Crystals are apparently stable in the solid state for prolonged periods of time.⁴⁴ Reaction with O₂ in pentane proceeds quickly at 20 °C upon stirring but is slow (5 min) at -20 °C. The amount of O₂ consumed is only 0.25 mol even at -20 °C. A purple pentane-soluble complex is formed which cannot be crystallized in pentane at -90 °C and appears to be an oily liquid. Its mass spectrum shows a molecular peak at *m/e* 366, indicating again the loss of one H atom. The ¹H and decoupled ¹³C NMR spectra are consistent with this. The uncoordinated arene carbon is found at δ 138.5 and the other olefinic carbon (exocyclic) at δ 68, both positions being shifted upfield compared to that of **2**. The ortho and meta peaks are split (arene C as well as C₂H₅) in accord with the substitution by CH₃ of the exocyclic double bond. The relatively slow rate of this reaction

(44) The thermal stability of **28** is not infinite at 20 °C. After more than 1 month in a sealed tube at 20 °C in the solid state, small amounts of Cp₂Fe, C₆Et₆, and Fe appear.

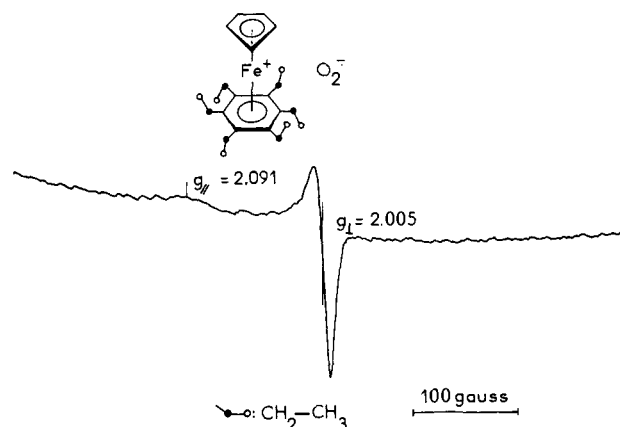
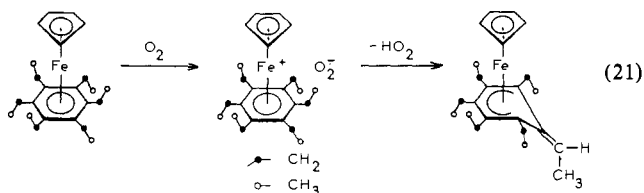


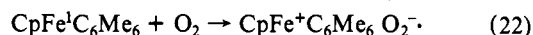
Figure 4. EPR spectrum of CpFe^IC₆Et₆ + O₂ at 77 K in frozen DME solution (O₂⁻).

at -20 °C allow its examination by EPR. Upon color change, green → red, the EPR spectra reveal the progressive appearance of the characteristic spectrum of O₂⁻. When the green color of **29** has completely disappeared, the clean spectrum of O₂⁻ can be seen above 77 K and shows the characteristic temperature dependence (Figure 4). Thus the sequence shown in eq 21 is ascertained.

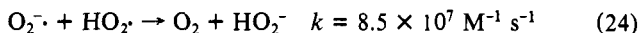


Discussion

A. Mechanism of H Atom Abstraction by O₂. According to the values of the ionization potentials found by J. C. Green from He I photoelectron spectra, the 19-electron complexes CpFe^I(arene) are the most electron-rich neutral species known to date.⁴³ They are also extremely air sensitive, and it is tempting to explain the H atom abstraction by O₂ in terms of an electron transfer from the sandwich to O₂ followed by deprotonation by O₂⁻.



The driving force of the electron transfer (eq 22) is all the greater as the difference between the redox potentials of the two reversible redox systems CpFeC₆Me₆/CpFe^{II}C₆Me₆ (≈ -1.8 V/SCE) and O₂/O₂⁻ (-0.7 V/SCE) is very large. The second step (eq 23) poses a problem in as much as O₂⁻ would be too weak a base to deprotonate **1**⁺ since the pK_a of HO₂ is only 4.8. However, the equilibrium can be shifted to the products because of the disproportionation of HO₂ (eq 24).



Indeed the superoxide radical anion can deprotonate substrates to an extent equivalent to that for the conjugate base of an acid with an approximate pK_a value of 23.^{45,46} The acidity of benzylic hydrogens in (arene)metal complexes has been known since Trahanovsky and Card found that (indane)Cr(CO)₃ is subject to replacement of benzylic H by D when promoted by amines.⁴⁷ This property has been used for a synthetic purpose, and we have found

(45) Yet, how these factors are changed in an inert solvent such as pentane is difficult to figure out. However, it is known that even in these circumstances electron transfer can occur between two radicals of different electronegativities to give ion pairs. Lawler, R. G.; Barbara, P. F.; Jacobs, D. *J. Am. Chem. Soc.* **1978**, *100*, 4912-4914.

(46) The effective basicity of superoxide radical anion has been underlined recently. Sawyer, D. T.; Gibian, M. J.; Morrison, M. M.; Sev, E. T. *J. Am. Chem. Soc.* **1978**, *100*, 627-628.

(47) Trahanovsky, W. S.; Card, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 2897-2898.

that $\text{CpFe}^+(\eta^6\text{-toluene})$ as well as $\text{CpFe}^+(\eta^6\text{-C}_6\text{Me}_6)$ could be deprotonated by *t*-BuOK and alkylated.^{20,48} Even weaker bases such as Na_2CO_3 can promote the transfer of a proton from a methyl group of $\text{CpFe}^+(\eta^6\text{-toluene})$.⁴⁹ Finally we have checked that KO_2 itself can deprotonate **1**⁺ to give **2** although the conditions used are somewhat different. Thus this process is feasible, but still we must consider the possibility of a radical mechanism which would proceed by a direct hydrogen atom abstraction. It is known that cobaltocene reacts with O_2 to give a peroxide⁵⁰ and similar reactions may occur in $\text{CpFe}^1(\text{arene})$ series.⁵¹ Decomposition of such a thermally unstable peroxides could generate a species capable of direct H abstraction. It is interesting to consider at this point that $\text{CpFe}^1(\text{arene})$ with less than six alkyl groups on the arene presumably leaves room for the attack of O_2 onto an unsubstituted arene carbon whereas the series $\text{C}_5\text{R}_5\text{Fe}^1\text{C}_6\text{R}'_6$ do not. The odd nature of these complexes can indeed provide a viable mechanistic alternative in as much as O_2 is known to react with organic radicals at a rapid rate. In paramagnetic d^7 complexes such as $\text{CpFe}^1(\text{arene})$, we know that the unpaired electron is located in an antibonding e^*_1 orbital which is essentially metal based but we also have examples at hand where the approach of a substrate induces a metal to arene electron transfer so that the paramagnetic sandwich finally behaves as an organometallic radical.^{25,52} However, in all cases known, these reactions resulting from an intramolecular metal to arene electron transfer are inhibited when the arene ligand bears six alkyl groups. It is also noteworthy in this respect that the purple salt $\text{Fe}(\text{C}_6\text{Me}_6)_2^+\text{PF}_6^-$ ⁵³ which does not react with O_2 , although it also belongs to the d^7 19-electron series, has similar electronic properties and in particular an unpaired electron in a e^*_1 orbital of high metal character as checked by our Mössbauer data.⁵⁴ The redox potential of the reversible system $\text{Fe}(\text{C}_6\text{Me}_6)_2^{2+}/\text{Fe}(\text{C}_6\text{Me}_6)_2^+$ is only -0.5 V/SCE⁵⁵ below that of O_2/O_2^- ; thus it appears that reactivity toward O_2 in the d^7 19-electron sandwiches strongly depends on the redox potential even though this series is paramagnetic. On the other hand, the yellow diamagnetic d^6 sandwich $\text{Cr}(\text{C}_6\text{Me}_6)_2$ is very air sensitive. It consumes 0.25 mol of O_2 in pentane like the title series and gives an orange, pentane-soluble, light-sensitive complex of as yet unknown structure, but which could well be the 17-electron H atom abstraction product.⁵⁶ Since $E_{1/2}$ for the reversible system $\text{Cr}(\text{C}_6\text{Me}_6)_2/\text{Cr}(\text{C}_6\text{Me}_6)_2^+$ is -1.3 V/SCE,^{57,58} it seems that the aerobic reactions described here do not depend on whether the sandwich is diamagnetic or paramagnetic but rather solely on whether its redox potential is higher or lower than that of O_2/O_2^- .

Another argument along this line comes from the fact that $\text{C}_5\text{Me}_5\text{FeC}_6\text{Me}_6$ reacts unstantaneously with O_2 at -80 °C whereas the same reaction with $\text{CpFeC}_6\text{Me}_6$ takes approximately 1 min. Since the former is more sterically hindered but has a more negative redox potential, this observation is in accord with an outer-sphere electron transfer to O_2 , presumably the rate-limiting step.

If so, it means that complexes which have a redox potential more negative than -0.7 V/SCE may lose one H atom upon contact

with air. This value is easily accessible and must indeed be attained by a great many complexes. Therefore the next question one has to address is the condition for the second step to occur, namely, the deprotonation by O_2^- , as observed here. We found that $\text{C}_5\text{Me}_5\text{FeC}_6\text{Me}_6$ loses specifically a hydrogen atom from C_6Me_6 . We also know that $\text{C}_5\text{Me}_5\text{Fe}^+\text{C}_6\text{H}_6$ does not lose a H atom from C_5Me_5 to give an $\text{Fe}^0(\text{fulvene})$ complex upon reaction with O_2 . C_5Me_5 is an odd ligand whereas C_6Me_6 is an even one. As has been clearly shown by Davies, Green, and Mingos,³⁹ the positive charge is much more delocalized onto an even than onto an odd ligand in a cationic complex and therefore C_6Me_6 is much more acidic than C_5Me_5 in **26**⁺. This regioselectivity is also consistent with the proposed mechanism involving deprotonation by O_2^- . At this stage it is possible to assume that neutral complexes with 18 valence electron (or more) on the metal, at least one even hydrocarbon ligand, and $E_{1/2} < -0.7$ V/SCE present a high probability of losing a H atom upon contact with air.

B. Structure and Properties of the Arene Ligand after the Loss of H: $\eta^5\text{-Benzyl}$. That deprotonation of coordinated arenes such as toluene and ethylbenzene can be useful for subsequent alkylation by organic halides has been clear since the work on chromium carbonyl complexes,⁵⁹ and much interest has been devoted recently to the deprotonation of coordinated arenes.^{60,61} In several instances, the deprotonated species are stabilized by conjugation in a strained system such as fluorene^{60,61a} or carbazole^{61a} or by heteroatoms such as O, S, or N.^{61a} In one case, the deprotonation of $\text{CpFe}^+(\text{fluorene})$ by *t*-BuOK, the crystal structure of the deprotonated complex was reported, indicating that the arene remains nearly planar after removal of the proton.⁶⁰ This was interpreted in terms of a zwitterionic structure. On the other hand, the deprotonation of $\text{CpFe}^+(\eta^6\text{-triphenylmethane})$ was viewed as stabilizing an exocyclic double bond.^{61a} Very recently, deprotonated $\text{CpFe}^+(\text{arene})$ complexes in which the arenes are simple alkylbenzenes such as toluene and mesitylene were entitled "zwitterions",⁴⁹ but so far these red unstable species have not been characterized except by alkylation. Even in stabilized series, deprotonated complexes of arenes are viewed as carbanions, for instance, $(\text{CO})_3\text{Cr}(\eta^6\text{-PhCH}^-)(\eta^6\text{-PhCr}(\text{CO})_3)$.⁶² To date the only characterization of exocyclic methylene complexes concerns **2**, **23**, and **27**. In all of them the arene ring is hexasubstituted. The deprotonation of CpFe^+ (pentamethylbenzene) gives a red powder which can be recrystallized at low temperature; however, the room-temperature, decoupled ¹³C spectrum indicates a complete polymerization although protonation allows the recovery of the cation.⁵⁶ Therefore, permethylation of the arene ligand provides a kinetic stabilization of **2** and related complexes (**1**, **22**, **26**, and **29** are thermally stable for the same reason). The crystal structure of **2** shows that the uncoordinated part of the arene makes an angle of 32° with the plane of the five coordinated carbons, slightly lower than that usually found in complexes of cyclohexadienyl (39–50°). The large solubilities in pentane indicate that **2**, **28**, **27**, and **30** are not zwitterions, as confirmed by the hydrogenation of **2** to **3**. **2** behaves as a neutral nucleophile rather than as a carbanion since its reaction with $\text{CpFe}^+(\eta^6\text{-PhCl})$ is an addition reaction whereas that of $\text{CpFe}^+(\text{fluorenyl}^-)$ on the same substrate was reported as a nucleophilic substitution of Cl^- ,⁴⁹ it also fails to react with $\text{CpFe}^+(\eta^6\text{-C}_6\text{H}_6)$ below room temperature whereas reactions of carbanions are fast at -80 °C.³⁶ Real zwitterions are those formed by reactions of **2** with CO_2 , CS_2 , and metal carbonyls. Another characteristic of **2** is its general and

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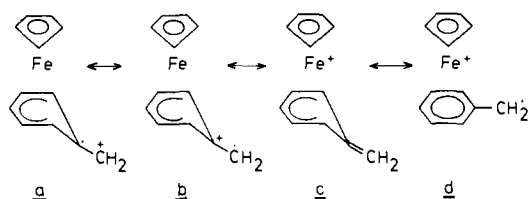
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Table I. Optical Data for Compounds 2, 3, 27, and 30 (λ , nm (ϵ , L mol⁻¹ cm⁻¹))

27	2	30	3
451 (1066)	434 (995)	420 (395)	410 (324)
388 (1240)	377 (1244)	358 (1185)	340 (902)
337 (4266)	333 (3732)	335 (2125)	315 (1725)
266 (40527)	267 (27785)	267 (18125)	301 (15228)
262 (38927)	263 (26126)	263 (17188)	286 (16751)
259 (42660)	260 (30274)	260 (20313)	276 (18528)
257 (39461)	258 (28822)	258 (19375)	266 (21320)
256 (38127)	254 (29029)	256 (19063)	243 (36802)
252 (35728)	252 (29237)	252 (20000)	
245 (31995)	246 (29029)	246 (20000)	
238 (34128)	240 (30481)	235 (21250)	
224 (49059)	229 (37946)	230 (21562)	

mild reactivity with halides of many elements which should prove very useful for binding the sandwich to electrodes and surfaces to take advantage of its properties of redox catalyst. Stoichiometrically clean reactions can be performed due to the ease of isolation of large amounts of **2** in the crystalline form. One limit is the electron transfer (eq 10 and 12) observed with some organometallic halides giving **1**⁺ and dimers when reactions with **2** were carried out at 20 °C, whereas such side reactions were never observed at -80 °C. Electron transfer from **2** involves the removal of a metal orbital rather than the exocyclic double bond since He I photoelectron spectra recorded by J. C. Green show nearly identical ionization potential values for **2** (6.14 eV) and **3** (6.17 eV). That these electron transfers **2** → **2**⁺ (also eq 15) are followed by H atom abstraction from the solvent by the exocyclic methylene unit is consistent with resonance forms **a-d**.⁶³ Attempts to use

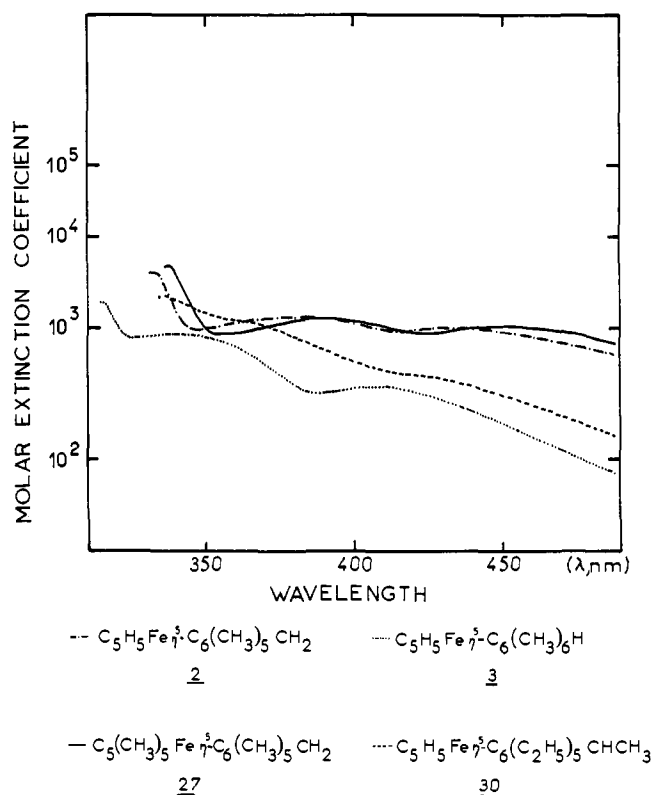
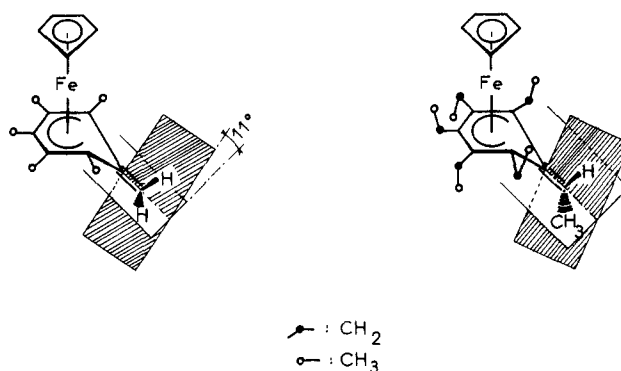


mild oxidizing agents providing such electron transfer to couple the sandwich through the CH₂ group of form **d** failed, but the reaction of I₂ with **2** provides this hoped for binuclear sandwich **22**²⁺ by what turned out to be a double nucleophilic substitution rather than an electron-transfer reaction. Binuclear sandwiches such as **22**²⁺ are useful in so far as they bear hexasubstituted arene ligands able to provide thermally stable bis "19-electron" complexes such as **22**, which are starting points "en route" to new mixed valence systems. Along this line a regiospecific reaction of **22** with O₂ would have been of interest to reach polymeric sandwiches in these series with high molecular weight. The lack of regioselectivity of the double H atom abstraction of O₂ from **22** precludes the isolation of such a polymer by reaction of **28** with I₂, but slightly different designs are in progress to reach this aim.

It is of great practical interest that, although **2** is isolable in the crystalline form, all the above chemistry can be achieved after simple contact with air at 20 °C for a few seconds of a complex of C₆Me₆, namely, **1**. Indeed the yield of **2** using the contact of **1** with air is higher than that for the deprotonation of **1**⁺ salts by bases. Only 3% of **1**⁺ OH⁻ is formed at 20 °C, but this amount reaches 8% at -80 °C because H₂O₂ formed at this temperature is more acidic than H₂O formed at 20 °C. This problem becomes more dramatic with the fully methylated complex **26** which gives 18.5% of **26**⁺ OH⁻ at 20 °C but as much as 55% at -80 °C. This indicates that the electron-releasing effect of Cp permethylation renders the exocyclic methylene more basic in **27** than in **2**.

The complex of C₆Et₆ (**29**) is peculiar in these series as it is the only one reacting slowly with O₂ at -20 °C which allows us

(63) That **2** has a low ionization potential (IP) is consistent with its good nucleophilic properties as well as its ability to donate one electron to an acceptor. Both properties can be linearly correlated to IP, but a distinction between them is not clear. See, for example, ref 9.

Figure 5. Visible spectra of η⁵-benzyl complexes of Fe(II).Figure 6. Distortion of the exocyclic double bond in **2** and in **30**.

to characterize O₂⁻ as a reaction intermediate. The purple complex resulting from the aerobic reaction of **29** must have a very distorted exocyclic double bond due to steric crowding, yet it is noteworthy in this context that an H atom can be abstracted from **29** by O₂. We already know from the X-ray study that the bulk of two ortho methyls induces a slight twist (11°) of the exocyclic methylene in **2**. This effect must be very much enhanced in **30**. That conjugation of the exocyclic double bond with the cyclohexadienyl ring is less marked in **30** than in **2** can be deduced from the UV-visible spectra (Table I). The d-d transitions in the visible or near-UV region are strongly perturbed by the presence and nature of the exocyclic double bond. There are three bands in this region (Figure 5). We have a good reference available, **3**, in which there is no exocyclic double bond. The three bands show a red shift and an increase of intensity (ϵ) in **2**, **27**, and **30** in which there is an exocyclic double bond. However, the major point of interest to our concern here is that this effect is very small for **30** due to distortion and subsequent lack of conjugation whereas it is large for **2** and **27**. This is particularly marked for ϵ of the 330-nm band and for both λ and ϵ for the 410-nm band. In this respect it is also noteworthy that **30** reacts very slowly with excess water in contrast with **2** and **27**. The splitting of the cyclohexadienyl pattern observed in ¹H and ¹³C NMR (ortho and meta positions) indicates that the distortion of

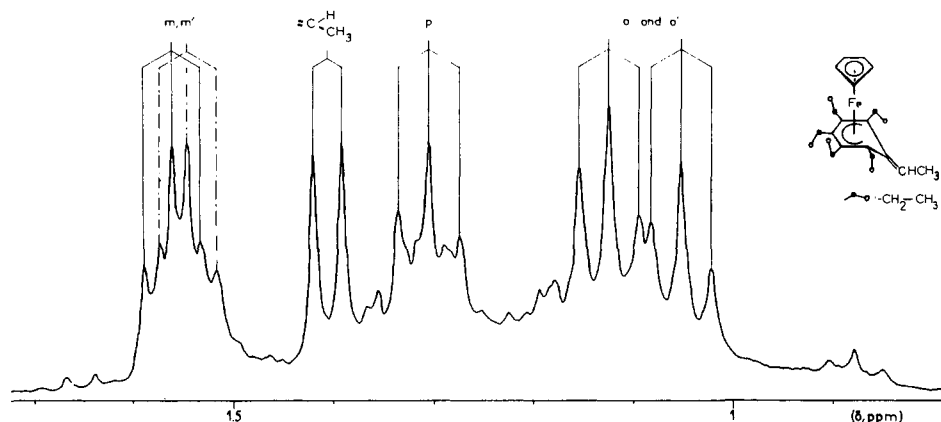


Figure 7. 250-MHz ^1H NMR spectrum of $\text{CpFe}^{\text{II}}(\eta^5\text{-C}_6(\text{C}_2\text{H}_5)_3\text{CHCH}_3)$ showing the CH_3 region.

the exocyclic double bond in **30** is less than 90° (no symmetry plane, see Figure 6 and the Me pattern in the 250-MHz ^1H NMR spectrum, see Figure 7).

Concluding Remarks

The unstantaneous loss of a hydrogen atom in the thermally stable complexes $\text{C}_5\text{R}_3\text{Fe}^{\text{I}}\text{C}_6\text{R}'_6$ upon contact with air in solution is a remarkably novel mode of activation of C–H bonds^{64,65} since further reaction with electrophiles provides C–C bonds as well as bonds between C and many other elements in high yields. The intermediates of benzylic activation after contact with air of the complexes of simple arenes, $\text{C}_6\text{R}'_6$, are well-characterized cyclohexadienyl complexes with exocyclic double bonds, suggesting that deprotonation of complexes of alkylarenes does not give zwitterions or carbanions when the arene is unstrained despite nucleophilic properties and electron-transfer reactions (which do involve metal orbitals) but the neutral η^5 -benzyl ligand.⁶⁶ We now have at hand a variety of convincing arguments indicating that aerobic H atom abstractions proceed by electron transfer to O_2 followed by deprotonation by O_2^- . There are, however, some unclear points such as, for example, why H_2O is formed at ambient temperature and H_2O_2 in low-temperature reactions and why d^7 complexes of the CpFe arene series with less than six alkyls do not react in the same fashion. A further critical study of the problem of solvation energies of the intermediates involved in the electron-transfer paths will no doubt shed light on these questions.

Experimental Section

Reagent grade tetrahydrofuran, diethyl ether, and 1,2-dimethoxyethane were predried on Na foil and distilled from sodium benzophenone ketyl under nitrogen just before use. Benzene and toluene were distilled and stored under nitrogen. Reagent grade pentane was degassed with nitrogen before use. All other chemicals were used as received. All manipulations were done by Schlenk technique, in a nitrogen-filled Vacuum Atmosphere drylab or in glovebags. Infrared spectra were recorded with a Pye-Unicam SP 1100 infrared spectrophotometer which was calibrated with polystyrene. Samples were prepared between KBr disks in Nujol. ^1H NMR spectra were recorded with Varian EM 360 (60 MHz) and XL 100 (100 MHz) and Brücker WP 80 (80 MHz) spectrometers (except for **30**). ^{13}C NMR spectra were obtained at 25 MHz in the pulsed Fourier transform mode with a Varian H-100 spectrometer or at 20.115 MHz with a Brücker WP 80 spectrometer. All chemical shifts are reported in parts per million (δ , ppm) with reference to tetramethylsilane (Me_4Si) and were measured relative to the solvent or Me_4Si unless specified otherwise. Mass spectra were recorded by Dr. P. Guénot at the Center of Physical Measurements of Rennes using a Varian MAT 311 spectrophotometer. Ultraviolet and visible spectra were recorded with a Beckman DB spectrophotometer. EPR spectra

were recorded with a Varian E 112 spectrometer at Grenoble (CENG). Mössbauer spectra were recorded with a ^{57}Co source on Rh using a symmetric triangular sweep mode. Isomer shifts are given relative to Fe. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne.

1. Reactions of $\text{CpFeC}_6\text{Me}_6$ with Dry Air or O_2 . A 1.41-g (0.5-mmol) sample of **1** is transferred into a Schlenk flask in a glovebag under N_2 . Then 60 mL of dry pentane is transferred through a steel cannula. The Schlenk flask containing the forest green solution is connected to dry air through the Schlenk line and a tube of KOH pellets. Upon depression and stirring, the solution immediately turns bright red. Alternatively the same result is obtained by adding 2.8 mL (0.125 mmol) of O_2 by syringe (20°C). A slight precipitate is formed. After filtration and removal of the solvent in vacuo, 1.34 g of crude **2** is obtained (96%). Recrystallizations from pentane at -40°C give 1.3 g of red-black crystals (92%). **2** is stable in CH_3CN and CH_2Cl_2 at 20°C for more than 1 h. Decomposition in acetone occurs more rapidly. **2** is stable in the solid state under pure O_2 but very hygroscopic; mp 110°C dec, 130°C (under N_2). Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{Fe}$: C, 72.35; H, 7.86; Fe, 19.79. Found: C, 72.32; H, 8.07; Fe, 19.61. Mass spectrum: M^+ calcd 282.107; found 282.106.

The precipitate of 1^+OH^- is collected, dried, weighed (0.055 g, 3%), and identified by ^1H NMR in D_2O (see ref 36). If the reaction mixture is hydrolyzed rather than extracted, titration by KMnO_4 indicates the presence of traces of H_2O_2 (1%). Before hydrolysis, the infrared spectrum shows an intense new band at 3400 cm^{-1} upon addition of O_2 to **1**.

Upon reaction at -78°C , the crude yields are different (**2**, 91%; 1^+OH^- , 8.6%). Alternatively hydrolysis followed by acidification by H_3PO_4 to pH 1.5 and titration by KMnO_4 (0.01 N) indicates the presence of 0.5 mol of H_2O_2 (1^+ can be precipitated as the PF_6^- salt before titration if desired). Titration of **1** by O_2 is realized by adding portions of 5% O_2 by syringe, and 1% near the equivalence. The stoichiometries (0.25 mol of O_2 at 20°C and 0.50 mol of O_2 at -78°C) are determined by color change from dark forest green to bright red, each experiment being repeated at least three times. The reaction between **1** and O_2 is fast at 20°C and takes 1 min at -78°C . The same results were obtained with DME instead of pentane.

2. Hydrogenation of **2.** To 0.282 g (1 mmol) of **2** in THF with 0.05 g of Pd/C (5%) is added by syringe 22.4 mL of H_2 at 20°C . The color of the solution changes in 2 h from bright red to orange. Pd/C is filtered, and the solvent is removed in vacuo. **3** is recrystallized from pentane at -80°C , which gives 0.26 g of microcrystals (90%); IR $\nu_{\text{CH}(\text{exo})}$ 2765 cm^{-1} , ^1H NMR (C_6D_6) δ 3.46 (Cp, 5 H), 2.12 (*p*- CH_3 , 3 H), 1.50 (*m*- CH_3 , 6 H), 1.04 (*o*- CH_3 , 6 H), 1.00 (d, CH_3 , 3 H), 0.94 (q, H, 1 H); ^{13}C NMR (C_6D_6) δ 76.5 (Cp), 17.1, 16.9, and 16.7 (Me_3), 89.3, 89.1 (C_6 , para and meta), 36.5 (C_6 , ortho), 33.7 (CHCH_3), 17.7 (CHCH_3).

Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{Fe}$: C, 71.84; H, 8.51; Fe, 19.65. Found: C, 71.80; H, 8.50; Fe, 19.70. Mass spectrum: M^+ calcd 284.119; found 284.122.

3. Reaction of **1 with O_2 from Air in the Solid State.** A polycrystalline sample of **1** is set into a plastic cell for Mössbauer spectroscopy in inert atmosphere, and Mössbauer spectra were recorded at various temperatures. Spectra at 293 and 77 K are reported respectively in parts 1 and 5 of Figure 1. Air is then allowed into the cell for 1 min and the spectra are recorded again (293 K, Figure 1(3); 77 K, Figure 1(6)). A monocrystalline sample of **1** is prepared by cooling down from 20 to -20°C a pentane solution of a microcrystalline sample in 48 h. Large plates were obtained (1.5–2 mm \times 0.5–0.7 mm \times 0.1 mm) and set beside one another in a Mössbauer cell onto a parafin surface, so as to make a mosaic covering most of the surface of the round cell (diameter 13.5

(64) For a survey of C–H activation in arenes by transition metals, see: (a) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113–117. (b) Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 43–263.

(65) Another mode of stoichiometric activation of arenes, nucleophilic substitution, has been developed in the (arene)Cr(CO)₃ series. For reviews, see: (a) Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36–51.

(66) For a theoretical discussion of this ligand, see: Hoffmann, R.; Hoffmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598–604.

mm). This sample gave a dissymmetrical doublet typical of a monocrystal. The relative intensity of the two lines (0.5, theory 0.33) confirms that the γ -ray crossing perpendicular to the cell is parallel to the electric field gradient (see central doublet to Figure 1(4)). Dry air is allowed into the cell for 1 h, and the Mössbauer spectrum is recorded again (20 °C, Figure 1(4)).

Cosublimed samples of **1** and **2** were prepared with different proportions in order to obtain a sample in which the proportions are close to those obtained in the oxidized monocrystal (32% of **2**). Figure 1(7) shows the spectrum at 77 K of such a sample (38% of **2**).

4. Deprotonation of 1⁺ by *t*-BuOK or KO₂. (a) *t*-BuOK. To a Schlenk tube containing 2.13 g (5 mmol) of 1⁺ PF₆⁻ and 0.8 g (7.12 mmol) of *t*-BuOK is added 50 mL of THF. The reaction mixture immediately becomes red. Stirring is continued for 5 min, and the solvent is removed in vacuo. A 60-mL sample of pentane is added, and the solution is allowed to stir for 15 min. After filtration, the solution is concentrated to 15 mL and slowly cooled down to -78 °C. Filtration allows 1.17 g of crystals of **2** (83%) to be collected.

(b) KO₂ in Me₂SO. In an apparatus for liquid-liquid extraction are placed 0.71 g (10 mmol) of dry KO₂, 2.13 g (5 mmol) of 1⁺ PF₆⁻, and 50 mL of Me₂SO. Extraction with pentane for 8 h gives a red solution. This solution is concentrated and filtered in dry heptane. Filtration and recrystallization of the solid gives 0.634 g of **2** (50%).

(c) KO₂ in THF with 18-Crown-6 Ether. A 0.71-g (10-mmol) sample of KO₂, 2.13 g (5 mmol) of 1⁺ PF₆⁻, and 18-crown-6 ether (5 mmol) are stirred in THF at 20 °C for 3 h, giving a red solution. After removal of the solvent in vacuo and extraction with pentane, fractional crystallization gives 0.75 g of **2** (59%).

5. Reaction of 2 with H₂O and D₂O. (a) H₂O. A 1.13-g (4-mmol) sample of **2** are dissolved in 50 mL of ether, and 0.4 mL (22 mmol) of water is added by syringe. After vigorous stirring, the precipitation is only partial and the solution is still red. No excess water is added in order to prevent the formation of an aqueous phase, 1⁺OH⁻ being very soluble in water. The precipitate is filtered and dried in vacuo, providing 1.11 g of a powder. Elemental analysis and ¹H NMR (CD₃COCD₃, δ 4.72 (Cp, s, 5 H), 2.6 (CH₃, s, 18 H), 3.06 (H₂O, large)) indicates the presence of excess water: ¹³C NMR (D₂O, TMPS) δ 100.8 (C₆), 80.4 (Cp), 19.1 (CH₃); IR (Nujol) 3400 cm⁻¹ (large, OH⁻); mass spectrum (analogous to that of **2**), *m/e* 282 (2⁺), 267 ((2-CH₃)⁺), 216 ((FeC₆Me₃CH)⁺), 214 ((FeC₆Me₃CH₂)⁺), 211 ((FeC₆Me₃(CH₃)₃)⁺), 186 ((Cp₂Fe)⁺), 162 ((C₆Me₆)⁺), 121 ((CpFe)⁺), 65 ((Cp)⁺) (*r*⁰ of the source, 130 °C at 70 eV).

When 1⁺OH⁻ is left under vacuum in a desiccator containing KOH pellets, it turns red (the color of **2**) after 8 h. Heating 1⁺OH⁻ with KOH in ethanol gives the same results rapidly as checked by the presence of the IR stretch at 1600 cm⁻¹ (exocyclic CH₂). If 10 mL of ether is added to 1⁺OH⁻ with KOH, the solution turns red, **2** being soluble in ether.

(b) D₂O. A 564-mg (2-mmol) sample of **2** is added to 10 mL of D₂O under N₂. After 1 day, 335 mg of NaPF₆ is added. The precipitate is dried with ether and deprotonated by *t*-BuOK. A mass spectrum of the neutral complex is recorded: *d*₀ 30%, *d*₁ 37%, *d*₂ 22.3%, *d*₃ 8.4%, *d*₄ 2.3% (values taking into account the isotopic contribution of C and Fe, temperature of the source, 120 °C at 70 eV). The average is 1.3 mol of D/mol. The same reaction in the presence of 10 mL of Me₂SO gives the same result.

6. Perdeuteration of the Methyls in 1 or 2. A 564-mg (2-mmol) sample of **2** is dissolved in 5 mL of DME and 5 mL of D₂O (99.9% D) and the solution is stirred 2 h with 300 g of Na/Hg (1%) in the presence of air, and then aqueous HPF₆ is added to the aqueous phase for metathesis. The intensity of the ¹H NMR peak for the methyls is ten times weaker than in 1⁺. Deuteration (90%) is also shown by the mass spectrum of the deprotonated complex as described in 5b. This experiment was repeated with **1**, which gives the same result.

7. Reaction of 2 with CO₂. A 564-mg (2-mmol) sample of **2** is dissolved in 30 mL of dry pentane in a Schlenk tube under N₂ at 20 °C, and then 45 mL of CO₂ is added (2 mmol). A yellow solid precipitates immediately. Dissolution with 20 mL of CH₃CN followed by concentration and addition of dry ether provides reprecipitation of 613 mg (94%) of a yellow-orange hygroscopic solid, **4**, very soluble in water (giving a neutral pH): mp 182 °C dec; ¹H NMR (CD₃CN) δ 4.42 (Cp, s, 5), 2.42 (CH₃, s, 3), 2.40 (CH₃, d, 6), 3.63 (CH₂, s, 2); ¹H NMR (D₂O, TMPS) 4.55 (Cp), 2.41 (CH₃), 3.00 (CH₂); ¹³C NMR (Me₂SO-*d*₆) δ 99.0, 98.1, and 97.5 (C₆ ring), 78.6 (Cp), 17.0 and 16.7 (CH₃), 77.9 (CH₂), 163.0 (CO₂⁻); ¹³C NMR (D₂O, TMPS) δ 101.1 (m, C₆ ring), 80.7 (Cp), 19.3 (m, CH₃), 80.2 (CH₂); 170.3 (CO₂⁻); IR (Nujol) 1630 cm⁻¹ (CO).

Anal. Calcd for C₁₈H₂₂O₂Fe: C, 66.27; H, 6.79; Fe, 17.11. Found: C, 65.77; H, 7.28; Fe, 16.61.

When 1 mL of aqueous HPF₆ (75%) is added to 652 mg of **4** in 100 mL of water, a yellow solid, **6**, precipitates. After filtration, washing with

water, and drying with ether, the acidic salt is recrystallized from acetone (516 mg, 60%): ¹H NMR (CD₃CN) δ 4.50 (Cp, s, 5 H), 2.40 (CH₃, m, 15 H), 3.03 (CH₂, s, 2 H); ¹³C NMR (CD₃COCD₃) δ 99.6, 98.6, and 98.2 (C₆ ring), 78.2 (Cp), 17.5 (CH₃), 78.7 (CH₂), 160.0 (CO₂H); IR (Nujol) 1712 cm⁻¹ (CO).

Anal. Calcd for C₁₈H₂₃O₂FePF₆: C, 45.78; H, 4.9; Fe, 11.82. Found: C, 45.26; H, 5.6; Fe, 11.34.

8. Reaction of 2 with CS₂. To 564 mg (2 mmol) of **2** in pentane is added 0.5 mL CS₂. A deep yellow precipitates is formed instantaneously, and 20 mL of CH₃CN is added to dissolve the solid **5**. After concentration and filtration, ether is added to reprecipitate **5**, followed by washing three times with ether. This provides 630 mg of yellow powdered **5** (89%), soluble in water (neutral pH), acetone, and acetonitrile. **5** is extremely soluble in Me₂SO with decomposition after a few hours: mp 170 °C dec; ¹H NMR (Me₂SO-*d*₆) δ 4.60 (Cp, s, 5), 2.54 (CH₃, m, 15), 3.37 (CH₂, s, 2); ¹³C NMR (CD₂Cl₂) δ 99.6 and 101.3 (m, C₆ ring), 83 (Cp), 21.0 and 22.6 (CH₃), 78.30 (CH₂), 148.60 (CS₂⁻).

Anal. Calcd for C₁₈H₂₂S₂Fe: C, 60.35; H, 6.18; Fe, 15.58. Found: C, 59.83; H, 6.78; Fe, 15.10.

A 716 mg (2-mmol) sample of the zwitterion **5** is dissolved in a hot mixture of water and acetonitrile; then 1 mL of aqueous HPF₆ (75%) is added. The precipitate of dithio acid **7** is formed immediately. After filtration at 20 °C and washing **7** with ether, it is dissolved in 20 mL of acetone with 1 mL of Me₂SO. This solution is filtered, and **7** is precipitated by addition of 30 mL of ether as a yellow-brown amorphous solid, **7** (585 mg, 58%), insoluble in water, moderately soluble in acetone and acetonitrile, and very soluble in Me₂SO with decomposition after a few hours: ¹H NMR (Me₂SO-*d*₆) δ 4.57 (s, Cp), 2.50 (m, CH₃), 2.37 (s, CH₂); ¹³C NMR δ 98.9, 98.7, and 98.2 (C₆ ring), 78.2 (Cp), 17.4, 16.8, and 16.6 (CH₃), 78.9 (CH₂), 143.0 (CS₂H).

Anal. Calcd for C₁₈H₂₃S₂FePF₆: C, 42.82; H, 4.59; Fe, 11.07. Found: C, 42.83; H, 5.19; Fe, 10.64.

9. Reaction of 2 with CH₃I. To a THF solution of 1.2 g (4.25 mmol) of **2** is added 0.26 mL of CH₃I in 10 mL of THF by cannula. The solution is allowed to stir for 15 min; metathesis with aqueous HPF₆, followed by addition of ether to an acetone solution, gives 1.25 g (66.5%) of **8** as a powder found pure by ¹H NMR. Recrystallization from hot ethanol gives 1.12 g (59.5% yield) of yellow needles: ¹H NMR (CD₃COCD₃) δ 4.73 (Cp, 5 H), 3.14 (q, CH₂, 2 H), 2.52 (Me₃, 15 H), 1.20 (t, CH₃, 3 H, *J* = 7.8 Hz); ¹³C NMR (CD₃CN) δ 79.2 (Cp), 17.7, 17.1, and 16.8 (Me₃), 100.7, 100.1, and 99.8 (C₆ ring), 103.2 (C quaternary), 23.8 (CH₂), 16.3 (CH₃).

Anal. Calcd for C₁₈H₂₅FePF₆: C, 48.90; H, 5.70; Fe, 12.63. Found: C, 49.02; H, 5.64; Fe, 12.64.

10. Reaction of 2 with PhCOCl. To a THF solution of 1.154 g (4.1 mmol) of **2** is added by syringe 0.48 mL of PhCOCl in 5 mL of THF. After the solution was stirred 1 h at room temperature, the workup proceeds as in **9**, yielding 1.217 g (50.4%) of yellow powder found pure by ¹H NMR. Recrystallization from hot ethanol gives 1.088 g of yellow plates (45.3% of **9**): IR (Nujol) 1748 (CO) cm⁻¹; ¹H NMR (CD₃COCD₃) δ 7.56 (C₆H₅, 5 H), 4.67 (Cp, 5 H), 2.65 (CH₂, 2 H), 2.54 (CH₃, 15 H).

Anal. Calcd for C₂₄H₂₇FeOPF₆: C, 54.13; H, 5.07; Fe, 10.52. Found: C, 54.51; H, 5.36; Fe, 10.65.

11. Reaction of 2 with SiMe₃Cl. To a THF solution of 1.92 g (6.8 mmol) of **2** is added 0.85 mL of SiMe₃Cl by syringe at 20 °C. The solution is allowed to stir for 45 min; then the solvent is removed in vacuo. After metathesis with aqueous HPF₆, the yellow solid is dissolved in CH₂Cl₂ and dried over MgSO₄, and reprecipitation by addition of excess ether provides 2.96 g (87%) of an hygroscopic powdered salt, **10**, found pure by ¹H NMR: ¹H NMR (CD₃COCD₃) δ 4.72 (Cp, 5 H), 2.76 (CH₂, 2 H), 2.58 (CH₃, 15 H), 0.02 (SiCH₃, 9 H); ¹³C NMR (CD₃CN) δ 7.91 (Cp), 99.4, 99.0, and 97.1 (C₆ ring), 105.7 (C quaternary), 18.7, 17.8 (Me₃), 22.2 (CH₂), -0.6 (SiMe₃).

Anal. Calcd for C₂₆H₃₁FeSiPF₆: C, 48.00; H, 6.25; Fe, 11.16; Si, 5.61. Found: C, 48.12; H, 6.20; Fe, 11.32; Si, 5.36.

12. Reaction of 2 with PPh₂Cl. To a solution of **2** (564 mg, 2 mmol) in 30 mL of benzene is added 0.4 mL of freshly distilled PPh₂Cl (448 mg, 2 mmol) by syringe. A yellow precipitate immediately forms. After the solution is stirred a few minutes, the solvent is removed in vacuo, and the residue is dissolved in 20 mL of acetone and precipitated by addition of 60 mL of ether. The precipitate is collected, washed with ether, and dissolved in dry acetone, and 324 mg of NH₄PF₆ (2 mmol) in acetone is added. NH₄Cl is filtered off, and ethanol is added to the liquor; cooling down to -20 °C for 1 day gives 823 mg of **11** as a yellow-orange microcrystalline solid (68%) stable in air and soluble in acetone and acetonitrile: ¹H NMR (CD₃CN) δ 4.62 (s, 5, Cp), 3.43 and 2.40 (s, CH₃), 2.08 (s, 2, CH₂), 7.02 (m, 10, PPh₂); ¹³C NMR (CD₃Cl₂) δ 99.4 (d) and 99.3 (C₆ ring), 78.8 (Cp), 17.9 and 18.5 (CH₃), 35.3 and 32.9 (CH₂), 132.8, 131.5, 131.1, 129.5, 129.0 (PPh₂), ³¹P NMR (acetone-*d*₆, H₃PO₄)

δ 102.3 (PPh₂), $J_{13C(CH_2)_3P} = 61.3$ Hz.

Anal. Calcd for C₂₉H₃₃P₂Fe: C, 56.9; H, 5.22; P, 10.12; Fe, 9.12. Found: C, 56.39; H, 5.81; P, 9.50; Fe, 8.67.

13. Reaction of 2 with CpFe(CO)₂Cl. To a solution of CpFe(CO)₂Cl⁶⁷ (424 mg, 2 mmol) in benzene (60 mL) at -20 °C is added dropwise 564 mg (2 mmol) of 2 by cannula. Precipitation of a yellow salt of 12 is immediate. Treatment as in 12 followed by recrystallization from acetone at -20 °C gives 670 mg (56%) of 12 as bright yellow plates. A 20% sample of crude Fp₂ is isolated from the liquor: ¹H NMR (CD₃CN) δ 4.39 (s, 5, Cp), 2.47, 2.43, 2.28 (s, CH₃), 2.70 (s, 2, CH₂), 5.0 (s, 5, Cp_{FP}); ¹³C NMR (CD₂Cl₂) δ 119.0, 98.5, 97.0, and 93.6 (C₆ rings); 78.2 (Cp), 17.8 (m, CH₃), 0.5 (CH₂, checked by off resonance with and without Me₄Si), 86.6 (Cp_{FP}), 229.6 (CO); IR (Nujol) 1941 and 1996 cm⁻¹ (CO).

Anal. Calcd for C₂₄H₂₇O₂Fe₂PF₆: C, 44.73; H, 4.47; Fe, 18.49. Found: C, 44.26; H, 4.97; Fe, 18.13.

Before metathesis, the chloride salt is stable and soluble in water. It can also be metathesized in water by addition of aqueous HPF₆ to the solution of the chloride salt in water.

If the reaction is carried out at 20 °C, large amounts of Fp₂ and 1⁺Cl⁻ are formed (80%).

12 is also characterized by the insertion of CS₂ into the Fe-carbon bond: to 630 mg (1 mmol) of 12 in 40 mL of acetone is added 1 mL of CS₂ (12 mmol), and the mixture is refluxed during 4 h, providing a color change from orange to dark brown. Concentration followed by addition of ether gives 625 mg (92%) of a powder found pure by ¹H NMR, which is recrystallized in acetone: ¹H NMR (acetone-*d*₆) δ 4.62 (Cp), 2.62 and 2.58 (CH₃), 2.98 (CH₂), 5.0 (Cp_{FP}); ¹³C NMR (CD₃CN) δ 119.1, 94.4, 97.7, 99.7 (C₆ ring), 79.1 (Cp), 17.9 (m, CH₃), 18.5 (CH₂), 87.5 (Cp_{FP}), 208.5 (CS₂), 217.1 (CO); IR (Nujol) 2000 and 1948 cm⁻¹ (CO).

Anal. Calcd for C₂₅H₂₇O₂S₂PF₆: C, 44.16; H, 3.97; Fe, 16.42. Found: C, 43.74; H, 4.47; Fe, 16.04.

14. Reaction of 2 with CpMo(CO)₃I.⁶⁷ To a solution of CpMo(CO)₃I (273 mg, 1 mmol) in THF at -20 °C is added dropwise a benzene solution of 2 (564 mg, 2 mmol). The formation of a precipitate is immediate. After stirring a few minutes and removing the solvent in vacuo, the reaction mixture is submitted to TLC on silica gel (eluant acetone-ether (30-70)), which gives 400 mg of 13 (59%), soluble in acetone and acetonitrile. This iodide is soluble in water and can be metathesized to the PF₆⁻ salt by addition of aqueous HPF₆: ¹H NMR (CD₃CN) δ 4.39 (s, Cp), 2.42, 2.37, 2.39 (s, CH₃), 2.65 (s, CH₂), 5.53 (s, CpMo); ¹³C NMR (CD₂Cl₂) δ 98.1, 96.7, 94.8 (C₆ ring), 78.2 (Cp), 17.8 (m, CH₃), -6.1 (CH₂, checked by off resonance with and without Me₄Si), 93.8 (CpMo), 229.6 (CO); IR (Nujol) 2050, 1945, 1930 cm⁻¹ (CO).

Anal. Calcd for C₂₅H₂₇O₃FeMoPF₆: C, 44.68; H, 4.01; Fe, 8.31; Mo, 14.20. Found: C, 45.02; H, 4.11; Fe, 9.0; Mo, 14.25.

The same reaction at 20 °C gives a good amount of Cp₂Mo₂(CO)₆ (30%) and 1⁺, the yield of 13 being close to 30%.

15. Reaction of 2 with Mn(CO)₅Br. A 0.834-g (2.96-mmol) sample of 2 and 0.813 g of Mn(CO)₅Br (2.96 mmol) are mixed together in the solid state, and 30 mL of THF is added by cannula at -78 °C. The solution is allowed to stir 1 h at -50 °C, and workup proceeds as in 13, giving 1.68 g of the PF₆⁻ salt (91% yield). Recrystallization from hot ethanol gives 1.43 g (77% yield) of 14 as yellow plates: IR (Nujol) 2120, 2070, 2030, 2010, 1985 cm⁻¹ (CO). ¹H NMR (CD₃COCD₃) δ 4.70 (Cp, 5 H), 2.56 (Me₅, CH₂, 17 H); ¹³C NMR (CD₃CN) δ 79.4 (Cp), 18.9, 17.8, and 17.7 (Me₅), 99.8, 98.2, and 93.6 (C₆ ring), 118.8 (C quaternary), 5.9 (CH₂), 211.8 (CO).

Anal. Calcd for C₂₂H₂₂O₅FeMnPF₆: C, 42.47; H, 3.56; Fe, 8.97; Mn, 8.83. Found: C, 42.61; H, 3.50; Fe, 9.00; Mn, 8.75.

16. Reaction of 2 with CpFe⁺η⁶-C₆H₅Cl.^{23b} To a THF solution of 1.286 g (3.39 mmol) of CpFe⁺η⁶-C₆H₅Cl is added a THF solution of 0.96 g of 2 (3.39 mmol) at -78 °C. When the solution is warmed up slowly, color change from deep red to yellow appears at -18 °C. After the solution is warmed up, the solvent is removed in vacuo and the solid is washed twice with 10 mL of pentane. Recrystallization from hot ethanol gives 2.0 g (89%) of 16 as a yellow-orange powder: ¹H NMR (CD₃COCD₃) δ 4.66 (Cp, 5 H), 2.27, 2.31, and 2.32 (Me₅ + CH₂, 17 H), 4.39 (Cp, 5 H), 6.44 (m, H para, 1 H), 6.06 (m, H meta, α -Cl, 1 H), 5.30 (m, H meta, γ -Cl, 1 H), 3.36 (m, H ortho, 1 H), 1.79 (m, CH, 1 H); ¹³C NMR (CD₃CN) δ 78.9 (Cp), 100.0, 99.7, 99.1 (C₆ ring), 89.2 (C quaternary), 18.3, 17.7 (Me₅), 47.7 (CH₂), 76.7 (Cp), 38.9 (C-Cl), 35.0 (α -C), 78.1, 77.6 (m-C), 79.9 (p-C), 65.3 (CH).

Anal. Calcd for C₂₈H₃₂FeClPF₆: C, 50.90; H, 4.88; Fe, 16.90; Cl,

5.36. Found: C, 50.72; H, 4.95; Fe, 17.01; Cl, 5.42.

17. Reaction of 2 with CpFe(CO)₃⁺PF₆⁻. To a THF solution of 1.156 g (3.30 mmol) of C₅H₅Fe⁺(CO)₃PF₆⁻⁶⁹ is added at -80 °C a THF solution of 932 mg of 2 (3.30 mmol), and the solution immediately turns orange. After the solution is stirred for 15 min at -80 °C and warmed up, 90 mg (0.21 mmol) of C₅H₅Fe⁺C₆Me₆PF₆⁻ is filtered; the solvent is removed in vacuo from the filtered orange solution and the solid is dried over MgSO₄ in acetone; reprecipitation by the addition of excess ether provides 1.80 g (86% yield) of orange-yellow powder found pure by ¹H NMR. Recrystallization from hot ethanol gives 1.62 g of 17 as yellow microcrystals (77.4%): IR (Nujol) 2050, 1975 cm⁻¹ (CO); ¹H NMR (CD₃COCD₃) δ 4.46 (Cp, 5 H), 2.46 and 2.47 (Me₅, 15 H), 2.53 (d, CH₂, *J* = 3.5 Hz), 1.10 (t, CH, *J* = 3.5 Hz), 3.20 (m, CH₂), 5.76 (m, CH₂); ¹³C NMR (CD₃CN) δ 213.1 (CO), 100.4, 100.1, 98.9 (C₆ ring), 87.7 (C quaternary), 85.7 (CH₂), 79.1 (Cp), 59.2 (CH₂), 56.7 (CH); 43.8 (CH₂), 18.2, 17.8, and 17.7 (CH₃).

Anal. Calcd for C₂₅H₂₇O₃Fe₂PF₆: C, 47.50; H, 4.30; Fe, 17.66. Found: C, 47.45; H, 4.35; Fe, 17.71.

When an analogous reaction is performed at 20 °C with 1.25 mmol of 2 and FpCO, the solution immediately turns purple. After the solution was stirred 1 h, a yellow precipitate is filtered and identified by ¹H NMR as 1⁺PF₆⁻ (340 mg, 64%). The solvent is removed from the liquor in vacuo, which gives 300 mg (70%) of crude Fp₂ identified by ¹H NMR, IR, and TLC.

18. Reaction of 2 with CpFe(CO)₂(C₂H₅)⁺BF₄⁻. To a THF solution of 584 mg (2 mmol) of CpFe⁺(CO)₂C₂H₅BF₄⁻ is added at -80 °C a THF solution of 564 mg (2 mmol) of 2. The solution is allowed to stir 1 h at -80 °C. After the solution is warmed up, a yellow solid is filtered, washed three times with THF, and dissolved in CH₂Cl₂, and reprecipitation with excess ether gives 720 mg (62.7%) of powder. Recrystallization from hot ethanol provides 650 mg (56.6% yield) of 18 as yellow microcrystals: IR (Nujol) ν_{CO} 2050, 1970 cm⁻¹ (CO); ¹H NMR (CD₃COCD₃) δ 5.43 (Cp_{FP}), 4.83 (Cp), 3.60 and 1.13 (CH₂, 6 H), 2.56 (CH₃, 15 H).

Anal. Calcd for C₂₆H₃₁O₂Fe₂BF₄: C, 54.35; H, 5.40; Fe, 9.75. Found: C, 54.50; H, 5.53; Fe, 10.01.

19. Hydrogenation of 27. Hydrogenation of 27 (644 mg, 1.82 mmol) in a 30 mL of toluene solution with Pd on charcoal at 20 °C during 15 h gives 522 mg (81% yield) of C₅Me₅Fe¹(η^5 -C₅Me₅H) as orange crystals after recrystallization from pentane: IR (pentane) $\nu_{CH(exo)}$ 2765 cm⁻¹; ¹H NMR (C₆D₆) δ 1.60 (C₅Me₅, 15 H), 2.07 (p-CH₃, 3 H), 1.43 (m-CH₃, 6 H), 1.02 (o-CH₃, 6 H), 0.95 (d, CH₃, 3 H, *J* = 4 Hz), 0.90 (q, H, 1 H, *J* = 4 Hz); ¹³C NMR (C₆D₆) δ 82.2 (C₅Me₅), 15.9, 15.1 and 14.9 (Me₅), 88.4, 86.6 (C₆ ring, p and m), 32.9 (C₆ ring, o), 38.6 (CH-CH₃), 17.6 (CHCH₃), 10.0 (C₅Me₅).

Anal. Calcd: C, 74.57; H, 9.60; Fe, 15.82. Found: C, 74.60; H, 9.65; Fe, 15.75. Mass spectrum: M⁺ calcd 354.019; found 354.023.

20. Reaction of 2 with Fe(CO)₅ and Fe₂(CO)₉. A benzene solution (70 mL) of 2 (564 mg, 2 mmol) containing 400 mg of Fe(CO)₅ (2 mmol) or 370 g of Fe₂(CO)₉ (1 mmol) is heated to 45 °C for 2 h. The color turns from red to brown-purple and a precipitate appears. The solvent is removed in vacuo, and the solid is washed with ether, dissolved in 20 mL of hot acetone, and reprecipitated by addition of 40 mL ether to the filtered liquor. Recrystallization from acetone at -20 °C provides 580 mg of glassy purple crystals of 19 (64%), soluble in CH₂Cl₂, acetone and acetonitrile and insoluble in ether and benzene. It is unstable and pyrophoric in air: ¹H NMR (CD₃CN) δ 4.58 (s, 5, Cp), 2.56 (m, 17, CH₃ and CH₂); ¹H NMR (CD₂Cl₂) δ 4.70 (s, 5, Cp), 2.70 (m, 15, CH₃), 2.50 (s, 2, CH₂); ¹³C NMR (CD₃CN) δ 120, 99.7 (m, C₆ ring), 79.2 (Cp), 19.9 (CH₃), 210.2 (CO); IR (CH₂Cl₂) 2030, 1990, 1925, 1900 cm⁻¹ (CO).

21. Reaction of 2 with Cr(CO)₆. A benzene solution containing 3.27 g (11.6 mmol) of 2 and 2.55 g (11.6 mmol) of Cr(CO)₆ is heated at 80 °C for 1 h. After the solution is cooled down, an orange precipitate is filtered and washed 5 times with 100 mL of dry ether. Recrystallization from hot acetonitrile provides 3.65 g (66%) of 20 as an orange powder: IR (Nujol) 2040, 1955, 1890, 1870 cm⁻¹ (CO); ¹H NMR (CD₃COCD₃) δ 4.34 (Cp, 5 H), 2.62 (CH₂, 2 H), 2.46, 2.42 (CH₃, 15 H).

Anal. Calcd for C₂₂H₂₂O₅FeCr: C, 55.69; H, 4.64; Fe, 11.81; Cr, 10.97. Found: C, 55.74; H, 4.72; Fe, 11.70; Cr, 10.88.

22. Reaction of 2 with Mo(CO)₆. A benzene solution of 2 (564 mg, 2 mmol) and 528 mg (2 mmol) of Mo(CO)₆ is refluxed 2 h, providing a color change from dark red to light red and a precipitate upon cooling. The solid is collected, washed several times with ether, and recrystallized in 50 mL of hot acetone containing 5 mL of CH₂Cl₂. This gives 881 mg of red crystals of 21 (75%): mp 180 °C dec; ¹H NMR (CD₂Cl₂) δ 3.99

(67) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1955**, *1*, 165-174.

(68) CpFe(CO)₃⁺PF₆⁻ is best synthesized by reaction between ferrocene and CO.³⁷

(69) Discussions with J. Torrance concerning the chemistry and physics of TCNQ⁻ salts are gratefully acknowledged. See also: Torrance, J. *Acc. Chem. Res.* **1979**, *12*, 79-86.

(s, 5, Cp), 2.36 and 2.30 (s, CH₃), 2.09 (CH₂) [by a Fourier transform mode (solubility 20 mg mL⁻¹); IR (CH₂Cl₂) 2080, 1922, 1970, and 1880 cm⁻¹ (CO)].

Anal. Calcd for C₂₂H₂₂O₅FeMo: C, 51.00; H, 4.24; Fe, 10.27; Mo, 18.55. Found: C, 51.91; H, 4.24; Fe, 10.94; Mo, 18.75.

23. Reaction of 2 with TCNQ.⁶⁹ To a THF solution of 360 mg (1.28 mmol) of **2** is added by cannula a THF solution of 261 mg of TCNQ (1.28 mmol) at 20 °C. The solution is allowed to stir 15 min. After filtration, the THF is removed in vacuo and 590 mg (95%) of a dark green powder is collected and dried in vacuo. The reduction of this solid in 1% Na/Hg in DME provides 309 mg (90% yield) of CpFeC₆Me₆ characterized by its mass spectrum. The dark green salt is also identified by its Mössbauer (I⁺) and optical (TCNQ⁻)⁴² spectra.

24. CpFe⁺C₆Me₅CH₂I PF₆⁻ from 2 and I₂. To a THF solution of 312.4 g of I₂ (1.23 mmol) is added a THF solution of 348 mg of **2** (1.23 mmol) at 20 °C by cannula. The reaction is instantaneous, and after filtration and washing twice with 20 mL of THF, the solid is dissolved in water, metathetized with aqueous HPF₆, and dried over MgSO₄ in acetone, and reprecipitation with excess ether provides 344 mg (62% yield) of **23** as a powdered salt. Recrystallization from hot ethanol gives 327 mg (59% yield) of yellow needles: ¹H NMR (CD₃COCD₃) δ 4.91 (Cp, 5 H), 2.68, 2.61, and 2.58 (Me₅, 15 H), 4.98 (CH₂, 2 H); ¹³C NMR (CD₃COCD₃) δ 79.6 (Cp), 18.0, 17.8, and 16.5 (Me₅), 100.8, 99.8, and 97.8 (C₆ ring), 101.2 (C quaternary), 2.6 (CH₂).

Anal. Calcd for C₁₇H₂₂FeIPF₆: C, 36.85; H, 4.00; Fe, 10.08; I, 22.90. Found: C, 36.95; H, 4.10; Fe, 10.35; I, 21.66.

25. CpFe⁺C₆Me₅CH₂Br PF₆⁻ from 2 and Br₂. To a THF solution of 325 mg of **2** (1.15 mmol) is added, at 20 °C by syringe, 1.25 mL of a solution of 0.5 mL of Br₂ in 9.5 mL of THF. The reaction is immediate: the yellow solid formed is filtered, washed twice with 20 mL of THF, dissolved in water, and metathetized with aqueous HPF₆; then the precipitate is dried over MgSO₄ in acetone and reprecipitation with excess ether gives 238 mg (47% yield) of powdered salt. Recrystallization from hot ethanol provides 220 mg (43% yield) of yellow needles (**25**): ¹H NMR (CD₃COCD₃) δ 4.92 (Cp, 5 H), 2.66, 2.62 (Me₅, 15 H), 5.15 (CH₂, 2 H); ¹³C NMR (CD₃CN) δ 79.6 (Cp), 18.0, 16.55 (Me₅), 101.0, 100.8, and 100.7 (C₆ ring) 101.8 (C quaternary), 30.3 (CH₂).

Anal. Calcd for C₁₇H₂₂FeBrPF₆: C, 40.26; H, 4.37; Fe, 11.01; Br, 15.76. Found: C, 40.37; H, 4.40; Fe, 11.40; Br, 15.48.

26. CpFe⁺C₆Me₅CH₂Cl PF₆⁻ from 2 and Cl₂. To a THF solution of 253 mg of **2** (0.9 mmol), at 20 °C under low pressure, is added by syringe, 20.15 mL of Cl₂ (0.9 mmol). The reaction is also instantaneous. The workup is exactly the same as in 11, and 235 mg (51% yield) of powdered salt is isolated. Recrystallization from hot ethanol gives 224 mg (48.5% yield) of yellow needles (**24**): ¹H NMR (CD₃COCD₃) δ 5.05 (Cp, 5 H), 2.72, 2.66 (Me₅, 15 H), 5.42 (CH₂, 2 H); ¹³C NMR (CD₃CN) δ 79.1 (Cp), 18.7, 17.9, and 16.5 (Me₅), 100.8, 100.7 (C₆ ring), 101.8 (C quaternary), 42.8 (CH₂).

Anal. Calcd for C₁₇H₂₂FeClPF₆: C, 44.13; H, 4.79; Fe, 12.07; Cl, 7.66. Found: C, 44.40; H, 4.82; Fe, 12.25; Cl, 7.52.

27. (CpFe⁺C₆Me₅CH₂)₂2PF₆⁻ from 2 + I₂ (or 2 + 23). To a THF solution of 522 mg (1.85 mmol) of **2** is added by cannula at 20 °C a THF solution of 235 mg (0.925 mmol) of I₂. The reaction is instantaneous, and the workup proceeds as above, yielding 750 mg (95% yield) of a powdered salt found pure by ¹H NMR. Recrystallization from hot ethanol gives 675 mg (85% yield). A similar reaction proceeds if **2** is reacted with **23** instead of I₂: ¹H NMR (CD₃COCD₃) δ 4.82 (Cp), 2.68, 2.62 (CH₃), 3.08 (CH₂); ¹³C NMR (Me₂SO-*d*₆) δ 78.3 (Cp), 17.2, 17.0, and 16.8 (CH₃), 99.1, 98.2, and 97.6 (C₆ ring), 99.7 (C quaternary), 29.6 (CH₂).

Anal. Calcd for C₃₄H₄₄Fe₂(PF₆)₂: C, 47.80; H, 5.19; Fe, 13.07. Found: C, 47.74; H, 5.25; Fe, 12.90.

28. Reaction of (η⁵-C₅Me₅)Fe^I(η⁶-C₆Me₆) with O₂. To a pentane solution of 1.136 g (3.22 mmol) of C₅Me₅FeC₆Me₆ is added at -80 °C, by syringe, 32 mL (1.61 mmol) of dioxygen. The reaction is instantaneous with precipitation of a yellow solid. After being warmed up, the solution is filtered and gives 475 mg (42% yield) of dark red crystals of **27** after recrystallization from pentane. The yellow solid is dissolved in water, metathetized with aqueous HPF₆, and dried over MgSO₄ in acetone, and reprecipitation with excess ether provides 840 mg of C₅Me₅Fe⁺C₆Me₆PF₆⁻ (**26**⁺PF₆⁻) characterized by its ¹H NMR spectrum: IR (toluene) 1570 cm⁻¹ (=CH₂); ¹H NMR (C₆D₆) δ 3.32 (CH₂, 2 H), 1.92 (p-CH₃, 3 H), 1.62 (m-CH₃, 6 H), 1.42 (o-CH₃, 6 H), 1.36 (C₅Me₅, 15 H); ¹³C NMR (C₆D₆) δ 80.9 (C₅Me₅), 15.1, 15.4, and 16.6 (C₆(C-H₃)₃), 70.3, 70.2, and 61.9 (C₆(CH₃)₃), 140.45 (uncoordinated C₆ ring C), 89.67 (CH₂).

29. Reaction of (η⁵-Cp)Fe(η⁶-C₆Me₅CH₂-CH₂C₆Me₅)Fe(η⁵-Cp) with O₂. A 3.78-g (6.70-mmol) of **22** sample obtained by Na/Hg reduction of **22**²⁺ (PF₆⁻)₂ in DME is transferred into a Schlenk tube in a glovebag under Argon, and 100 mL of dry pentane is transferred through a steel cannula. Then 150 mL (6.70 mmol) of dioxygen is added by syringe, and the forest green solution immediately turns red. A slight precipitate is formed. After filtration and crystallization at -80 °C, 3.39 g (6.03 mmol) of a powdered mixture of **28** is obtained (90%): ¹³C NMR (C₆D₆) δ 76.5, 76.3, and 75.7 (Cp), 19.2, 17.6, 16.8, 16.4, and 14.1 (Me₄), 90.1, 89.9, 89.6, 89.5, 89.3, 89.0, 85.7, 83.5, 68.2, and 57.2 (C₆), 145.0, 136.2, and 131.7 (uncoordinated C₆ ring C), 77.3, 77.2, and 76.9 (=C-H₂), 36.5, 34.4, and 33.7 (CH₂). The mixture of ortho-, meta-, and para-substituted complexes (**28**) is represented by peaks of similar magnitude for each set of carbons.

30. Reaction of (η⁵-Cp)Fe(η⁶-C₆Et₆) with O₂. To a pentane solution of 828 mg (2.25 mmol) of CpFeC₆(C₂H₅)₆ (**29**) is added at -20 °C by syringe 12.6 mL of dioxygen (0.56 mmol). The green solution turns red after 5 min with precipitation of a yellow solid. The solution is filtered and the solid washed twice with 5 mL of pentane. A 780-mg sample of a red oil (**30**, 94.5% yield) is isolated by removing the solvent in vacuo. The workup for the solid proceeds as in **28** and gives 58 mg of CpFe⁺C₆(C₂H₅)PF₆⁻, characterized by its ¹H NMR spectrum.

The reaction was followed in the cavity of an EPR spectrometer using various solvents (DME, pentane, Me₂SO). The solutions of **29** are prepared in a glovebag, and O₂ is introduced by syringe in portions into the EPR tube above the frozen solution and then allowed to diffuse in the gel. The spectrum characteristic of Fe(I) was progressively replaced by that of O₂⁻.^{14b} The spectrum of O₂⁻ was found after completion of the reaction (color change from green to red) as seen on Figure 3: IR (pentane) 1640 cm⁻¹ (=CHCH₃); ¹H NMR (C₆H₆, Bruker WM 250 spectrometer, 250 MHz, cf. Figure 5) δ 3.92 (Cp, 5 H), 1.05 and 1.12 (t, o-CH₃), 1.53 and 1.55 (t, m-CH₃), 1.30 (t, p-CH₃), 2.65 (q, p-CH₂), 1.81-2.46 (o- and m-CH₂) [24 signals indicating that the CH₂'s are not equivalent even within the methylene units], 1.39 (d, CHCH₃), 4.20 (q, CHCH₃, *J* = 7 Hz); ¹³C NMR (C₆D₆) δ 74.9 (Cp), 16.3, 15.7, 15.4, 13.6, and 13.2 (CH₃Et), 25.3, 23.7, 23.2, and 22.7 (CH₂Et), 101.7, 94.0, 91.4, 51.4, and 50.9 (C₆Et₅), 138.5 (uncoordinated C₆ ring C), 68 (CHCH₃), 17.7 (CHCH₃).

Acknowledgment. We are grateful to Professor F. Varret and J. P. Mariot, Le Mans, for helpful assistance and discussions of the Mössbauer data and to Dr. P. Guénot and S. Sinbandhit (Centre de Mesures Physiques pour la Chimie, Rennes) for their diligent help in recording the mass and ¹³C NMR spectra. Useful discussions with Professor M. J. McGlinchey (Rennes, sabbatical leave) and financial support of the CNRS (ATP No. 3801) are also gratefully acknowledged.