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Formation of Carbon–Carbon Bond by Reaction of CO_2: Functional Organometallic Electron Reservoirs[1]

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Reactions of ferrocene with Al_2Cl_6 and arenes (benzene, mesitylene, hexamethylbenzene, naphthalene) neat or in heptane under CO_2 for 1 h at 50–60 °C, followed by 8 h at 80–100 °C, provide the carboxylated salts $[(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-arene})]X^-$. $[(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)]$ (**6**, a redox catalyst) is deprotonated by NaOH in ethanol, which affords the water-soluble zwitterion $[(\eta^5\text{-}C_5H_4CO_2^-)Fe^+(\eta^6\text{-}C_6Me_6)]$ (**7**). The redox electrochemistry of **6** and **7** is compared. Compounds **6** and **7** are reduced by Na/Hg in THF at 20 °C giving, respectively, the blue thermally unstable air-sensitive acid $(\eta^5\text{-}C_5H_4CO_2H)Fe^I(\eta^6\text{-}C_6Me_6)$ (**8**) and the purple, thermally stable, very air-sensitive radical anion $(\eta^5\text{-}C_5H_4CO_2^-)Fe^I(\eta^6\text{-}C_6Me_6)$ (**9**). The latter is the active form of the redox catalyst in basic media. Compounds **8** and **9** are characterized as Jahn–Teller active d^7 Fe(I) complexes by EPR (**8**, **9**) and Mössbauer (**9**) spectroscopies. The Na/Hg reduction of **6** finally gives **9** via **8** which rapidly thermally decomposes to **7**. Compounds **8** and **9** can also be rapidly generated at −50 °C from **6** and **7**, respectively, using $LiAlH_4$ as a single electron-transfer reagent in THF, this pathway being shown by EPR spectroscopy.

The carboxylation of aromatics has been of interest since the 125-year old Kolbe–Schmitt reaction of CO_2 with sodium phenoxide[2] found an outstanding application with the synthesis of aspirin.[3] Ferrocene, as a superaromatic, was a candidate for carboxylation, providing a synergistic activation of CO_2 could proceed. Indeed, it was found that under Friedel–Crafts conditions, namely, in the presence of $AlCl_3$, CO_2 reacts as an electrophile to carboxylate one ferrocene ring at 50 °C[4] (eq 1). Aluminum chloride plays multiple roles in ferrocene chemistry:[5,6] it can complex a Cp ring or the iron (eq 2 and 3). The first mode of complexation induces ring cleavage and replacement by an arene or CO's.[7] The second mode inhibits the ring cleavage, and the Fe–Al bond may be hydrolyzed for ferrocene recovery.[5b] In chlorinated solvents, Friedel–Crafts alkylation of ferrocene is induced. In summary, the two most useful roles of $AlCl_3$ are (i) inducing electrophilic attack on a ring and (ii) the replacement of one ring by an arene or three CO's. The combination of these two roles in a one-pot reaction was of special interest to us in the case of CO_2 because it could open the route to carboxylated $CpFe^+$ arene salts. When this salt was used as a redox catalyst, we need both the oxidized (Fe^{II}) and reduced (Fe^I) forms to be stable and soluble in water.[8-11] The carboxylate function is a suitable choice for this purpose. In more general terms, the functionalization of this electron-reservoir system can be very useful for chemical modification of polymers or electrodes to achieve specific electron-transfer properties.

$$Cp_2Fe \xrightarrow[CO_2]{AlCl_3} \underset{\mathbf{1}}{(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CO_2H)} \qquad (1)$$

$$Cp_2Fe\text{–}AlCl_3 \xrightarrow[H_2O]{AlCl_3} Cp_2Fe \xrightarrow{AlCl_3} AlCl_3CpFeCp \qquad (2)$$

$$AlCl_3CpFeCp \xrightarrow[\Delta]{L_3} CpFe^+L_3 \qquad (3)$$

$$L_3 = \text{arene or 3CO}$$

Several hundred $CpFe^+(\eta^6\text{-arene})$ salts have been synthesized[6] since Coffield's[12] and Nesmeyanov's[13] discoveries of the first syntheses (eq 4 and 5), either by using the convenient direct ligand exchange reaction from ferrocene or by suitable modification subsequent to complexation of a given arene. However, upon one-electron reduction at 20 °C (Na/Hg in THF or DME or cathodic reduction) decomposition of the Fe^I complexes always occurs unless

$$CpFe(CO)_2Cl \xrightarrow[\text{arene}]{AlCl_3} CpFe^+(\eta^6\text{-arene})AlCl_4^- \qquad (4)$$

$$\text{arene} = \text{benzene, mesitylene}$$

$$Cp_2Fe \xrightarrow{AlCl_3} CpFe^+(\eta^6\text{-arene})AlCl_4^- \qquad (5)$$

$$\text{arene} = C_6H_6,\ C_6H_5Me,\ C_6H_5Cl,\ \text{naphthalene, etc.}$$

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the arene is sterically crowded.[6,10,11] If a sterically crowded arene bears a functional group in an exocyclic position, such as in $C_6Me_5NH_2$,[14] the $CpFe^I(\eta^6\text{-arene})$ complex also decomposes very rapidly at 20 °C. As a general rule, the presence of an heteroatom (halogen, N, O) or of a functional group renders the $CpFe^I$(arene) complex very unstable (this is particularly true in THF, the solvent of synthesis). Thus it was appropriate to examine the possibility of functionalization of the Cp ring in the $CpFe^+$(arene) cations. Doing so, we could use the arene C_6Me_6 as the ligand because we know that Fe(I) complexes of C_6Me_6 are stable at 20 °C. We have also examined other arene complexes in order to generalize the synthetic method.

It was of further interest to investigate the one-electron reduction of $CpFe^+(\eta^6\text{-arene})$ complexes which have been functionalized on the Cp ring to know how their Fe(I) oxidation state behaves under ambient conditions. This paper includes such studies and ensuing redox chemistry. Two preliminary communications have appeared, one concerning the carboxylation[9] and the other the functional electron reservoir.[15]

Results and Discussion

I. Reactions of CO_2 with Ferrocene–$AlCl_3$–Arene. In benzene at 50 °C, carboxylation of ferrocene occurs in the presence of $AlCl_3$ in 50% yield. This temperature is too low to induce the replacement of a cyclopentadienyl ligand of ferrocene by an arene. The carboxylation and the ligand exchange are not in competition at 50 °C. It is feasible to carboxylate ferrocene to ferrocenylcarboxylic acid **1** without a side reaction. The same reaction medium, at 80 °C, results in Cp replacement. Thus, it is possible to perform both reactions sequentially in one pot by letting the reaction mixture stand first at 50 °C and then at 80 °C (eq 6). At 80 °C, the reaction mixture contains both ferrocene and **1**. Ferrocene gives $CpFe^+C_6H_6$ (**3**), whereas **1** loses the unsubstituted cyclopentadienyl ring rather than the substituted one. We know that an electron-withdrawing group diminishes the electron density and the $Cp–AlCl_3$ bond strength, thus inhibiting the cleavage of the substituted ring.[13] This is even more marked in the case of an exocyclic carbonyl (eq 7). Under these conditions, **2** is the major product of the ligand exchange reaction between **1** and benzene in the presence of $AlCl_3$ at 80 °C. Compound **3** is formed in two ways. First, it is made from non-carboxylated ferrocene; second it also is a minor product of the ligand exchange reaction of **1**. Before hydrolysis, the salts formed are tetrachloroaluminates (**a**). After hydrolysis with ice water at 0 °C, water-soluble chlorides (**b**) are obtained, and metathesis with $M'BF_4$(M′ = H, Na) or, better, MPF_6(M = H, NH_4, Na) precipitates the BF_4 (**c**) or PF_6 (**d**) salts. However, in basic medium, the organometallic carboxylates $(\eta^5\text{-}C_5H_4CO_2^-)Fe^+(\eta^6\text{-}C_6H_6)BF_4^-$ (or PF_6^-) are water-soluble, whereas **3c** (or **3d**) is not. Filtration allows the separation of **3c** or **3d**, and the salts **2c** or **2d** can then be precipitated in acidic aqueous medium.

$$\mathrm{Cp_2Fe + AlCl_3 + CO_2 + arene} \xrightarrow{50\ ^\circ\mathrm{C}} \underset{\mathbf{1}}{(\eta^5\text{-}C_5H_4CO_2H)FeCp} \xrightarrow{80\ ^\circ\mathrm{C}} (\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-arene}) \quad (6)$$

2, arene = C_6H_6
4, arene = naphthalene
5, arene = mesitylene

$$(\eta^5\text{-}C_5H_4CO_2H)FeCp \xrightarrow[\mathrm{AlCl_3}]{\text{benzene}} (\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6H_6) \gg CpFe^+(\eta^6\text{-}C_6H_6) \quad (7)$$

The reaction conditions are optimum when the arene is a liquid at 50–80 °C, e.g., with benzene and mesitylene. Thus both **2d** and $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6H_3Me_3)PF_6^-$ (**5d**) are obtained in 25% and 34% yields, respectively, which is reasonable, given the complexity of the reaction described above and the 50% maximum yield of ferrocene carboxylation. Compound **2c** was obtained before by $KMnO_4$ oxidation of $(\eta^5\text{-}C_5H_4Et)Fe^+(\eta^6\text{-}C_6H_6)$ (eq 8).[6b]

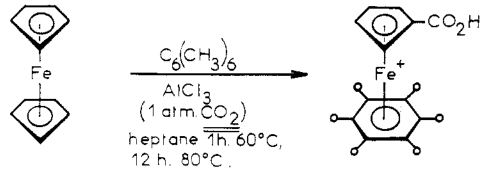
$$Cp_2Fe \rightarrow (\eta^5\text{-}C_5H_4Et)_2Fe \xrightarrow[\mathrm{AlCl_3,\ Al}]{C_6H_6} \underset{32\%}{(\eta^5\text{-}C_5H_4Et)Fe^+(\eta^6\text{-}C_6H_6)} \xrightarrow{\mathrm{KMnO_4}} \underset{\mathbf{2}}{(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6H_6)} \quad (8)$$

The latter is accessible from $(\eta^5\text{-}C_5H_4Et)_2Fe$[13] which is obtained in two steps from ferrocene.[6a] The overall yield from ferrocene in the latter route is limited by the 32% yield of the ligand exchange between $(\eta^5\text{-}C_5H_4Et)_2Fe$ and benzene.[13]

Another route which we had previously used[16] consists of exchanging the free ring of acetylferrocene for benzene and then oxidizing $(\eta^5\text{-}C_5H_4COCH_3)Fe^+(C_6H_6)$ by $KMnO_4$ (eq 9). These two routes are in any case applicable only to the synthesis of the benzene complex and give lower yields. Making and isolating **1** would be an alternative, necessarily longer procedure and would not take advantage of a one-pot synthesis.

$$Cp_2Fe \rightarrow CpFe(\eta^5\text{-}C_5H_4COCH_3) \xrightarrow{C_6H_6} (\eta^5\text{-}C_5H_4COCH_3)Fe^+(\eta^6\text{-}C_6H_6) \xrightarrow{\mathrm{KMnO_4}} (\eta^5\text{-}C_5H_4CO_2H)Fe^+(C_6H_6) \quad (9)$$

Since our chief aim was the synthesis of the C_6Me_6 complex **6**, we had to use a nonaromatic hydrocarbon solvent for the reaction (eq 9a). Under these conditions, the yields are lower. $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)X^-$ (X^- = BF_4^- (**6c**) or PF_6^- (**6d**)) is obtained in 15% yield after recrystallization from acetone. $(\eta^5\text{-}C_5H_4CO_2H)Fe^+$(naphthalene)$PF_6^-$ (**4d**) is obtained similarly in 12% yield. In order to ensure the success of these reactions, it is essential that the first step be carried out with an efficient bubbling of CO_2 at 50 °C. Alternatively, the reaction may be carried out in a closed steel reactor under pressure of CO_2. The yields decreased in this way, but less care is necessary concerning the contact of CO_2 with the other reactants, and thus the system may be considered convenient and it gives reproducible yields.



(9a)

II. Redox and Acid–Base Chemistry of $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)$ (6). In basic aqueous medium (NaOH or 0.1 N LiOH), the acid **6** is in the carboxylate form **7**, a zwitterion. The cathodic reduction of **7** in this

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medium on Hg at −1.8 V vs. SCE gives the Fe^I radical anion which was not observable given its high reactivity. It reduces water and nitrates very rapidly. It is known that **6** is a redox catalyst for the cathodic reductions $H_2O \rightarrow H_2$ and $NO_3^- \rightarrow NH_3$ on Hg.[8] The solubility of both the oxidized and reduced forms of this redox catalyst allowed the determination of the rate of reduction of NO_3^-.[8]

Since these electrochemical conditions are not suitable for the isolation and characterization of the reactive reduced Fe^I form, we searched classical synthetic techniques to investigate the chemistry of $(\eta^5\text{-}C_5H_4CO_2H)Fe^I(\eta^6\text{-}C_6Me_6)$ (**8**) and that of $(\eta^5\text{-}C_5H_4CO_2^-)Fe^I(\eta^6\text{-}C_6Me_6)$ (**9**). First, we designed suitable solvent conditions to isolate the zwitterionic carboxylate **7** free of other salts such as $Na^+PF_6^-$. An ethanolic solution of **6** was treated with 1 equiv of NaOH (eq 10). If a large excess of acetone is added to this solution, **7** precipitates, whereas $Na^+PF_6^-$ is still soluble. Compound **7** isolated in this way is pure. The solubility of complex **7** is, contrary to that of **6**, high in water and ethanol but low in acetone and acetonitrile. The carbonyl stretch in the infrared spectra is shifted from 1730 cm^{-1} for **6** to 1650 cm^{-1} for **7**. The hexamethylbenzene signal in the ^1H NMR spectra remains at the same values (δ 2.39 (CD_3CN)), but the cyclopentadienyl protons (two triplets) are shifted further upfield for **7** (δ 4.39 and 4.66) than for **6** (δ 4.72 and 4.91). The Mössbauer parameters are also significantly lower for **7** (QS = 1.86 mm s^{-1}; IS = 0.54 mm s^{-1}) than for **6** (QS = 1.96 mm s^{-1}; IS = 0.45 mm s^{-1}), the latter being similar to the value for $CpFe^+(C_6Me_6)PF_6^-$ (**10**). This indicates a slightly lower symmetry in **7** as compared to **6** and **10**, probably due to a slight change of the shape of the conjugated sandwich **7**.[17] The cathodic reduction of **6** and **7** on Hg in DMF (0.1 M $n\text{-}Bu_4N^+ClO_4^-$, 0.1 V/s) shows a reversible one-electron reduction to Fe^I at −1.27 and −1.67 V vs. SCE, respectively. The cyclic voltammetry indicates differences between the cathodic and anodic peaks of 70 and 110 mV, respectively, with i_a/i_c close to 1 in both cases (quasi-reversibility). Thus the negative charge shifts the reduction by 0.4 V. The irreversible reduction of the acidic group in **6** occurs at −1.39 V vs. SCE. These data are consistent with previous electrochemical studies.[22] They tell us that the Na/Hg reduction of both **6** and **7** should give the carboxylate radical anion **9** of the Fe^I form (eq 11–13).

$$\underset{\textbf{6d}}{(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)PF_6^-} \xrightarrow[\text{ethanol}]{\text{NaOH}} \underset{\textbf{7}}{(\eta^5\text{-}C_5H_4CO_2^-)Fe^+(\eta^6\text{-}C_6Me_6)} + Na^+PF_6^- + H_2O \quad (10)$$

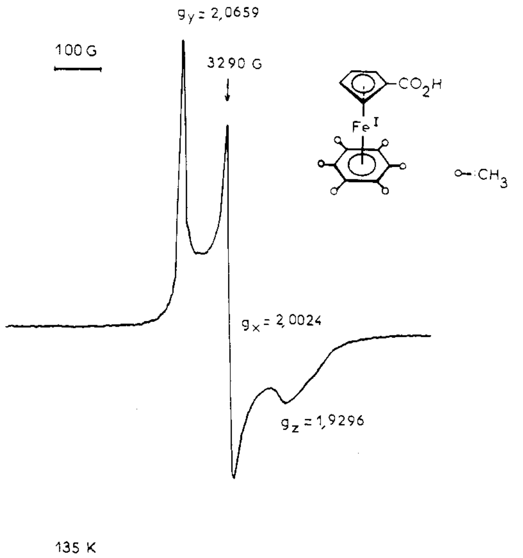

Figure 1. EPR spectrum of **8** at 135 K, generated from **6d** and $LiAlH_4$ in THF, at 223 K.

$$\underset{\textbf{6d}}{(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)PF_6^-} \xrightarrow{-1.27\text{ V}} \underset{\textbf{8}}{(\eta^5\text{-}C_5H_4CO_2H)Fe(\eta^6\text{-}C_6Me_6)} \quad (11)$$

$$\underset{\textbf{6d}}{(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)PF_6^-} \xrightarrow{-1.39\text{ V}} \underset{\textbf{9}}{(\eta^5\text{-}C_5H_4CO_2^-)Fe^+(\eta^6\text{-}C_6Me_6)} + {}^1/{}_2H_2 \quad (12)$$

$$\underset{\textbf{7}}{(\eta^5\text{-}C_5H_4CO_2^-)Fe^+(\eta^6\text{-}C_6Me_6)} \xrightarrow{-1.67\text{ V}} \underset{\textbf{9}}{(\eta^5\text{-}C_5H_4CO_2^-)Fe(\eta^6\text{-}C_6Me_6)} \quad (13)$$

III. Synthesis and Electronic Structure of $(\eta^5\text{-}C_5H_4CO_2H)Fe^I(\eta^6\text{-}C_6Me_6)$ (8) and $(\eta^5\text{-}C_5H_4CO_2^-)Fe^I(\eta^6\text{-}C_6Me_6)$ (9). The Na/Hg reduction of **6d** was carried out at room temperature in THF. It was assumed that hexamethylbenzene Fe(I) complexes are stable under these conditions. The reaction proceeds rapidly (a few minutes) to give a blue species. After 15 min of reduction, the blue color disappears and a purple compound starts to appear. The reaction is complete after 2 h, the purple compound being the final reduction product.

The Na/Hg reduction of **7** is much slower than that of **6d**, but the purple complex is directly obtained in 2 h. The relative rates of Na/Hg reduction are not surprising given the 0.4-V difference in the reduction potentials and the fact that **7** is much less soluble than **6d** in THF (solubilities of both Fe^{II} complexes are very low, but they determine the rates of electron transfer).

Pentane was added to the transcient blue species produced by reduction of **6d**, in order to stop the reduction; however, removal of the solvent after filtration left a yellow solid showing the infrared stretch at 1650 cm^{-1} and thus the formation of **7**. On the other hand, one-electron reduction of **6d** at −50 °C in THF using $LiAlH_4$ (instead of Na/Hg) also produces the blue species, which was characterized as a 19-electron d^7 Fe(I) complex by EPR (three *g* values close to 2) in frozen THF solution at 135 K (Figure 1).

We know that $LiAlH_4$ reduces $CpFe^+(\eta^6\text{-arene})$ complexes to $CpFe(\eta^5\text{-cyclohexadienyl})$ complexes[33] but this

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(17) For comprehensive analyses of the Mössbauer spectroscopy of the iron sandwich compounds in various oxidation states and for extensive characterization of Jahn–Teller active Fe^I species using this technique see: ref 18–21 and (a) Mariot, J.-P.; Astruc, D.; Batail, P.; Varret, F. *J. Phys. C* **1980**, *1*, 319. (b) Mariot, J. P.; Michaud, P.; Lauer, S.; Astruc, D.; Trautwein, A. X.; Varret, F. *J. Phys.* (*Les Ulis, Fr.*) **1983**, *44*, 1377. (c) Mariot, J.-P.; Michaud, P.; Lauer, S.; Astruc, D.; Trautwein, A. X.; Varret, F. *Hyperfine Interact.* **1984**, *14*(4), 336; **1986**, *28*, 761.

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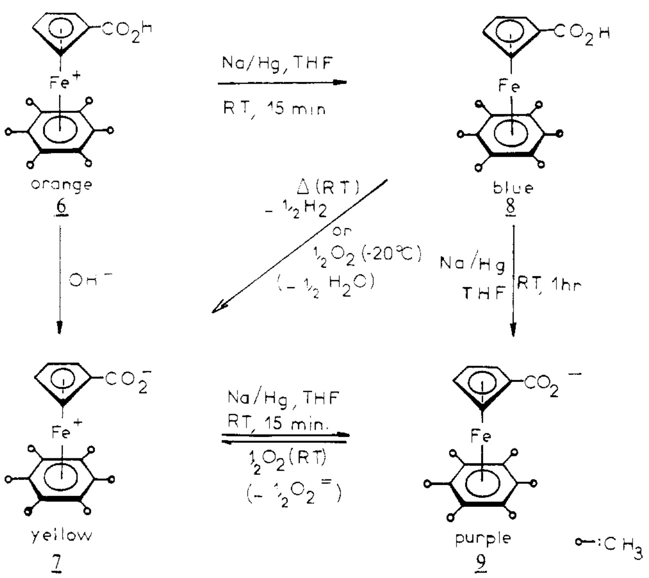
Scheme I



hydride transfer has been shown recently to proceed first by electron transfer at the low contact temperature between −90 and −50 °C;[23b] further H atom transfer proceeds at higher temperatures (typically −20 to 0 °C). This mechanism appears to be general, and it is thus logical to expect the one-electron reduction of 6 and 7 using $LiAlH_4$ at −50 °C (eq 14). The thermal decomposition of the blue

$$\mathrm{RCpFe^+(\eta^6\text{-}C_6Me_6)} \xrightarrow[\text{THF, -50 °C}]{\mathrm{LiAlH_4}} \mathrm{RCpFe(\eta^6\text{-}C_6Me_6)} \quad (14)$$

$$\mathrm{R = H, CO_2^-}$$

19-electron Fe^I complex 8 proceeds by intramolecular electron transfer from the iron(I) center to the acid chain (eq 15). Although the Fe^{II}/Fe^I redox system has a less

$$\underset{8}{(\eta^5\text{-}\mathrm{C_5H_4CO_2H})\mathrm{Fe^I}(\eta^6\text{-}\mathrm{C_6Me_6})} \xrightarrow{\Delta\ (20\ °\mathrm{C})} \underset{7}{(\eta^5\text{-}\mathrm{C_5H_4CO_2^-})\mathrm{Fe^+}(\eta^6\text{-}\mathrm{C_6Me_6})} + {}^1/_2\mathrm{H_2} \quad (15)$$

negative potential than that of the reduction of the acid substituent, the electron transfer must be fast because (i) the reduction of the acid substituent is irreversible and gives a gas (H_2), which displaces the Fe^{II}/Fe^I equilibrium and (ii) the carboxylic substituent is conjugated to the Fe(I) sandwich frame as indicated by the color shift of the Fe(I) complex (Fe(I) complexes are forest-green; 8 is blue). During the Na/Hg reduction of **6d**, 8 clearly appears as the first intermediate, but the reduction can then continue by direct reduction of the acid substituent to carboxylate and H_2. It is likely that both routes proceed, but the intermediacy of 7 accounts for most of the reduction path (Scheme I). The thermal stability of the purple radical anion 9 obtained either by Na/Hg reduction of **6d** or 7 allows more extensive characterization. However, the manipulation of 9 is extremely delicate given its sensitivity to air due to its strong reducing power. It can also be produced by one-electron reduction of its cationic precursor 7 using $LiAlH_4$ in THF at −50 °C.[6b,23b] The EPR spectrum of 9 conveniently generated under these conditions was obtained in frozen THF at 133 K and shows

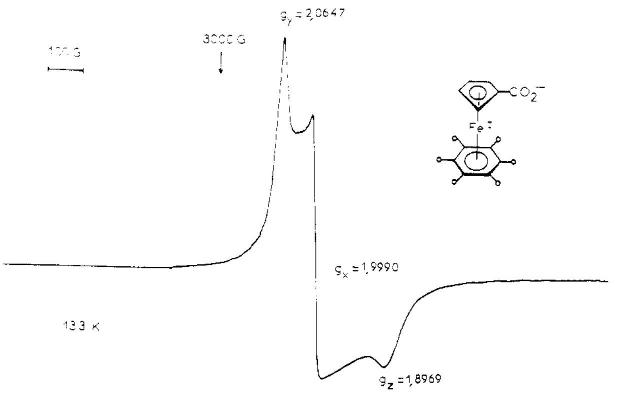
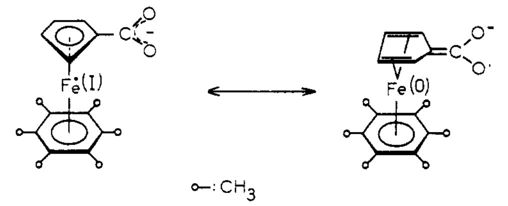


Figure 2. EPR spectrum of **9** at 133 K, generated from **7** and $LiAlH_4$ in THF, at 223 K.



9A 9B

Figure 3.

three signals corresponding to three *g* values around 2, a characteristic of 19-electron d^7 Fe(I) complexes (rhombic distortion).[23] Although the spectrum and the *g* values differ slightly from those of 8, it is clear that both the blue complex 8 and the purple complex 9 belong to the same d^7 Fe(I) family as all the forest-green $CpFe^I$(arene) complexes (Figure 2).[23,24] Compound 9 could also be characterized by its infrared spectrum. The carbonyl stretch of the carboxylate is observed at 1625 cm^{-1} (compare 7, 1650 cm^{-1}). The 25 cm^{-1} shift also shows the conjugation between the iron center and the carboxylate substituent. This conjugation is best represented by a small contribution of a fulvene Fe(O) mesomer, **9B**. The UV spectra could not be recorded by using standard conditions because 9 is so air-sensitive. At the low concentration necessary for UV spectroscopy, air could not be avoided. However, the color shift from $CpFe^I(\eta^6\text{-}C_6Me_6)$ to 9 (green to purple) indicates a change of the levels of the e^*_1 ($d_{xz,yz}$) and e_2 (C_6Me_6) orbitals which are responsible for the $e^*_1 \rightarrow e_2$ transition.[11] These changes are attributable to the change of sandwich symmetry and to the small contribution of the mesomeric form **9B**.

The Mössbauer spectrum of 9 under zero field was recorded at 77 K. It shows a single quadrupole doublet (QS = 1.54 mm s^{-1}, IS = 0.83 mm s^{-1}). These parameters are also typical of Fe(I) complexes.[17] They indicate that the contribution of the mesomeric fulvene Fe(O) form **9B** is weak. Note that, under these conditions, $CpFe^I(\eta^6\text{-}C_6Me_6)$ shows two quadrupole doublets of equal intensities and isomer shifts, only differing by the QS values. The splitting into two doublets is a result of the cooperative distortion induced by the packing in the solid state,[10,17] whereas frozen solutions exhibit only a single doublet. The carboxylate group inhibits the specific alternating packing found by the X-ray structure of $CpFe^IC_6Me_6$. Indeed, the X-ray crystal structure of $(\eta^5\text{-}C_5H_4CO_2H)CoCp$ shows it is a dimer bridged by the carboxylic substituents.[25] The

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[23] For an extensive study of the EPR spectroscopy of Jahn–Teller active Fe^I sandwich compounds, see: (a) Rajasekharan, M. V.; Giezynski, S.; Ammeter, J. H.; Ostwald, N.; Hamon, J. R.; Michaud, P.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 2400. (b) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

[24] For specific discussions on the electronic structure of Fe(I) complexes see ref 6b, 10, 11, 20, 21, and 23 and: Green, J. C.; Kelly, M. R.; Payne, M. P.; Seddon, E. A.; Astruc, D.; Hamon, J.-R.; Michaud, P. *Organometallics* **1983**, *2*, 211.

carboxylate group in **9** has different solid state interactions, but certainly dramatic ones.

IV. Reaction of (η^5-$C_5H_4CO_2H$)Fe^I(η^6-C_6Me_6) (8) and (η^5-$C_5H_4CO_2^-$)Fe^I(η^6-C_6Me_6) (9) with O_2. The reactions of $CpFe^I$(arene) complexes with O_2 are of interest because they provide good systems to examine the reactivity of $O_2^-\cdot$ ion pairs:[26]

$$CpFe^I(\eta^6\text{-arene}) + O_2 \rightarrow [CpFe^{II}(\eta^6\text{-arene})^+,O_2^-\cdot]$$

We previously showed that in the absence of a salt such as $Na^+PF_6^-$ in THF,[27] $CpFe^I$(arene) complexes react with O_2 to give benzylic H atom abstraction which leads to Fe^{II}(cyclohexadienyl) complexes.[18,28] When the arene ligand of the Fe^I complex does not bear benzylic hydrogens, a dimeric cyclohexadienyl peroxide is obtained.[27,29]

$$CpFe^I(\eta^6\text{-}C_6H_5CH_2R) \xrightarrow{O_2} CpFe^{II}(\eta^5\text{-}C_6H_5{=}CHR)$$

$$R = H, \text{alkyl}$$

$$CpFe^I(\eta^6\text{-}C_6H_3R_3) \xrightarrow{O_2} [CpFe^{II}(\eta^5\text{-}C_6H_3R_3\text{-}O\text{-})]_2$$

$$R = H \text{ or } t\text{-Bu}$$

In the presence of a salt such as $NaPF_6$ in THF solution, these cage reactions are totally inhibited because of the ion exchange between the two pairs[27]

$$[CpFe^+(\eta^6\text{-arene}),O_2^-\cdot] + [Na^+,PF_6^-] \rightarrow [CpFe^+(\eta^6\text{-arene}),PF_6^-] + [Na^+,O_2^-\cdot]$$

giving two new ion pairs: a large organoiron cation with a large PF_6^- anion and a small Na^+ cation with a small $O_2^-\cdot$ anion.

The reactions of the present Fe^I complexes bearing either a carboxylic group or an anionic charge differ from the analogous reaction of $CpFe^I$(arene) compounds. Blue, THF-soluble (η^5-$C_5H_4CO_2H$)Fe^I(η^6-C_6Me_6) (**8**) immediately reacts with 0.5 mol of O_2 at 20 °C, giving a colorless solution and a yellow precipitate of (η^5-$C_5H_4CO_2^-$)Fe^+(η^6-C_6Me_6) (**7**). The carboxylic proton is more acidic than the arene methyl proton; thus no cyclohexadienyl structure is obtained.

This reaction presumably follows the general mechanism of the reactions of Fe(I) compounds with O_2 involving deprotonation in the cage by superoxide anion.[18,27]

$$(\eta^5\text{-}C_5H_4CO_2H)Fe^I(\eta^6\text{-}C_6Me_6) \xrightarrow{O_2} [(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6),O_2^-\cdot] \xrightarrow{\text{“}-HO_2\text{”}} (\eta^5\text{-}C_5H_4CO_2^-)Fe^+(\eta^6\text{-}C_6Me_6)$$

The reaction of purple (η^5-$C_5H_4CO_2^-$)Fe^I(η^6-C_6Me_6)Na^+ with O_2 at 20 °C also gives (η^5-$C_5H_4CO_2^-$)Fe^+(η^6-C_6Me_6) and Na_2O_2 (ν = 800 cm^{-1}), the latter resulting from the disproportionation of $Na^+O_2^-$. It was hoped that anionic compounds such as **9** would transfer a single electron to O_2, leaving O_2^-, but this is not the case. The presence of Na^+ presumably inhibits the cage reaction of O_2^-. However, the disproportionation to O_2^{2-} and O_2 (which is further reduced) is always observed under this type of reaction conditions (it is probably catalyzed by Na^+).[27c] The production of reactive superoxide anion must await further studies, and the present work indicates that anion$^-$/Na^+ systems are presumably not adequate for this purpose.

Scheme II

$$CpFe^I(\eta^6\text{-}C_6Me_6) \xrightarrow{O_2} CpFe^{II}(\eta^5\text{-}C_6Me_5CH_2) \xrightarrow{CO_2} CpFe^+(\eta^6\text{-}C_6Me_5CH_2CO_2^-) \xrightarrow{Na/Hg} CpFe^I(\eta^6\text{-}C_6Me_5CO_2^-)$$

Conclusion and Outlook

We have found a reproducible one-pot synthesis of the carboxylic acids $[CpCO_2HFe^{II}(\eta^6\text{-arene})]^+PF_6^-$ using CO_2 and cheap, commercially available raw materials (ferrocene, aluminum chloride, arene). Na/Hg reduction of both the acid **6d** and of the zwitterionic carboxylate **7** gives the extremely reactive, but thermally stable, purple radical anion **9**. Since all attempts to reduce $[CpFe^{II}(\eta^6\text{-arene})]^+$ complexes with exocyclic arene functions failed, Cp functionalization turns out to be the successful alternative for functionalization of this redox catalyst. This location of the functional group is all the more convenient in that it leaves room for hexalkylarenes which are the necessary ligands to obtain thermally stable Fe(I) complexes. It should be noted that the reaction of O_2 with $CpFe^I$(η^6-C_6Me_6) gives $CpFe^{II}$(η^5-$C_6Me_5CH_2$) which quickly and quantitatively reacts with CO_2[6b,28b] to give the zwitterion $CpFe^+$(η^6-$C_6Me_5CH_2CO_2^-$) and that Na/Hg reduction of the latter also gives a forest-green thermally stable Fe(I) radical anion[30] (Scheme II).

Note that the introduction of $CpFe^{II}$(η^5-$C_6Me_5CH_2$) in aqueous media (pH 13) produces $CpFe^+$(η^6-C_6Me_6)OH^- which is also soluble. The electroreduction gives the transcient Fe(I) complex which is not observed "de visu" in the electrochemical cell; it is too reactive to allow the observation of its precipitate. The purple color of the radical anion **9** was never observed either in the electrochemical cell because its steady-state concentration is too low.[30] In summary, the absence of the PF_6^- counteranion is sufficient to allow solubilization and to provide an homogeneous redox catalyst in water. However, functionalization using the carboxylate chain on the Cp ring as well as on the η^5-pentamethylbenzyl ligand also offers opportunities to modify electrodes with this redox catalyst, to attach it to polymers,[31] and to provide biological tracers.[32]

Experimental Section

Reagent grade tetrahydrofuran[12] (THF) and diethyl ether were distilled from sodium benzophenone ketyl under nitrogen just before use. Acetonitrile and dichloromethane were distilled from phosphorous pentoxide. Benzene and toluene were distilled from sodium. All other chemicals were used as received. All manipulations were done by using Schlenk techniques under prepurified nitrogen or argon. Infrared spectra were recorded on a Pye-Unicam SP 1100 infrared spectrometer either as a Nujol mull between KBr disks or in solution using 0.1-mm cells with KBr windows. Wavenumbers are given in inverse centimeters by using polystyrene as reference. ^1H NMR spectra were recorded with a Varian EM 360 (60 MHz, room temperature) or a Brüker WH

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Table I. ^{13}C NMR Data for $[(\eta^5\text{-}C_5H_4R)Fe(\eta^6\text{-arene})]^+PF_6^-$ (R = H, CO_2H)[a]

		R = CO_2H				R = H		
solv	arene	CH_3	C_5H_4	arene	COOH	CH_3	C_5H_5	arene
$Me_2SO\text{-}d_6$	C_6H_6		80.4					
			78.2	89.2	167			
			76.9					
CD_3COCD_3	$C_6H_3(CH_3)_3$	17.7	81.3	91.7	167.1	20.1	81.8	88.1
			81.2					
CD_3COCD_3	$C_6(CH_3)_6$	16.9	79.0	100.7	167	18.6	80.1	91.0
			80.7					
			82.0					
$Me_2SO\text{-}d_6$	naphthalene		78.2	87.6[b]	160		77.2	86.0[b]
			78.7	88.8[b]				87.6[b]
				96.9[c]				96.6[c]
				131.3[d]				132.7[d]
				134.2[d]				131.8[d]

[a] Chemical shifts in δ; internal standard Me_4Si. [b] Coordinated. [c] Quaternary. [d] Uncoordinated.

Table II. ^1H NMR Data for $[(\eta^5\text{-}C_5H_4R)Fe(\eta^6\text{-arene})]^+PF_6^-$ (R = H, CO_2H)[a]

	R = CO_2H				R = H		
arene	H_{arene}	C_5H_4	CH_3	OH (large)	arene	C_5H_4	CH_3
C_6H_6	6.2	4.82 (m)		3.8			
$C_6H_3(CH_3)_3$	6.0	4.9 (m)		4.1	6.20	5.0 (s)	2.50 (s)
$C_6(CH_3)_6$		4.91 (t)	2.39 (s)	4.1		4.69 (s)	2.54 (s)
		4.72 (t)					
$C_{10}H_8$	6.4 (q)[b]	4.9 (q)		3.5	6.32 (q)	4.4	
	7.2 (q)[b]				7.16 (q)		
	7.9 (s)[c]	4.9 (q)		3.5	7.82 (m)		

[a] Chemical shifts in δ; internal standard Me_4Si; solvent CD_3CN/Me_4Si; 100 MHz. [b] Coordinated. [c] Uncoordinated.

80 (80 MHz, FT mode, low-temperature spectra) instrument. ^{13}C NMR spectra were recorded on a Brüker WH 80 spectrometer (20.115 MHz, FT mode). All chemical shifts are reported in parts per million (δ) with reference to internal tetramethylsilane (Me_4Si). Mössbauer spectra were recorded with a 25-mCi ^{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 for microanalyses of the CNRS at Lyon-Villeurbanne. See NMR data in Tables I and II.

1. **Synthesis of $(\eta^5\text{-}C_5H_4CpCO_2H)Fe^+(\eta^6\text{-}C_6H_6)PF_6^-$ (2d).** A stream of CO_2 was passed into 200 mL of a C_6H_6 solution of ferrocene (7 g, 37.6 mmol) for 4 min (well-ventilated hood), and then 20 g of Al_2Cl_6 was added (75.2 mmol). Carbon dioxide was bubbled into the reaction mixture at 60 °C for 1 h with magnetic stirring (the reaction flask was equipped with a condenser). During this period, the reaction mixture, initially brown, became purple and HCl gas was evolved. This carboxylation process is monitored by thin-layer chromatography (TLC) on silica gel using hexane as the eluent (aliquots were hydrolyzed before TLC analysis). After completion of the CO_2 fixation step, 670 mg (37.6 mmol) of water was added, the temperature was raised to 80 °C, and the reaction mixture was refluxed overnight with stirring under a CO_2 atmosphere. During this time ligand exchange took place and the color changed from purple to brown. The reaction mixture was then cooled to 0 °C, and the organic phase was decanted and hydrolyzed with 150 g of ice water. The aqueous phase was separated and washed three times with 40 mL of ether. To the aqueous layer solution was added a solution of 20% aqueous NaOH dropwise until the pH reached 12–13. After filtration, the aqueous phase was added to a saturated aqueous HPF_6 solution (6.2 g in 20 mL). The unsubstituted complex $CpFe^+(\eta^6\text{-}C_6H_6)PF_6^-$ (**3d**)[12] was isolated as a yellow precipitate and purified by precipitation with ether from a filtered acetone solution (12.5 g, 49% yield). The basic solution from which the unsubstituted complex has been removed was washed with CH_2Cl_2; then concentrated aqueous HCl was added dropwise until pH 1 was reached; then 2 mL of 75% aqueous HPF_6 was added. The acidic salt $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(C_6H_6)PF_6^-$ (**2d**) slowly precipitated at 3–5 °C in 12 h and was recrystallized from water (4.9 g, 34% yield). Infrared: ν_{COOH} 2580, 2400 (doublet); ν_{CO} 1730 cm^{-1}. Total conversion of ferrocene to **3d** and **2d**: 83%. Anal. Calcd $C_{12}H_{11}O_2FePF_6$: C, 37.22; H, 2.84; Fe, 14.83. Found: C, 37.47; H, 2.83; Fe, 14.82.

2. **Synthesis of $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6H_3(CH_3)_3)PF_6^-$ (5d).** In a similar way, starting from 40 mmol of ferrocene, 40 mmol of water, 60 mmol of Al_2Cl_6, and mesitylene as the solvent (200 mL), 4.28 g (25%) of $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6H_3Me_3)PF_6^-$ (**5d**) was obtained after recrystallization from water; mp 190 °C dec. Infrared: ν_{COOH} 2600, 2680 cm^{-1} (doublet); ν_{CO} 1725 cm^{-1}. Total conversion of ferrocene into **5d** and $CpFe^+(\eta^6\text{-}C_6H_3Me_3)$ (**10**): 63%. Anal. Calcd for $C_{15}H_{17}O_2FePF_6$: C, 41.97; H, 3.96; Fe, 13.0. Found: C, 42.41; H, 3.96; Fe, 13.01.

3. **Synthesis of $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-naphthalene})PF_6^-$ (4d).** From 50 mmol of ferrocene, 75 mmol of Al_2Cl_6 and 50 mmol of naphthalene in 400 mL of heptane as solvent, one obtains 7.9 g (12%) of dark red crystals of **4d** after recrystallization from water (pH 1; 3–5 °C, in the dark). Note that water is not added before the ligand exchange reaction since it causes decomposition and that too long reaction times also cause decomposition (optimal time: 2–3 h in refluxing heptane). **4d** is very light sensitive; mp 190 °C dec. Infrared: ν_{COOH} 2600, 2680 (doublet); ν_{CO} 1730 cm^{-1}. Total conversion of ferrocene to **4d** and $CpFe^+(\text{naphthalene})PF_6^-$ (**11**): 30%. Anal. Calcd for $C_{16}H_{13}O_2FePF_6$: C, 43.9; H, 2.9; Fe, 12.7. Found: C, 43.70; H, 3.07; Fe, 12.25.

4. **Synthesis of $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)PF_6^-$ (6d). (a) Using CO_2 at 1 atm.** From 100 mmol of ferrocene, 150 mmol of Al_2Cl_6, 100 mmol of C_6Me_6, and 100 mmol of water, 11.75 g (15%) of orange crystals of $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)$ (**6d**) was obtained (as described for **2d**) after recrystallization from water at pH 1. Total conversion of ferrocene to **6d** and $CpFe^+(\eta^6\text{-}C_6Me_6)PF_6^-$ (**12**):[33] 40%.

(b) Using CO_2 at a 50-atm Pressure in an Autoclave. In a 500-mL steel autoclave, 100 mL of heptane was deaerated with Ar and 9.3 g of ferrocene (50 mmol), 8.1 g of C_6Me_6 (50 mmol), and 26.7 g of Al_2Cl_6 (100 mmol) were added under Ar. The autoclave was purged, and a CO_2 pressure of 50 atm was introduced. The reaction mixture is heated for 1 h at 60 °C under mechanical stirring (carboxylation) and then at 110 °C for 15 h (ligand exchange). After the pressure and the temperature were allowed to reach ambient conditions, the autoclave was cooled to 0 °C, the reaction mixture was hydrolyzed under nitrogen with ice–water and filtered. The aqueous phase was separated and treated as indicated for the preparation of **2d**. $CpFe^+(\eta^6\text{-}C_6Me_6)PF_6^-$ (**12**; 2.8 g, 13%) and $(\eta^5\text{-}C_5H_4CO_2H)Fe^+(\eta^6\text{-}C_6Me_6)PF_6^-$ (**6d**; 1.7 g 8%) were obtained as orange needles after recrystallization in boiling ethanol. Infrared (cm^{-1}): 3400, 3200 (s, ν_{OH}); 1730 (s, ν_{CO}); 855 (s, ν_{PF}). Mössbauer parameters (293 K): QS = 1.96 mm s^{-1}; IS = 0.45 mm s^{-1}. Anal. Calcd for $C_{18}H_{23}O_2FePF_6$: C, 45.79; H, 4.91; Fe, 11.83. Found: C, 45.72; H, 5.20; Fe, 11.75

(method b).

5. **Synthesis of (η^5-$C_5H_4CO_2^-$)Fe^+(η^6-C_6Me_6) (7).** **6d** (472 mg, 1 mmol) was dissolved in 50 mL of ethanol, and 40 mg of NaOH (1 mmol) was added. A large excess of acetone was then added to the solution. the zwitterion precipitates at −20 °C, the $NaPF_6$ salt being still soluble. Pure **7** (200 mg, 53%) was obtained as a yellow powder. The absence of $NaPF_6$ in these samples was checked by infrared spectroscopy (no PF band at ν_{PF} = 855 cm^{-1}). However, the zwitterion is obtained as a trihydrate. ^1H NMR (CD_3CN, δ, Me_4Si): 4.66 (t, 2 H, C_5H_4), 4.39 (t, 2 H, C_5H_4), 2.39 (s, 18 H, $C_6(CH_3)_6$), 2.32 (s, H_2O). ^{13}C NMR (D_2O, δ, DSS): 173.1 (CO_2), 101.3 ($C_6(CH_3)_6$), 88.7 (substituted CpC), 82.2 (Cp); 80.2 (Cp), 18.4 ($C_6(CH_3)_6$). Infrared (Nujol, cm^{-1}): 1650 (s, ν_{CO}), 3400 (s, ν_{OH}). Mössbauer parameters (293 K): QS = 1.86 mm s^{-1}; IS = 0.54 mm s^{-1}. Anal. Calcd for $C_{18}H_{22}O_2Fe{\cdot}3H_2O$: C, 56.85; H, 7.42; Fe, 14.68. Found: C, 56.64; H, 7.28; Fe, 15.00.

6. **Synthesis of (η^5-$C_5H_4CO_2^-$)Fe^I(η^6-C_6Me_6) (9) from 7. (a) Characterization by EPR Spectroscopy.** **7** (10 mg, 0.031 mmol) were mixed with 10 mg of $LiAlH_4$ (0.27 mmol). The well-ground mixture was introduced into an EPR tube. The latter was purged with argon and then cooled to −50 °C; 2 mL of degassed THF, previously cooled to −50 °C, was added. EPR spectrum at 133 K: g_x = 1.9990; g_y = 2.0647; g_z = 1.8969.

(b) Synthesis and Characterization of 9. In a Schlenk tube, 652 mg of **7** (2 mmol), 23 g of 1% Na/Hg (10 mmol), and 100 mL of degassed THF were introduced. After 2 h of reduction at 20 °C, the purple suspension was isolated by transfer into another Schlenk tube. The purple precipitate was filtered and rinsed with 10 mL of THF. **9** was slightly THF soluble; 412 mg (60%) of powder was obtained. **9** was extremely air-sensitive in solution and in the solid state: upon contact with air, it was instantaneously transformed to **7**. Infrared (Nujol, cm^{-1}): 1625 (s, ν_{CO}). Mössbauer parameters (77 K): QS = 1.54 mm s^{-1}; IS = 0.83 mm s^{-1}. Anal. Calcd for $C_{18}H_{22}O_2FeNa$: C, 61.91; H, 6.35. Found: C, 61.75; H, 6.39.

7. **Reduction of [(η^5-$C_5H_4CO_2H$)Fe(η^6-C_6Me_6)]$^+PF_6^-$ (6). (a) Characterization of (η^5-$C_5H_4CO_2H$)Fe^I(η^6-C_6Me_6) (8).** Cation **6** (10 mg, 0.021 mmol) and 10 mg of $LiAlH_4$ (0.27 mmol) were mixed and introduced into an EPR tube; the latter was purged with argon and cooled to −50 °C. Degassed THF (2 mL) was introduced at −50 °C. In 1 min, the solution turned green-blue; the tube was then cooled to 77 K. EPR (135 K): g_x = 2.0024; g_y = 2.0659; g_z = 1.9296 (these values are characteristic of Fe^I sandwichs).

(b) Characterization of (η^5-$C_5H_4CO_2^-$)Fe^+(η^6-C_6Me_6) (7). In a Schlenk tube, 170 mg of **6** (0.36 mmol), 4.1 g of 1% Na/Hg (1.8 mmol of Na) and 10 mL of degassed THF were introduced under argon at 20 °C. The solution immediately became blue, indicating the formation of the neutral Fe^I compound **8**. After 15 min of reduction at 20 °C, the blue color of the solution disappeared; 100 mL of pentane was added to impede further reduction. After filtration, 150 mg of a yellow powder was recovered. The infrared spectrum showed a strong band at 1650 cm^{-1} (ν_{CO}), characteristic of the zwitterionic compound **7**. The absence of ν_{CO} at 1730 cm^{-1} and of ν_{OH} at 3400 cm^{-1} indicated that **6** has been fully reduced. A strong PF band at 855 cm^{-1} indicated the presence of $NaPF_6$. The latter was removed by recrystallization from acetone, and **7** was identified by comparison with an authentic sample.

(c) Synthesis and Characterization of (η^5-$C_5H_4CO_2^-$)Fe^I(η^6-C_6Me_6) (9). In a Schlenk tube, 472 mg of **6** (1 mmol), 11.5 g of 1% Na/Hg (5 mmol of Na), and 100 mL of degassed THF were introduced under argon at 20 °C. The solution immediately became blue, and this color disappeared after 15 min; then the suspension progressively turned purple. After 2 h of reduction at 20 °C, the purple suspension was transferred to another Schlenk tube to remove the amalgam and then filtered. A purple powder (250 mg) was obtained, which still contained $NaPF_6$. Washing several times with THF did not remove all the $NaPF_6$. On the other hand, the extremely air-sensitive compound **9** was not stable in acetone or in acetonitrile. It has been characterized by Mössbauer spectroscopy (see above) and by an EPR spectrum at 3.5 K of a solid-state sample (g = 1.9725; for a solution spectrum, see above).

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Reaction of Decamethylstannocene with Lithium Alkyls

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The attack of alkyllithiums on (η^5-Me_5C_5)$_2$Sn (**1**) resulted in an overall nucleophilic substitution at the tin atom with pentamethylcyclopentadienide as the leaving group. Thus, the reaction of **1** with $(Me_3Si)_2CHLi$ yielded Me_5C_5Li and $((Me_3Si)_2CH)_2Sn$ (**2**). Treatment of **1** with MeLi produced Me_5C_5Li and apparently a mixture of oligomeric stannylenes $[Me_2Sn]_n$; the initial formation of a short-lived [bis(pentamethylcyclopentadienyl)alkyltin]lithium species (η^1-Me_5C_5)$_2$Sn(Me)Li (**3**) was demonstrated by trapping experiments with methyl iodide and methyl-d_3 iodide, which yielded (η^1-Me_5C_5)$_2$Sn(CH_3)$_2$ (**4**) and (η^1-Me_5C_5)$_2$Sn(CH_3)(CD_3) (**5**), respectively. The intermediate **3** is postulated also during reduction of (η^1-Me_5C_5)$_2$Sn(Me)Cl (**6**) with $Li_2C_8H_8$.

Introduction

The use of the cyclopentadienyl ligand in tin(II) chemistry led to the first synthesis of a monomeric diorganotin(II) species, dicyclopentadienyltin,[1] the parent compound of what has become a long series.[2] Since the compound is a π-complex with tin as central atom, it was named stannocene in analogy to the well-known iron compound. Investigation of its reactions with electrophiles

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