Electron-Transfer Chemistry of the 20-Electron Complex $[Fe^0(C_6Me_6)_2]$ and of the 19-Electron Complex $[Fe^I(C_6Me_6)(\eta^5\text{-}C_6Me_6H)]$: Mild C–H Activation by O_2 via Superoxide Ion and Functionalization of the Exocyclic Methylenes in the Resulting Complexes $[Fe^0(C_6Me_6)(\eta^4\text{-polyene})]$[†,1]

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Activation of methyl substituents by mild reactions with O_2 has been achieved in paramagnetic bis(arene)iron complexes and followed by functionalization of the nucleophilic exocyclic methylene groups. The 20e complex $[Fe^0(C_6Me_6)_2]$ (**2**), best synthesized from $[Fe^{II}(C_6Me_6)_2]^{2+}(PF_6^-)_2$ (**1**) and Na/Hg in THF at 20 °C, shows a Mössbauer doublet with isomer shift IS = 1.02 mm s^{-1} vs Fe and quadrupole splitting QS = −1.35 mm s^{-1} (293 K). It reacts at −40 °C with $^1/_2$ mol of O_2 in toluene to give the thermally unstable *o*-xylylene complex $[Fe^0(C_6Me_6)\{\eta^4\text{-}C_6Me_4({=}CH_2)_2\}]$ (**4**), characterized by NMR spectroscopy in $C_6D_5CD_3$ at −50 °C (δ_{CH_2}: ^1H, 4.42 and 5.04 ppm; ^{13}C, 144.8 ppm; vs TMS). Complex **4**, in which the *o*-xylylene ligand is unusually coordinated by the double bonds of the ring, reacts with HPF_6 in THF to give only **1** and with PhCOCl in THF to give $[Fe^{II}(C_6Me_6)\{\eta^6\text{-}C_6Me_5CH(COPh)_2\}]^{2+}$, isolated as its PF_6 salt **5**, in which the enolic tautomer predominates. The reaction of **2** with O_2 at 20 °C in toluene or at −40 °C in THF in the presence of 1 equiv of $NaPF_6$ gives the 19e complex $[Fe^I(C_6Me_6)_2]^+(O_2^{2-})_{1/2}$ (**3a**). The 19e complex $[Fe^I(C_6Me_6)(\eta^5\text{-}C_6Me_6H)]$ (**7**), obtained by one-electron reduction of its monocationic 18e precursor **6** with 1 equiv of the 19e complex $[Fe^ICp(C_6Me_6)]$, reacts with $^1/_2$ mol of O_2 to give $[Fe^0(C_6Me_6)\{\eta^4\text{-}C_6Me_5H({=}CH_2)\}]$ (**8**), a model reaction for the second H atom abstraction from **2** by O_2. The 18e complex **6** reacts with *t*-BuOK to give **8** as well, consistent with the electron transfer $O_2 \rightarrow O_2^{\bullet-}$ followed by deprotonation in the reaction of **7** with O_2. Complex **8** reacts with the electrophiles CH_3CO_2H, PhCOCl, $Ph_3C^+PF_6^-$, I_2, and $[Fe^{II}(C_6H_6)(\eta^5\text{-}C_6H_7)]^+PF_6^-$ (**11**) to give the respective complexes $[Fe^{II}(C_6Me_6)(\eta^5\text{-}C_6Me_5HCH_2X)]^+PF_6^-$ (X = H (**6**), COPh (**9**), CPh_3 (**10**), I (**13**), $[Fe^{II}(C_6H_6)(\eta^4\text{-}C_6H_7)]$ (**12**)). Complex **8** deprotonates **9** to give **6** and $[Fe(C_6Me_6)\{\eta^4\text{-}C_6Me_5H({=}CHCOPh)\}]$ (**14**). The 18e complex $[Fe^{II}(C_6H_3Me_3)(\eta^5\text{-}2,4,6\text{-}C_6H_4Me_3)]^+PF_6^-$ (**15**), obtained by hydride reduction of $[Fe^{II}(C_6H_3Me_3)]^{2+}(PF_6^-)_2$, reacts similarly with *t*-BuOK in THF at −60 °C to give the thermally unstable complex $[Fe^0(C_6H_3Me_3)\{\eta^4\text{-}3,5\text{-}C_6H_4({=}CH_2)\}]$ (**16**). The latter reacts with PhCOCl to give **15** and the dibenzoylated complex $[Fe^{II}(C_6H_3Me_3)\{C_6H_2Me_2CH(COPh)_2\}]^+PF_6^-$ (**17**).

Introduction

Electron-transfer pathways provide powerful means of activating aromatic hydrocarbons by metals.[2] They also bring about the structural transformation of aromatic ligands in organometallic complexes.[2-4] The reactions of molecular oxygen appeared useful to us for the activation of aromatics in electron reservoir complexes because exergonic electron transfer (ET) obtained in these reactions[5] gives ion pairs in which the superoxide ion, $O_2^{\bullet-}$,[6,7] reacts cleanly within seconds at −80 °C. As already shown with $Fe^ICp(arene)$ complexes, the fast reaction of $O_2^{\bullet-}$ in the cage is either a deprotonation[7e] of the organoiron cation at the benzylic position or a nucleophilic addition onto the arene ligand in the absence of benzylic hydrogen.[8] Both cage reactions are totally inhibited by $Na^+PF_6^-$ (because of double ion exchange)[8d,e] and by the enzyme superoxide dismutase.[9] Following deprotonation of the alkylarene ligand, the nucleophilic exocyclic methylene of the η^5-bound cyclohexadienyl ligand was shown to react with a variety of electrophiles EX, giving back meanwhile the η^6-arene ligand[8] (Scheme I).

[†] Dedicated to the memory of Dr. Bianka Tchoubar (see Note Added in Proof).

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(5) The $E°$ value for the redox system O_2/O_2^- is about −0.7 V vs SCE in DMF or pyridine.[6] Neutral organometallic complexes that contain only hydrocarbon ligands have $E°$ values[8] (neutral/monocation) which are usually more negative and have an exergonic ET with O_2. Even if this is not the case, ET is driven by the decomposition or any other reaction of the organometallic radical cation and by the dismutation of $O_2^{\bullet-}$.[6] ($OM + O_2 \rightleftharpoons [OM^+,O_2^-] \rightarrow$ reaction.)

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Scheme I

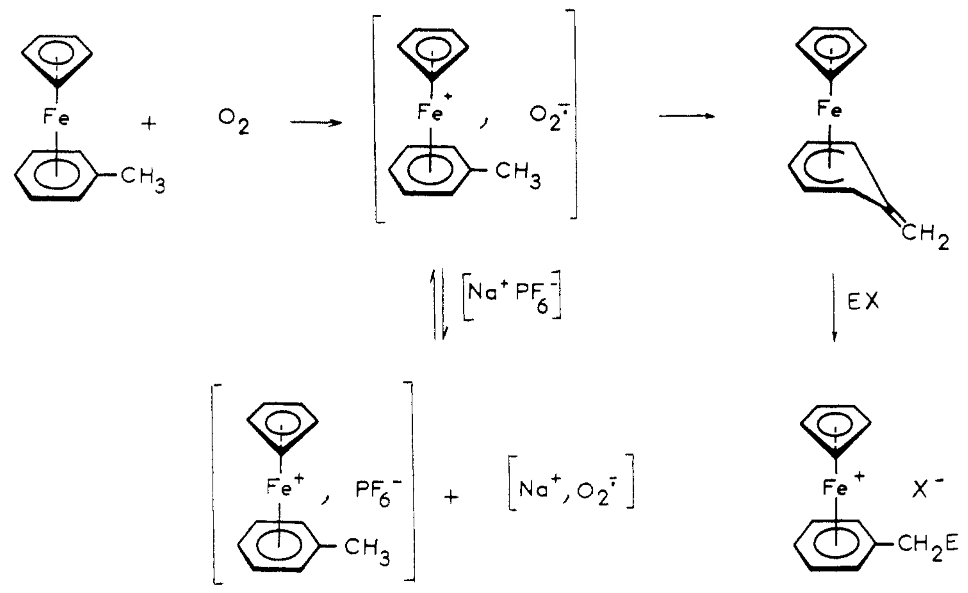
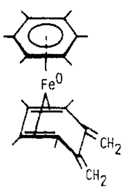
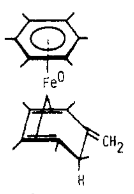


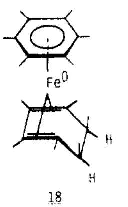
Table I. Comparison of the Mössbauer Parameters for the 18e Fe^0(polyene) Complexes 4, 8, and 18[a,16]



4



8



18

	Mössbauer doublet		
	4 (77 K)	8 (293 K)	18 (293 K)
no. of exocyclic double bond(s)	2	1	0
isomer shift (IS) vs Fe, mm s^{-1}	0.43	0.48	0.33
quadrupole splitting (QS), mm s^{-1}	1.02	0.92	0.98

[a] The slight temperature correction for the 18e iron complexes would give, for 4, IS = 0.33 and QS = 0.92 at 293 K.

The complexes bis(arene)iron are easily accessible and show a rich redox series of three isolable oxidation states (0–2).[10–12] By reaction with 1 equiv of $NaBH_4$, the dicationic 18e complexes $[Fe^{II}(arene)_2]^{2+}(PF_6^-)_2$ give the heat- and air-stable complexes $[Fe^{II}(arene)(\eta^5\text{-cyclohexadienyl})]^+$. The latter are isoelectronic with the [Fe(arene)Cp] series and are isolable in the oxidation states Fe^{II} (18e, cationic)[11,13] and Fe^I (19e, neutral).[11a]

In separate full papers[11g–i] we have described the reactions of nucleophiles with the 18e complexes $[Fe^{II}(arene)_2]^{2+}$ and $[Fe^{II}$(arene)(cyclohexadienyl)] and subsequent functionalization of aromatics via temporary complexation to Fe^{II}. Here, we describe details of the activation of the permethylated benzene and cyclohexadienyl ligands by O_2 using the ET pathway in the 20e complex $[Fe(C_6Me_6)_2]$ (2) and in the 19e complex $[Fe(C_6Me_6)(\eta^5\text{-}C_6Me_6H)]$ (7) and the functionalization of the resulting Fe^0(polyene) complexes by reaction of electrophiles at the exocyclic

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(12) (a) In a 60-kG field, the Mössbauer spectrum of **9** splits into a doublet (left) and a triplet (right), indicating the negative sign of QS; see: Collins, R. L. *J. Chem. Phys.* **1965**, *42*, 1072. (b) The shift of the QS induced by the presence of one electron in an orbital of e^*_1 symmetry is 2 mm s^{-1}.[12c] Thus, the estimation of the character of e^*_1 is (3.35 mm s^{-1})/[2(2 mm s^{-1})] = 0.84. (c) Varret, F. *J. Chem. Phys.* **1976**, *6*, 437. (d) The Mössbauer parameters of **1** at 300 K are IS = 0.82 mm s^{-1} vs Fe and QS = 2 mm s^{-1}. These values are analogous to those reported for $[Fe(mesitylene)]^{2+}$: Stukan, R. A.; Vol'kenau, N. A.; Nesmeyanov, A. N.; Goldanskii, V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, *8*, 1472. Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 500. (e) The metal-vapor synthesis of $Fe(arene)_2$[12f,g] was reported to give, inter alia, the 20e complex $[Fe(\eta^6\text{-arene})_2]$, assigned by analogy of the Mössbauer parameters (arene = benzene) with those given in our preliminary communication.[11b] This metal-vapor synthesis also gives, in the reaction mixtures, the complex $[Fe(\eta^6\text{-arene})(\eta^4\text{-arene})]$ (arene = benzene, toluene[12g–j]), analogous to $[Ru(\eta_6\text{-}C_6Me_6)(\eta_4\text{-}C_6Me_6)]$.[12k,m] (f) Timms, P. L. *J. Chem. Soc., Chem. Commun.* **1969**, 1033. (g) Parker, S. F. *J. Organomet. Chem.* **1984**, *272*, 411. (h) Ozin, G. A.; Francis, C. G.; Huber, H. X.; Andrew, M.; Nazar, L. *J. Am. Chem. Soc.* **1981**, *103*, 2453. (i) Zenneck, U.; Franck, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 831. (j) Morand, P. D.; Francis, C. G. *Organometallics* **1985**, *4*, 1653. (k) Fischer, E. U.; Elschenbroich, C. *Chem. Ber.* **1970**, *103*, 162. (l) Huttner, G.; Lange, S. *Acta Crystallogr., Sect. B* **1972**, *B25*, 2049. (m) Timms, P. L.; King, R. B. *J. Chem. Soc., Chem. Commun.* **1978**, 898.

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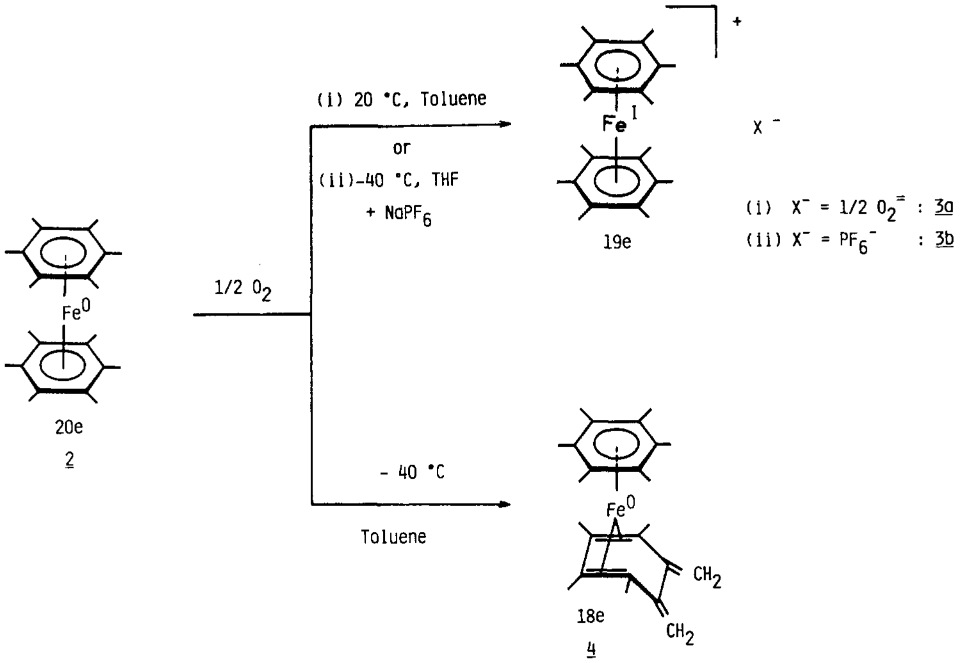
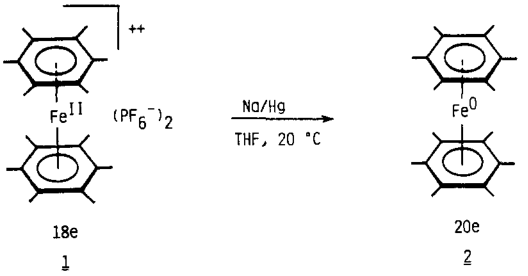
Scheme II



double bond(s). This work has been the subject of a preliminary communication.[11c]

Results

Synthesis of [$Fe(C_6Me_6)_2$] (2) and Double C–H Activation by O_2. The 20e complex 2 has long been known from the work of Fischer et al.,[10b] and its low-yield synthesis was improved by Brintzinger et al.[10d] using sodium naphthalenide reduction of the dicationic precursor 1; however, separation of naphthalene from 2 is tedious. The synthesis of 2 was simplified and improved by using Na/Hg reduction at 20 °C of the dry complex 1 (eq 1).



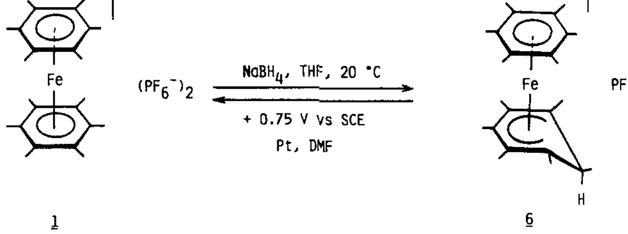
(1)

These conditions are essential in order to impede hydrogenation of 2. An 80% yield of black crystals of 2 was obtained in this way. As shown before,[10d] complex 2 is not thermally stable above 20 °C. Being a triplet, it is ESR silent (the paramagnetism was reported by Fischer[10b]). It exhibits a quasi-temperature-independent Mössbauer doublet with an isomer shift (IS) of 1.02 mm s^{-1} vs Fe at 293 K and 1.20 mm s^{-1} at 1.7 K, characteristic of an Fe^0 sandwich complex, and a very negative quadrupole splitting (QS) of −1.35 mm s^{-1} at 293 K and −1.47 mm s^{-1} at 1.7 K. No spontaneous magnetization (zero field) was observed down to 1.7 K. The applied field of 60 kG at 100 K showed the sign of the QS to be negative[11b,12a] and a hyperfine field below 100 K due to the paramagnetism (S = 1). The QS is 1.6 mm s^{-1} lower than that of 1, indicating that the antibonding e^*_1 orbital has around 84% metal character.[12b-d]

The reaction of 2 with $^1/_2$ mol of O_2 at 20 °C gives the purple 19e complex [$Fe^I(C_6Me_6)_2$]$^+$(O_2^{2-})$_{1/2}$ (3a) in 62% yield (Scheme II). The cation shows a Mössbauer spectrum at 293 K characteristic of Fe^I [11b] (IS = 0.82 mm s^{-1} vs Fe; QS = 0.63 mm s^{-1}).

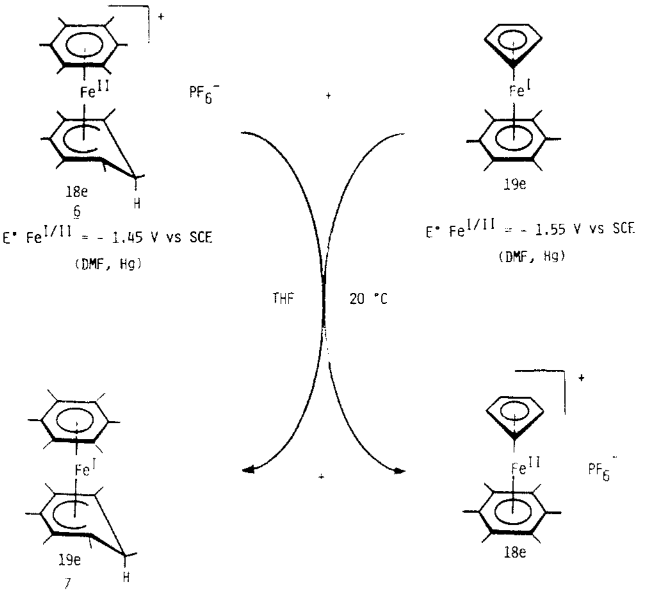
The anion is characterized by infrared spectroscopy ($\nu_{O_2^{2-}}$ = 840 cm^{-1}). Metathesis with $NaPF_6$ gives the PF_6 salt 3b.[10b] The reaction of 2 with $^1/_2$ mol of O_2 in THF with 1 equiv of $NaPF_6$ at −40 °C also gives a purple precipitate of 3b and $^1/_2$ equiv of Na_2O_2. If the reaction of 2 with $^1/_2$ mol of O_2 is effected in toluene at −40 °C in the absence of $NaPF_6$, a red color develops in 5 min. In toluene-d_8, the ^1H and ^{13}C NMR spectra show the features of the neutral o-xylylene Fe^0 complex [$Fe^0(C_6Me_6)\{\eta^4\text{-}C_6Me_4(=CH_2)_2\}$] (4): two distinct multiplets for the methylene protons are observed in the ^1H NMR spectrum at δ = 4.42 and 5.04 ppm, and the methylene signal is found at δ = 88 ppm in the $^{13}C\{^1H\}$ NMR spectrum, whereas the signal of the two decoordinated ring carbons is located at δ = 145 ppm. Crystallization at −80 °C gave a red powder, thermally unstable above −20 °C, which showed the Mössbauer parameters (at 77 K) IS = 0.44 mm s^{-1} and QS = 1.05 mm s^{-1} for the temperature-independent quadrupole doublet, consistent with an 18e complex and comparable with values for other Fe^0 18e complexes of analogous geometries (vide infra).

Synthesis of [$Fe^I(C_6Me_6)(\eta^5\text{-}C_6Me_6H)$] (7) and Single C–H Activation by O_2. The $NaBH_4$ reduction of 1 at 20 °C in THF was reported to give the hydride-transfer product 6 selectively[11a,e] (eq 2), a reaction which parallels that reported by Nesmeyanov[13] for the unsubstituted complex [$Fe(C_6H_6)_2$]$^{2+}$. The cyclic voltammograms of 6



(2)

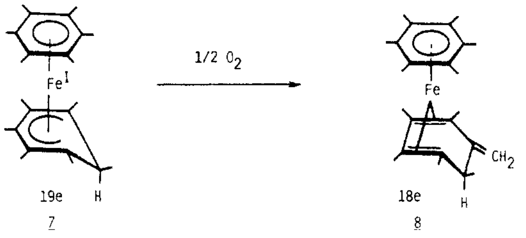
(DMF, Hg, 20 °C) show a reversible wave at −1.45 V vs SCE and irreversible waves at −2.20 V (Hg, to 7) and +0.75 V (Pt, to 1).[14] The Na/Hg reduction of 6 is not clean, but reaction of **6** in THF at 20 °C with 1 equiv of [Fe^{I}Cp(C$_6$Me$_6$)] gives pure [Fe^I(C$_6$Me$_6$)(η^5-C$_6$Me$_6$H)] (**7**) and the precipitate of [Fe^{II}Cp(C$_6$Me$_6$)]$^+$PF$_6^-$ (eq 3). The 19e



(3)

complex **7** is thermally stable and very air-sensitive; it is amber brown (UV (pentane, 20 °C): λ = 428 nm, ϵ = 434 L mol^{-1} cm^{-1}), and recrystallization at −80 °C gave brown-black crystals that gave the correct analysis (77% yield). The ESR spectrum was recorded in the solid state at 3 K and showed three *g* values typical for a Jahn–Teller-active Fe^I species (g_x = 2.017; g_y = 2.144; g_z = 1.996). The Mössbauer spectra of **7** showed a quadrupole doublet with parameters typical for Fe^I: IS = 0.46 mm s^{-1} and QS = 0.91 mm s^{-1} at 293 K. The variation of these values with the temperature is rather low, IS = 0.58 mm s^{-1} and QS = 1.04 mm s^{-1} at 77 K, indicating a weak rhombic distortion.[15]

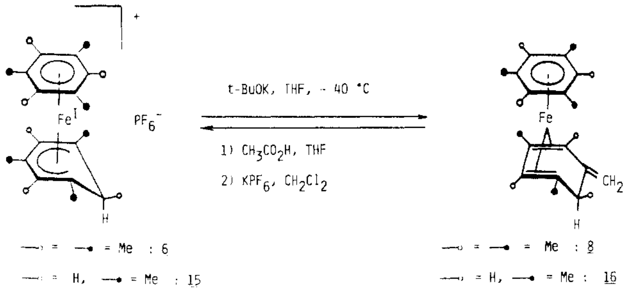
The 19e complex **7** reacts rapidly with $^1/_2$ mol of O$_2$ (20 °C, THF) to give a color change of the solution from brown to light red, and the pure 18e complex [Fe^0(C$_6$Me$_6$){η^4-C$_6$Me$_5$H(=CH$_2$)}] (**8**) is isolated as red crystals in 88% yield (eq 4). The exocyclic methylene group is observed



(4)

in C$_6$D$_6$ as two distinct multiplets centered at δ = 4.45 and 4.65 ppm in the ^{1}H NMR spectrum and as a singlet at δ = 92.7 ppm in the ^{13}C{^{1}H} NMR spectrum. The latter shows the decoordinated sp^2 carbon at δ = 157.7 ppm, whereas the decoordinated sp^3 carbon is found at δ = 39.4 ppm. The Mössbauer spectrum shows a quadrupole doublet with parameters close to those of **4** and of the cyclohexadiene complex [Fe^0(C$_6$Me$_6$)(η^4-C$_6$Me$_6$H$_2$)], as expected for comparable oxidation states and geometries (no significant variation is found in the series; see Table I).

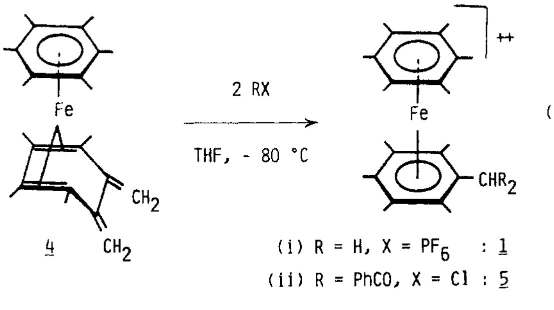
The deprotonation of **6** with *t*-BuOK in THF at −80 °C also cleanly gives **8** in 97% yield (eq 5). This contrasts



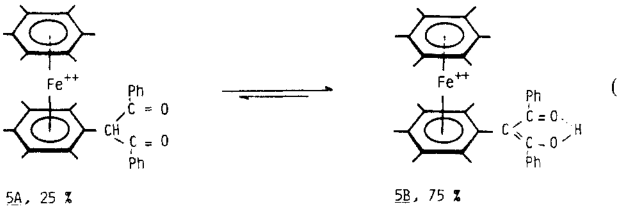
(5)

with the reaction of *t*-BuOK with **1**, which did not give **4** but only the ET product **3b**. Similarly, the mesitylene complex **15** (analogous to **6**) is cleanly deprotonated by 1 equiv of *t*-BuOK in THF-d_8 at −40 °C to give the red complex **16**, analogous to **8**. Complex **16** is not thermally stable above 0 °C, but its ^{13}C{^{1}H} NMR spectra were recorded at −35 and −10 °C without change in this solvent and showed that pure **15** was formed. The THF solutions of **15** could be used at low temperature for functionalization, and the reactivities of **8** and **15** can be compared.

Reactivity of the Exocyclic Methylene Groups in the Fe^0(polyene) Complexes 4, 8, and 16. The protonation of **4** in THF at −80 °C with HPF$_6$ gave exclusively a pink precipitate of **1**, whatever the stoichiometry. No cyclohexadienyl intermediate was detected. Similarly, the benzoylation of **4** in THF at −80 °C gave exclusively the orange dibenzoylated dicationic complex **5** (eq 6), isolated as a PF$_6$ salt after metathesis with aqueous HPF$_6$. The latter was found by ^{1}H NMR spectroscopy to consist of a 75/25 mixture of enol/ketone in tautomeric equilibrium (eq 7).



(6)



(7)

The protonation of **8** and **16** in THF solutions was effected with HPF$_6$ or CH$_3$CO$_2$H and immediately gave precipitates of the protonated complexes **6** and **15**. If CH$_3$CO$_2$H is used, protonation is followed by metathesis with KPF$_6$ in water to regenerate the PF$_6$ salt (eq 5).

The reaction of **8** with carbon electrophiles and with I$_2$ proceeded cleanly at low temperature without side reac-

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(14) It is probable that the 17e species [Fe(C$_6$Me$_6$)(η^5-C$_6$Me$_6$H)]$^{2+}$ generated upon anodic oxidation of **6** loses a H atom to form **1**; this H atom transfer can also be concomitant with the anodic oxidation of **6**. Similarly, it is probable that the reaction of **8** with Ph$_3$C$^+$ follows a comparable mechanism: monoelectronic oxidation would first give Ph$_3$C$^\bullet$ and the 17e monocation, which would then abstract a H atom from the medium. As in organic chemistry, 17e organometallic radicals can lose or gain a H atom to give stable 18e complexes.

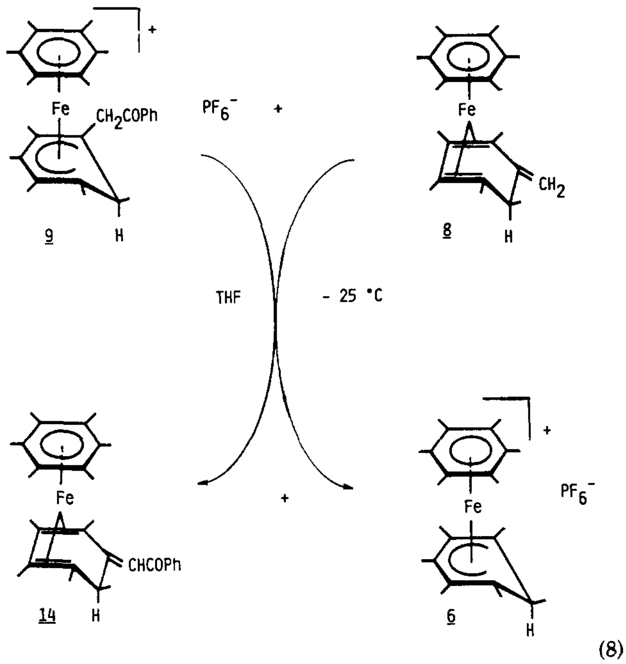
(15) A small variation of QS with temperature is noted in sterically bulky Fe^{I}Cp(arene) complexes (i.e. arene = C$_6$Et$_6$, C$_6$Me$_5$CH$_2$CH$_2$C$_6$Me$_5$): Varret, F.; Mariot, J.-P.; Hamon, J.-R.; Astruc, D. *Hyperfine Interact.* **1988**, *39*, 67. However, the origin of the small variation for **7** may instead be electronic.

(16) Complex **18** was obtained by NaBH$_4$ reduction of **6** at 50 °C.[11g]

tions (side ET processes occurring in reactions carried out at 20 °C must be avoided). Thus, **8** formed carbon–carbon bonds between the exocyclic methylene group and the carbon electrophile by reactions with PhCOCl, $Ph_3C^+PF_6^-$, and [$Fe(C_6H_6)(\eta^5-C_6H_7)$]$^+$. Formation of a C–I bond occurred upon reaction with I_2. These reactions were carried out between −80 and −25 °C (Scheme III).

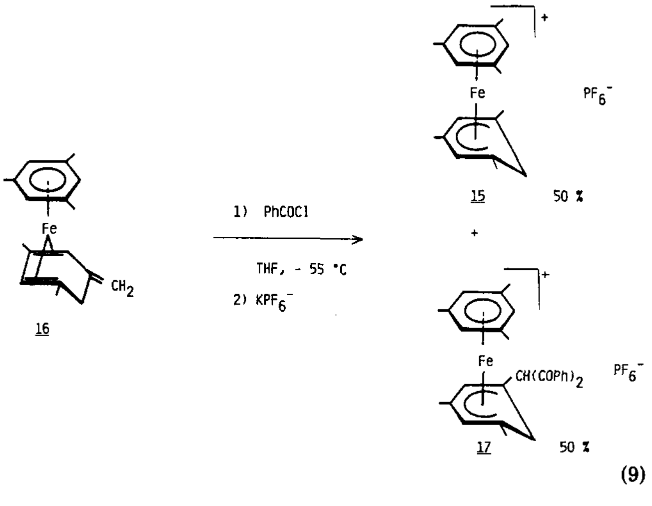
If the reaction between **8** and $Ph_3C^+PF_6^-$ is carried out at −55 °C and immediately followed by warming up to 20 °C over 90 min, only **6** is formed (as in the protonation reaction of eq 5).

In the case of an electron-withdrawing group such as PhCO– in **9**, the methylene hydrogens are very acidic and the complex can be deprotonated. Indeed, **8** can act as a base to deprotonate **9** in THF at −25 °C, giving **6** and the birefringent complex **14** (eq 8), already known as an intermediate in the iron-mediated functionalization of C_6Me_6.[11g,i]



(8)

The deprotonation of **9** to give **14** opens the route to another electrophilic attack of the exocyclic double bond, as in double benzoylation. Indeed, reaction of the mesitylene complex **16** with PhCOCl at −55 °C in THF directly gives equal amounts of the dibenzoylated cation **17** and **15** (eq 9), as indicated by the ^1H and $^{13}C\{^1H\}$ NMR spectra of the reaction mixture (also showing both tautomers of **17**).



(9)

Discussion

The reaction of the 20e complex **2** with O_2 does not involve coordination of O_2 to the sterically and electronically crowded iron center[17] but fast outer-sphere ET due to the exergonicity of eq 10.

$$Fe^0(C_6Me_6)_2 + O_2 \rightarrow [Fe^0(C_6Me_6)_2^+,O_2^-] \qquad (10)$$

Indeed, the difference in redox potentials between the two reversible redox systems [$Fe(C_6Me_6)_2$]$^{0/+}$ and $O_2^{0/-}$ is $\Delta E° = E°_{1/3} - E°_{O_2/O_2^-}$ = 1.37 V[14] − 0.75 V[6] = 0.62 V. The reaction is exergonic by 14.2 kcal mol^{-1} (59.6 kJ mol^{-1}).

According to the Marcus theory,[18] ET (eq 10) should be fast but, in contrast with the ET between [$Fe^ICp(C_6Me_6)$] (**18**) and O_2, it does not proceed at −80 °C, only at −40 °C. The ET of eq 10 is shown by the isolation of the 19e monocation **3**, with peroxide anion resulting from the dismutation of superoxide anion. It is also consistent with the salt effect[19] disrupting the cage of eq 10, as also experienced with **18**.

We observe competition between the cage reaction of superoxide, which deprotonates the 19e cation [$Fe(C_6Me_6)_2$]$^+$, and the escape of superoxide to disproportionate. The latter process is noted at 20 °C, as deprotonation is more difficult than with [$FeCp(C_6Me_6)$]$^+$ (**19**), because of the weaker acidity in the symmetric sandwich. The salt effect markedly accelerates the escape of superoxide from the cage because of double ion exchange, complete inhibition of the cage reaction being noted in the presence of $NaPF_6$ at −40 °C. These mechanistic features leading to the proposed intermediate [$Fe^I(C_6Me_6)(C_6Me_5CH_2)$] (**20**) are summarized in Scheme IV.

The 19e intermediate **20** is not observed, and the ESR spectra taken in the course of the reaction of **2** with O_2 to give **4** show three *g* values of Fe^I species, but their large lattice dependency[20a] does not allow us to obtain more precise structural information beyond that of the oxidation state.

However, we know that **20** is expected to be more reactive toward O_2 than **2** because it is isoelectronic with **18**, which reacts faster than **2** with O_2. A good model of **18** is **7**. The reaction of **7** with O_2 as well as its electronic structure were investigated for this reason. Indeed, the electronic properties of **7** are comparable to those of **18**; it is a Jahn–Teller-active, d^7, 19e Fe^I species (as is **3**).[20] The reversible redox system **6**/**7** has an $E°$ value of −1.45 V vs SCE in DMF at an Hg electrode, intermediate between those of **2** and **18**. Thus, the exergonicity of the reaction of **7** with O_2 is larger than that of **2** with O_2 (ΔE = 0.7 V; 16.1 kcal mol^{-1}; 66.3 kJ mol^{-1}), and indeed, **7** reacts with

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(17) (a) For an excellent study of reactions of ligands with the 20e complex **2**, see ref 10d. The reactions reported in ref 10d are much slower than the reaction of **1** with O_2. (b) For electrochemical data on the complex [$Fe(arene)_2$]$^{2+}$, see: Braitsch, D. M.; Kumarappan, R. *J. Organomet. Chem.* **1975**, *84*, C37.

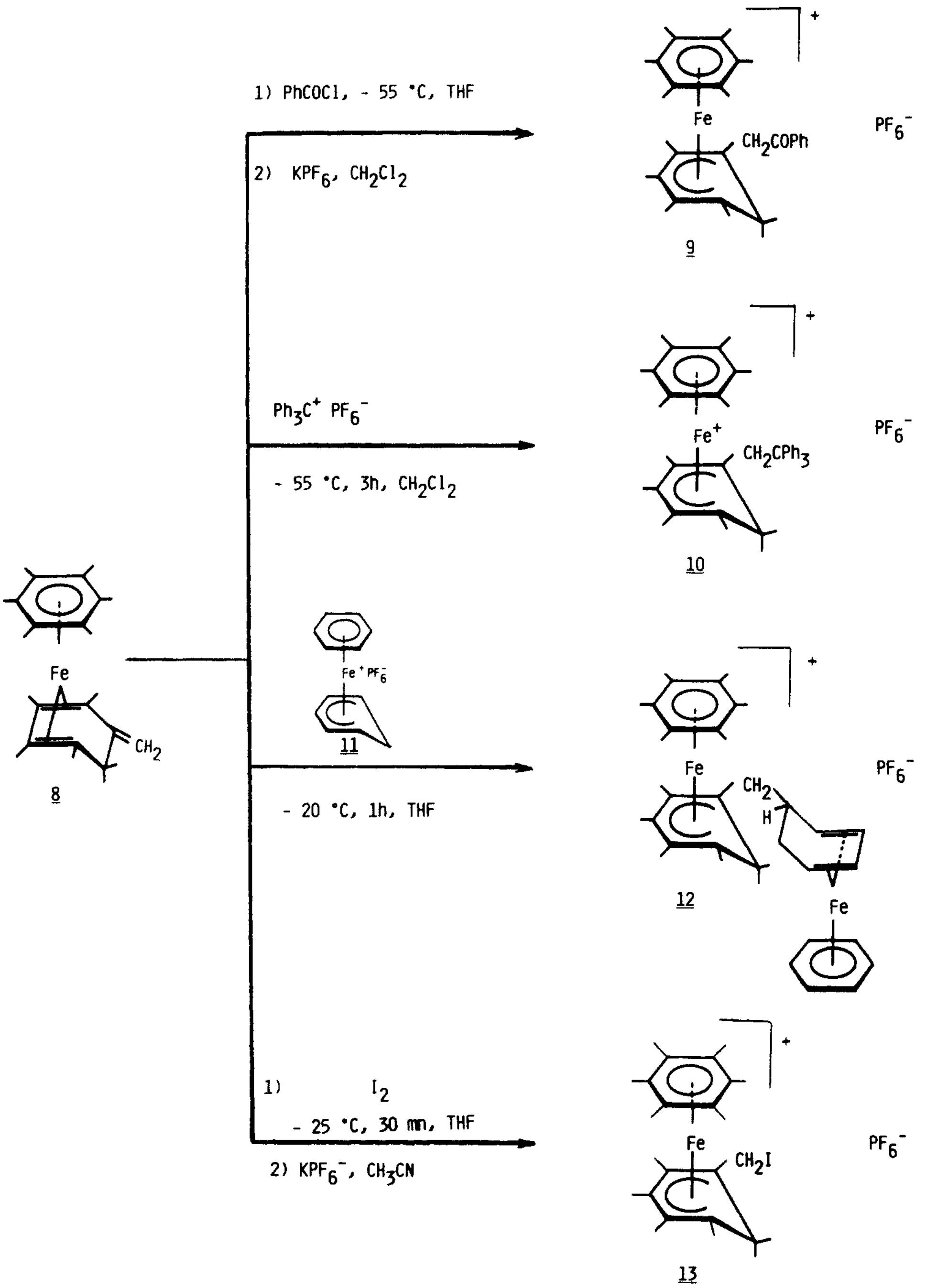
(18) Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 213.

(19) (a) Loupy, A.; Tchoubar, B. *Effets de Sel en Chimie Organique et Organométallique*; Bordas: Paris, 1988. (b) The salt has no effect on ET since the latter is exergonic, but it inhibits the cage reaction. The double ion pair exchange in Scheme IV must also be exergonic, since this exchange produces a pair of small ions [Na^+,O_2^-]. Moreover, Na^+ presumably catalyzes the dismutation of O_2^-: Hamon, J.-R.; Astruc, D. *Organometallics* **1988**, *7*, 1036.

(20) For extensive studies of the electronic structure of Fe^I sandwich complexes 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) Green, J. C.; Kelly, M. R.; Payne, M. P.; Seddon, E. A.; Astruc, D.; Hamon, J.-R.; Michaud, P. *Organometallics* **1983**, *2*, 211. (c) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.

(21) Helling, J. F.; Braitsch, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 7207. Helling, J. F.; Cash, G. G. *J. Organomet. Chem.* **1974**, *73*, C10.

Scheme III



O_2 faster than 1. Since 18 can reasonably be expected to behave like 7, its reaction with O_2 is faster than that of 2, which explains the failure of its isolation or observation. Another interesting comparison of the reactivities of 7 and 20 is the analogy of the reaction products 4 and 8. The observed regiospecificity of the deprotonation of 6 and the cation 21 is opposite to that found by Helling in the reaction of nucleophiles with the complexes [Fe-($C_6H_3Me_3$)(η^5-1,3,5-$Me_3C_6H_3R$)] (21), analogues of 15, later rationalized by Davies in term of charge control.[22,23] Even the deprotonation of 15 follows a regioselectivity similar to that encountered for 6 and 21. The deprotonation of a methyl group in 6, 15, and 21 is not perturbed by steric constraints, in contrast with nucleophilic attack on 15. This regioselectivity, now better explained in terms of orbital control,[8h] is rather favorable in our search for activation and functionalization of aromatics[11,25] since, in the bis(arene)iron series, one of the arene ligands has an ancillary role while multiple functionalization is performed on the other one. The analogy between the mechanism

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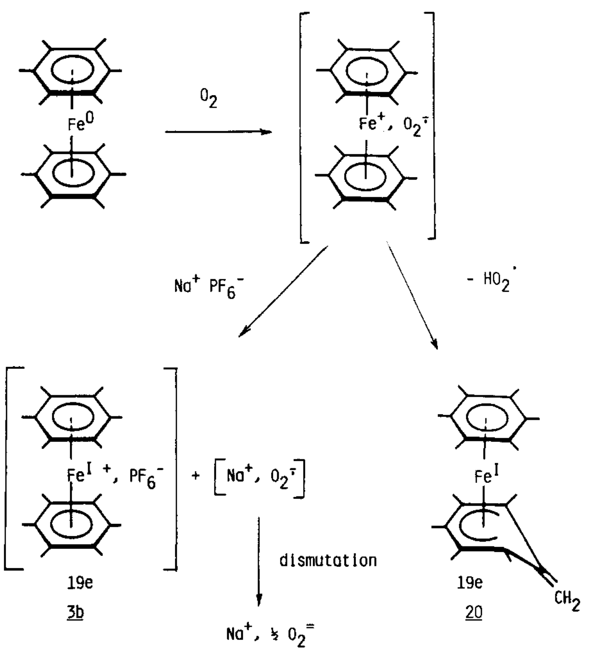
[22] Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. Tetrahedron Report No. 57. *Tetrahedron* **1978**, *34*, 3047.

[23] Davies, S. G. *Organotransition Metal Chemistry: Application to Organic Synthesis*; Pergamon Press: Oxford, England, 1982.

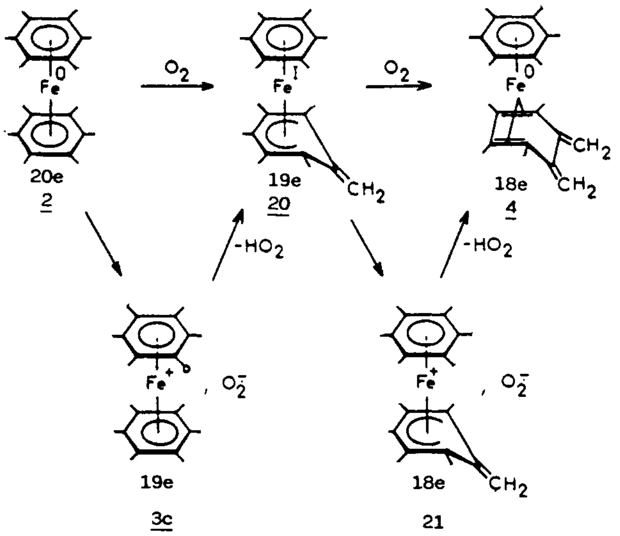
[24] Astruc, D.; Michaud, P.; Madonik, A. M.; Saillard, J.-Y.; Hoffmann, R. *Nouv. J. Chim.* **1985**, *9*, 41.

[25] For strategies by other groups concerning the transition-metal-mediated functionalization of aromatics, see: (a) Semmelhack, M. F. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 36. (b) Jaouen, G. *Ibid.* **1977**, *295*, 59. (c) Kundig, P.; Simmons, D. P. *J. Chem. Soc., Chem. Commun.* **1983**, 1320. (d) Rose-Munch, F.; Rose, E.; Semra, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1108; **1987**, 942. (e) Mutin, R.; Lucas, C.; Thivolk-Cazat, J.; Dufaud, V.; Dany, F.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1988**, 896. (f) Tam, W.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *216*, 97. (g) Brookhart, M.; Lukacs, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161. (h) Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 2388. (i) Hull, J. W.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 1716. (j) Abd-El-Aziz, A. S.; Lee, C. C.; Piorko, A.; Sutherland, R. G. *J. Organomet. Chem.* **1988**, *348*, 95. (k) Cameron, T. S.; Clerk, M. D.; Linden, A.; Sturge, K.; Zawarotko, M. J. *Organometallics* **1988**, *7*, 2571.

Scheme IV



Scheme V

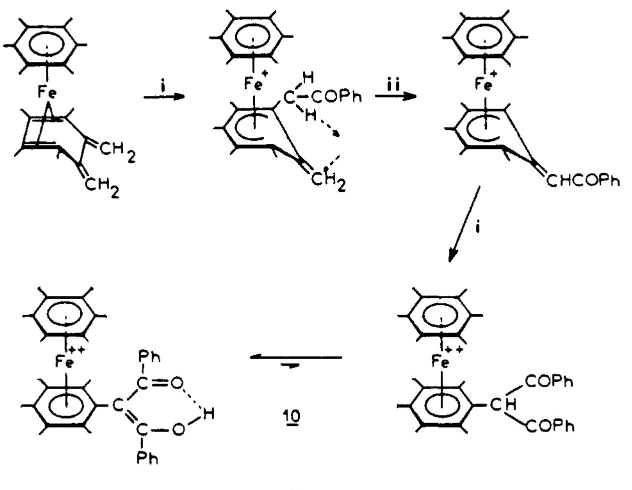


of reaction with O_2 of **7** and **18** (including the acidities of **19**, **6**, and **15**) allows us to extend it to **20** and propose the general Scheme V for the reaction of **2** with O_2, involving ET followed by deprotonation by O_2^- in the cage for each C–H activation step.

The double C–H activation by O_2 in which the key steps are deprotonation in the cage by reactive O_2^- is all the more precious since deprotonation of **1** by bases fails. On the other hand, deprotonation of **19** and **6** is feasible. Both are acidic 18e intermediates in the reactions of O_2 with the 19e complexes **18** and **7**. The ruthenium analogue of **1** $[Ru(C_6Me_6)_2]^{2+}$ was shown by Gladfelter[25i] to react cleanly with bases, giving the ruthenium analogue of **4** by double deprotonation. The reaction of **1** with various bases only gives the ET products **3** and **2**.

The reaction of electrophiles with exocyclic double bonds, which results from C–H activation, can only lead to bond formation if side-ET pathways are avoided[26] by using low-temperature processes for extended periods. The η^4-polyene unit then gives η^5-cyclohexadiene cationic complexes.[26] Yet electron-withdrawing groups such as COPh increase the acidity of the exocyclic protons. Deprotonation can occur intramolecularly by the other basic methylene group in **4**, by the starting material in **16**, or in a subsequent reaction with *t*-BuOK for **8**. In all these cases, double benzoylation can be achieved,[28] but the better control in the reaction of **8** allows isolation of the monofunctionalized complex **9** before it reacts in situ again, potentially opening the route to chiral exocyclic carbon centers. On the other hand, the double benzoylations of **4** and **16** are remarkably comparable (intra- versus intermolecular deprotonation: Scheme VI versus eqs 8 and 9) but the theoretical yield of the intermolecular functionalization of **16** is limited to 50% (formation of **15**), a restriction that does not apply to the intramolecular proton transfer in **4**.

Scheme VI



i, PhCOCl   ii, isomerization

Conclusion

(1) The synthesis of $[Fe(C_6Me_6)_2]$ (**2**) has been improved to make it readily available and isolable. Its Mössbauer spectrum shows a quadrupole doublet with a very negative quadrupole spitting and confirms the 20e configuration with high metal character of the antibonding HOMO.

(2) Double C–H activation by O_2 in the 20e complex **2** occurs efficiently under very mild conditions according to a pathway that consists of ET followed by deprotonation in the cage by $O_2^{\bullet-}$ for each C–H activation step. The Fe^0(*o*-xylylene) complex formed shows an unusual intracyclic coordination[29] to the metal, which leaves two reactive exocyclic double bonds for reactions with electrophiles. In the latter, functionalization is achieved by double carbon–carbon bond formation with benzoyl chlo-

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[26] Compare with the FeCp(arene) series, in which the nucleophilic exocyclic methylene reacts with a large variety of electrophiles but where problems of side ET were also found. For a detailed discussion, see ref 8c.

[27] (a) For a pioneering book on organoiron chemistry, see: *The Organic Chemistry of Iron*; Koerner Von Gustorf, E. A., Grevels, F.-W., Fischler, I., Eds.; Academic Press: New York, 1978. In particular, see the chapter on diene-iron complexes in Vol. I, pp 525–625. (b) Deprotonation of $[Fe(\eta^5\text{-}C_6Me_7)(CO)_3]^+$: Shubin, V. G.; Berezina, R. G.; Piottukh-Peletski, V. N. *J. Organomet. Chem.* **1973**, *54*, 239.

[28] For multiple deprotonation–alkylation sequences, see: (a) Hamon, J.-R.; Saillard, J.-Y.; Le Beuze, A.; McGlinchey, M.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549. (b) Moulines, F.; Astruc, D. *Angew. Chem.* **1988**, *100*, 1394; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1347. (c) Moulines, F.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1989**, 614.

[29] For exocyclic coordination, see: (a) Bennett, M. A.; McMahon, I. J.; Turney, T. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 379. (b) Chapell, C. D.; Cole-Hamilton, D. J.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1982**, 1867.

ride, which gives back the arene-type ligand subsequent to intramolecular proton transfer.

(3) The second C–H activation in the reaction of **2** with O_2 is mimicked by investigation of the 19e complex $[Fe^I(C_6Me_6)(\eta^5\text{-}C_6Me_6H)]$ (**7**), a close model of the transient intermediate **20** resulting from the first C–H activation of **2** by O_2. The electronic structure and the reactivity of **7** with O_2 indicate that **7** and **20**, both 19e Fe^I species, react with O_2 as $[Fe^ICp(C_6Me_6)]$ more rapidly than **2** according to an outer-sphere ET followed by deprotonation by $O_2^{\bullet-}$ in the cage. The clean deprotonation of the 18e cationic precursor **6** of **7** and of the mesitylene analogue **15** is consistent with this mechanism.

(4) The η^4-triene ligands coordinated to Fe^0 by the intracyclic double bonds are clearly related to the *o*-xylylene ligand. Both ligands can react with 2 equiv of electrophile, but stepwise control is better achieved in the former. Addition of a variety of electrophiles leads to carbon–electrophile bond formation if reactions are carried out at low temperature in order to avoid side-ET reactions.

(5) This study shows how to take advantage of ET pathways to activate bonds and how to avoid ET pathways when they impede bond activation or formation. A careful control of the reaction medium (temperature, salt effect) was shown to be necessary in order to drive reactions in the desired way, although the required reaction conditions to activate or form bonds were very mild.

Experimental Section

General Data. All reactions were carried out under an atmosphere of dry N_2 with use of Schlenk techniques and a HE Vacuum Atmospheres Dri-Lab. Reagent grade tetrahydrofuran (THF), dimethoxyethane (DME), diethyl ether, toluene, and pentane were predried over Na foil and distilled from sodium benzophenone ketyl under argon just before use. Benzoyl chloride was purified by using a standard procedure.[30] All other chemicals were used as received. ^1H NMR spectra were obtained with a Varian EM 360 (60-MHz) spectrometer. The low-temperature ^1H NMR spectra and the ^{13}C spectra were recorded at 80 and 20.115 MHz, respectively, in the pulse Fourier transform mode with a Bruker WP 80 spectrometer by Dr. S. Sinbandhit (Centre de Mesures Physiques de l'Ouest (CMPO), Rennes, France). All chemical shifts are reported in parts per million (δ, ppm) relative to Me_4Si. Mass spectra were recorded with a Varian MAT 311 (70-eV) instrument by Dr. P. Guénot (CMPO, Rennes, France). Infrared spectra were recorded with a Pye-Unicam SP 1100 infrared spectrophotometer, which was calibrated with a polystyrene film. Samples were prepared between KBr disks in Nujol or in 0.1 mm thick cells in solutions. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbane, France. In the reaction of O_2 with frozen THF solutions of Fe^0 or Fe^I (containing a salt or not), O_2^- was characterized by ESR spectroscopy as already reported.[20c]

Improved Preparation of $[Fe(C_6Me_6)_2]$ (2). The complex $[Fe^{II}(C_6Me_6)_2]^{2+}(PF_6^-)_2$ (**1**) was synthesized according to the method of Tsutsui and Zeiss[10e] by reaction of $FeCl_2$ with 2 equiv of C_6Me_6 and 2 equiv of $AlCl_3$ in refluxing heptane overnight, followed by hydrolysis at 0 °C, metathesis with aqueous $H^+PF_6^-$, recrystallization from acetone, and drying in vacuo. Complex **1** (2 g, 3 mmol) was stirred at 20 °C with Na/Hg (1%, 70 g, 15 mmol) and 20 mL of distilled dimethoxyethane (DME). The suspension first turned from orange to purple after a few minutes (the 19e complex can be isolated at this time if desired), and stirring was continued for a few hours. When the solution was dark brown, DME was removed in vacuo and **2** was extracted with 3 × 10 mL of distilled toluene. Adding distilled pentane (50 mL) and cooling to −95 °C gave **2** as black crystals (800 mg, 75% yield). The Mössbauer spectra were essentially temperature-independent but appeared as a strongly dissymmetrical doublet because of the texture: IS (vs Fe) = 1.02 mm s^{-1}, QS = −1.35 mm s^{-1} (300 K); IS = 1.20 mm s^{-1}, QS = −1.47 mm s^{-1} (1.7 K). Single ET to **1** or from **2**, giving **3**, was characterized by the Mössbauer spectra of **3** (PF_6 salt, **3b**), at 300 K: IS = 0.82 mm s^{-1}, QS = 0.63 mm s^{-1} (compare **1**: IS = 0.56 mm s^{-1}, QS = 2.06 mm s^{-1} at 300 K). Complex **2** was already reported and characterized by Fischer et al.[10b] and by Brintzinger et al.[10d]

Reaction of O_2 with $[Fe(C_6Me_6)_2]$: Formation of $[Fe^0(C_6Me_6)\{\eta^4\text{-}C_6Me_4(=CH_2)_2\}]$ (4). To complex **2** (95 mg, 0.25 mmol) in 2.5 mL of toluene-d_8 was added O_2 by syringe (5.6 mL, 0.25 mmol) at −50 °C. After a few minutes of stirring at −40 °C, the solution, which was initially brown-black, turned red. This solution was transferred into an NMR tube at −50 °C (complex **4**): ^1H NMR ($C_6D_5CD_3$, −50 °C) δ 5.04 and 4.42 (2 s, 4 H, $=CH_2$), 1.73 (s, 18 H, C_6Me_6), 1.71 (s, 6 H, β-CH_3), 1.15 (s, 6 H, α-CH_3); ^{13}C NMR ($C_6D_5CD_3$, −50 °C) δ 144.8 (s, $C=CH_2$), 90.5 (C_6Me_6), 88.0 (t, $C=CH_2$), 81.6 (β ring C), 59.1 (α ring C), 23.1 (β-CH_3), 14.8 (C_6Me_6); Mössbauer (mm s^{-1} vs Fe, 77 K) IS = 0.43, QS = 1.02.

Complex **2** (418 mg, 1.1 mmol), in 30 mL of toluene, reacted at 0 °C with 7 mL of O_2 (brown solution → purple precipitate). The purple solid was filtered, washed with 2 × 20 mL of toluene and 20 mL of pentane, and dried in vacuo (253 mg, 62% yield of **3a**). Infrared (Nujol): $\nu_{O_2^{2-}}$ = 840 cm^{-1}. The product is insoluble in THF, CH_3COCH_3, and CH_3CN. The cation was identified as **3** by recording the Mössbauer spectrum at 193 K, the latter being identical with that of an authentic sample.[11b] The purity of the samples of **2** and **3** was checked by using the Mössbauer spectra.

Benzoylation of 4. To a red toluene solution of **4** (1-mmol scale), obtained from **2** + O_2 at −40 °C, was added dropwise, at −60 °C, 0.5 mL of PhCOCl (excess). The mixture was warmed up to 20 °C, toluene was removed in vacuo, KPF_6 (380 mg, 2 mmol) and acetone (15 mL) were added, and the mixture was stirred 15 min and then decanted and filtered. Ether was added to the solution, which precipitated **5** as orange microcrystals (720 mg, 98% yield based on **2** titrated with $H^+PF_6^-$). Infrared (KBr): ν_{CO} 1735 cm^{-1}, $\nu_{C=C}$ 1630 (m) cm^{-1}. ^1H NMR (CD_3COCD_3, δ): 7.83 and 5.58 (2 m, 10 H, Ph); 7.15 and 3.31 (2 s, 1 H, OH and CH); 2.60 (s, 18 H, C_6Me_6); 2.77, 2.70, 2.53, 2.49, and 2.43 (5 s, 15 H, CH_3). $^{13}C\{^1H\}$ NMR (CD_3CN, δ): 156.3 ($C(OH)=C<$); 135.8, 133.8, 132.2, 131.2, 130.3, 130.2, 128.8, 127.2 (2 Ph); 107.6 (α ring C); 105.5 (C_6Me_6); 105.4 (β ring C); 104.9 (γ ring C); 104.6 (δ ring C); 101.9 ($C(OH)=C<$); 17.4 (α-CH_3); 16.8 (C_6Me_6); 16.5 (β-CH_3); 16.1 (γ-CH_3). Anal. Calcd for $C_{38}H_{44}F_{12}FeO_2P_2$: C, 51.95; H, 5.05. Found: C, 51.62; H, 5.15.

Preparation of $[Fe(C_6Me_6)(\eta^5\text{-}C_6Me_6H)]$ (7). The precursor $[Fe(C_6Me_6)(\eta^5\text{-}C_6Me_6H)]^+PF_6^-$ ($7^+PF_6^-$) was synthesized according to the reported procedure by reduction of **1** with $NaBH_4$ at 20 °C.[11g] The complex $7^+PF_6^-$ (6.8 g, 12.9 mmol) was stirred for 1 h at 20 °C with the 19e complex $[FeCp(C_6Me_6)]$ (5.46 g, 12.9 mmol) in 10 mL of THF; then the solvent was removed in vacuo and the brown complex **7** was extracted with 3 × 40 mL of pentane and recrystallized from this solvent at −80 °C. After this reaction, the THF-insoluble complex $[FeCp(C_6Me_6)]^+PF_6^-$ was recovered quantitatively. Complex **7** was obtained in 77% yield (3.80 g). Mössbauer parameters (mm s^{-1}): IS = 0.46, QS = 0.91 (293 K); IS = 0.58, QS = 1.04 (77 K). Anal. Calcd for $C_{24}H_{37}Fe$: C, 75.50; H, 9.70; Fe, 14.70. Found: C, 75.10; H, 9.73; Fe, 15.17. UV–visible (pentane): λ = 428 nm; ϵ = 434 L mol^{-1} cm^{-1}. ESR (solid state, 3 K, ν = 9.2483 GHz): g_x = 2.017; g_y = 2.114; g_z = 1.996.

Reaction of O_2 with $[Fe(C_6Me_6)(\eta^5\text{-}C_6Me_6H)]$ (7): Synthesis of 8. To a THF solution (100 mL) of complex **7** (90 mg, 0.24 mmol) was added 2.7 mL of O_2 (0.12 mmol) to give the color change from brown to light red. After removal of THF in vacuo and extraction with 3 × 10 mL of pentane, the red complex **4** was recrystallized from this solvent at −80 °C (80 mg, 88% yield). ^1H NMR (C_6D_6, δ): 4.67, 4.47 (2 s, 2 H, $=CH_2$); 1.88 (s, 18 H, C_6Me_6); 1.73 (s, 3 H, endo-Me); 1.27, 1.18, 1.13, 0.94 (4 s, 13 H, 4 Me, exo-H). ^{13}C NMR (C_6D_6, δ): 157.7 ($C=CH_2$); 92.7 ($C=CH_2$); 91.2 (C_6Me_6); 83.8 (β′-C); 59.0 (β-C); 39.8, 39.4 (α,α′-C); 39.4 (CH–Me); 16.7 (C_6Me_6); 21.7, 20.2, 16.0, 15.6, 13.5 (5 Me). Mössbauer parameters (mm s^{-1}): IS = 0.48, QS = 0.92 mm s^{-1} (293 K). Anal. Calcd for $C_{24}H_{36}Fe$: C, 75.78; H, 9.54; Fe, 14.68. Found: C, 76.09; H, 10.26; Fe, 14.66.

Deprotonation of $[Fe(C_6Me_6)(\eta^5\text{-}C_6Me_6H)]^+PF_6^-$ (6). To complex **6** (1.05 g, 2 mmol) in a THF suspension (30 mL) was

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[30] Perrin, D. D.; Amarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Compounds*; Pergamon: New York, 1966. See also ref 8c.

added freshly sublimed *t*-BuOK (240 mg, 2 mmol) at −90 °C. The color turned light red as the solution became homogeneous upon warming up to −40 °C. After the solution was warmed to 20 °C, THF was removed in vacuo and the solid residue was extracted with 3 × 20 mL of pentane. Recrystallization from this solvent at −90 °C gave complex **8** (370 mg, 97% yield), identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample obtained as above.

Protonation of [Fe(C$_6$Me$_6$){η^4-C$_6$Me$_4$(=CH$_2$)$_2$}] (4) and of [Fe(C$_6$Me$_6$){η^4-C$_6$Me$_5$H(=CH$_2$)}] (8). **4**: To a toluene solution of **4** prepared as above was added, dropwise by syringe, H$^+$PF$_6^-$ in THF. The toluene solution became colorless as **1** precipitated, as characterized by comparison of its ^{1}H NMR spectrum with that of an authentic sample[10e] (335 mg, 50% yield from **2**).

8: To a THF solution of **8** (380 mg, 1 mmol) was added, dropwise by syringe, 0.5 mL of CH$_3$CO$_2$H. After the solution was warmed to 20 °C, THF was removed in vacuo, KPF$_6$ (190 mg, 1 mmol) and 15 mL of CH$_2$Cl$_2$ were added, the mixture was stirred 15 min and then filtered, and ether was added to the solution, which precipitated microcrystalline **6** as the PF$_6$ salt (520 mg, 99% yield), characterized similarly by its ^{1}H NMR spectrum.[11g]

Benzoylation of 8. To a THF solution of **8** (380 mg, 1 mmol) was added dropwise, at −55 °C, 0.5 mL of PhCOCl (excess). The mixture was warmed up to 20 °C, THF was removed in vacuo, KPF$_6$ (190 mg, 1 mmol) and CH$_2$Cl$_2$ (15 mL) were added, and the mixture was stirred 15 min and then decanted and filtered. Ether was added to the solution, which precipitated **9** as carmine red microcrystals (620 mg, 98% yield). ^{1}H NMR (CD$_3$COCD$_3$, δ): 0.95 (s, 3 H, endo Me); 1.26 (m, 4 H, *o*-Me, exo H); 1.83 (s, 3 H, *m*-Me); 1.93 (s, 3 H, *m'*-Me); 2.10 (s, 18 H, C$_6$Me$_6$); 2.60 (s, 3 H, *p*-Me); 3.60 (m, 2 H, CH$_2$); 7.50, 7.90 (m, 5 H, Ph). ^{13}C NMR (CD$_3$CN, δ): 14.1, 14.5, 15.1, 15.6, 16.8 (Me); 16.4 (C$_6$*Me*$_6$); 38.6 (*C*H-CH$_3$ ipso); 39.2 (CH$_2$); 46.3, 51.1 (*o,o'*-dienyl); 93.0, 95.7 (*m,m'*-dienyl); 96.9 (*p*-dienyl); 101.3 (C$_6$Me$_6$); 129.2, 129.9, 134.7, 137.1 (Ph); 195.3 (CO). Infrared (Nujol): $\nu_{C=O}$ = 1690 cm^{-1}. Anal. Calcd for C$_{32}$H$_{41}$F$_6$FeP: C, 59.06; H, 6.55. Found: C, 59.32; H, 6.62.

Reaction of Ph$_3$C$^+$PF$_6^-$ with 8. To a methylene chloride solution of **8** (380 mg, 1 mmol) at −55 °C was added Ph$_3$C$^+$PF$_6^-$ (390 mg, 1 mmol). The reaction mixture was stirred 3 h at −55 °C and then warmed up to 20 °C; after removal of the solvent in vacuo, the residue was dissolved in acetonitrile, the solution was filtered, and slow addition of ether precipitated the red microcrystalline complex **10** (610 mg, 80% yield). ^{1}H NMR (CD$_3$CN, δ): 0.91 (m, 4 H, endo Me, exo H); 1.36, 1.60 (2 s, 5 H, *o*-Me, CH$_2$); 2.06 (s, 3 H, *m*-Me); 2.15 (s, 3 H, *m'*-Me); 2.21 (s, 18 H, C$_6$Me$_6$); 2.38 (s, 3 H, *p*-Me); 7.2–7.4 (m, 15 H, Ph). ^{13}C NMR (CD$_2$Cl$_2$, δ): 13.9, 15.1, 16.8, 18.5 (endo, *o,m,m',p*-Me); 16.2 (C$_6$Me$_6$); 39.4 (ipso *C*HMe); 41.5 (CH$_2$); 47.9, 60.7 (*o,o'*-dienyl); 91.3, 94.9, 96.1 (*m,m',p*-dienyl); 100.2 (*C*$_6$Me$_6$); 126.9, 128.4, 130.2, 147.1 (Ph). Anal. Calcd for C$_{43}$H$_{51}$F$_6$FeP: C, 67.1; H, 6.64. Found: C, 66.7; H, 6.60.

On the other hand, if the reaction mixture was not kept at −55 °C but warmed up to 20 °C over 90 min, **3b** was obtained (260 mg, 50% yield) but not **10**.

Reaction of [Fe(C$_6$H$_6$)(η^5-C$_6$H$_7$)]$^+$PF$_6^-$ (11) with 8. To a THF solution of **8** (380 mg, 1 mmol) at −50 °C was added [Fe(C$_6$H$_6$)(η^5-C$_6$H$_7$)]$^+$PF$_6^-$ (**11**) (360 mg, 1 mmol) with stirring. No reaction appeared to occur below −20 °C. At this temperature, the salt dissolved and reacted (1 h). The reaction mixture was warmed up to 20 °C, filtered, and concentrated, and pentane was added, which precipitated the thermally labile adduct **12** (440 mg, 60% yield) after washing with 4 × 15 mL of ether. The THF-insoluble residue was extracted with acetone and characterized as **3b** (75 mg, 15% yield) by ^{1}H NMR spectroscopy. **12**: ^{1}H NMR (CD$_3$CN, δ) 1.04 (m, 5 H, endo Me, endo diene H), 1.30 (m, 5 H, *o*-Me, exo H, exo diene H), 1.69 (2 s, 5 H, *m*-Me, CH$_2$), 1.79 (s, 3 H, *m'*-Me), 2.07 (s, 18 H, C$_6$Me$_6$), 2.44 (s, 3 H, *p*-Me), 4.51, 4.30, 5.04 (m, 3 H, diene H), 3.36, 3.31 (m, 2 H, diene H), 5.03 (s, 6 H, C$_6$H$_6$); ^{13}C NMR (CD$_2$Cl$_2$, −10 °C, δ) 12.3, 14.0, 14.5, 15.7, 16.2 (endo, *o,m,m',p*-Me), 15.1 (C$_6$*Me*$_6$), 25.0 (CH$_2$), 37.3 (*C*H-Me), 49.3 (*o*-dienyl), 90.7, 93.3, 94.0 (*m,m',p*-dienyl), 98.8 (*C*$_6$Me$_6$), 39.3, 49.5, 67.3 (diene C), 28.7, 23.8 (sp^3 ring C), 89.7 (C$_6$H$_6$).

Contact of a THF solution of **12** with air at 20 °C gave a heterogeneous mixture in 1 min. After removal of THF in vacuo and extraction with acetone, the two cationic complexes [Fe(C$_6$H$_6$)(C$_6$H$_7$)]$^+$PF$_6^-$ (**11**) and **6** were characterized by their ^{1}H NMR spectra (1/1 mixture) subsequent to metathesis with aqueous HPF$_6$.

Reaction of I$_2$ with 8. The slow addition of a THF solution of I$_2$ (300 mg, 1.2 mmol) at −25 °C to a THF solution of **8** (450 mg, 1.2 mmol) at −25 °C immediately gave a precipitate. The mixture was stirred 30 min at −25 °C and then warmed to 20 °C, and THF was recovered in vacuo; KPF$_6$ (225 mg, 1.2 mmol) and acetonitrile were added, and the mixture was stirred 15 min. The mixture was filtered, and slow addition of ether gave the complex **13** as red microcrystals (550 mg, 70% yield). ^{1}H NMR (CD$_3$CN, δ): 1.10, 1.30 (m, 4 H, endo Me, exo H); 1.72 (m, 6 H, *o,m*-Me); 1.81 (s, 3 H, *m*-Me); 2.12 (s, 18 H, C$_6$Me$_6$); 2.48, 2.38 (m, 5 H, *p*-Me, CH$_2$). ^{13}C NMR (CD$_3$CN, δ): 14.3, 15.3, 15.9, 16.3, 17.4 (Me); 25.2 (CH$_2$I); 37.8 (ipso *C*HMe); 49.8, 52.7 (*o,o'*-dienyl); 95.3, 94.4, 95.8 (*m,m',p*-dienyl); 100.9 (*C*$_6$Me$_6$). Anal. Calcd for C$_{24}$H$_{36}$F$_6$FeIP: C, 44.2; H, 5.52; I, 19.49; Fe, 8.59. Found: C, 44.2; H, 5.25; I, 19.43; Fe, 8.04.

If this reaction is carried out with excess I$_2$, it leads to decomposition.

Deprotonation of [Fe^{II}(C$_6$Me$_6$)(C$_6$Me$_5$HCH$_2$X)]$^+$PF$_6^-$ (X = COPh, 9) by [Fe^0(C$_6$Me$_6$){η^4-C$_6$Me$_5$H(=CH$_2$)}] (8). To a THF solution (20 mL) of **8** (380 mg, 1 mmol) at −80 °C was added **9** (630 mg, 1 mmol). The red, heterogeneous mixture was stirred and slowly warmed; it turned brown at −25 °C. THF was removed in vacuo at 0 °C, and the residue was extracted with ether, which gave a birefringent solution (green by reflection, red by transmission) of the complex **14**, thermally unstable at 0 °C. An analogous deprotonated birefringent complex was characterized and reported elsewhere.[11h] Addition of H$^+$PF$_6^-$ in THF of the THF solution of **14** at −80 °C immediately gave back **9** quantitatively. The ether-insoluble residue from the reaction between **9** and **8** was extracted with CH$_2$Cl$_2$, and the extracts were filtered and concentrated; slow addition of ether gave a precipitate of microcrystalline **6** (520 mg, 99% yield) after washing with 2 × 20 mL of ether and drying in vacuo. It was characterized by its ^{1}H NMR and infrared spectra by comparison with those of an authentic sample.

Preparation and Benzoylation of [Fe(C$_6$H$_3$Me$_3$){η^4-C$_6$H$_4$Me$_2$(=CH$_2$)}] (16). To a THF-d_8 suspension of [Fe(C$_6$H$_3$Me$_3$)(η^5-C$_6$H$_4$Me$_3$)]$^+$PF$_6^-$ (**15**) (350 mg, 0.8 mmol), prepared by reaction of [Fe(mesitylene)$_2$]$^{2+}$(PF$_6^-$)$_2$ and 1 equiv of NaBH$_4$ in THF at 0 °C,[11i] was added freshly sublimed *t*-BuOK (95 mg, 0.8 mmol) at −60 °C. The red heterogeneous mixture became homogeneous at −40 °C. The solution of **16** was filtered into an NMR tube at −35 °C. The ^{13}C NMR spectra were recorded at both −35 and −10 °C, but no difference was noted and the spectra were very clean. The complex is thermally unstable at 0 °C. ^{13}C NMR (THF-d_8, δ): 19.6 (arene Me); 21.7 (diene Me); 33.2 (*t*-*Bu*OH); 38.0 (ipso CH$_2$); 55.9, 87.4 (Me—*C*=); 60.8, 77.5 (H*C*=); 85.5 (arene CH); 92.4 (C=*C*H$_2$); 93.3 (arene *C*—Me); 149.5 (*C*=CH$_2$).

To a THF solution of **16** (1 mmol) prepared as above was added 0.5 mL of PhCOCl (excess) at −55 °C with stirring. The reaction was immediate; the mixture was warmed to 20 °C, THF was removed in vacuo, and then K$^+$PF$_6^-$ (190 mg, 1 mmol) and acetone were added. After the mixture was stirred 15 min, filtration, concentration, and slow addition of ether gave 540 mg of the microcrystalline product. The ^{1}H and ^{13}C NMR spectra indicated that this product was a mixture of **15** and the dibenzoylated product **17** in equal amounts. These two PF$_6^-$ salts were not separated. ^{1}H NMR of **17** (CD$_3$COCD$_3$, δ): 1.60 (m, 5 H, *o*-Me, ipso CH$_2$); 2.53 (s, 9 H, C$_6$H$_3$Me); 2.88 (s, 3 H, *p*-Me); 4.60 (m, 2 H, dienyl CH); 5.90 (s, 1 H, enolic H); 5.96 (s, 3 H, C$_6$*H*$_3$Me$_3$); 7.66, 8.15 (m, 10 H, Ph). Infrared (KBr): $\nu_{C=O}$ = 1700 and 1750 cm^{-1}. The reaction products are the same if the order of addition is reversed.

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Note Added in Proof. This series of articles on the functionalization of the complexes $Fe(arene)_2$, which includes ref 11g–i, is dedicated to the memory of Dr. Bianka Tchoubar (deceased April 24, 1990), who hosted D.A. in Sivergue (Provence, France) when ref 11g–i were written up in July 1988. Dr. Tchoubar, an outstanding soul in the French chemistry of this century, has inter alia contributed a book on salt effects[19a] and many stimulating discussions.

Registry No. **1**, 53382-63-1; **2**, 55280-55-2; **3a**, 89278-40-0; **3b**, 53382-61-9; **4**, 89278-41-1; **5**, 127355-88-8; **6**, 81971-77-9; **7**, 81971-78-0; **8**, 89278-52-4; **9**, 127355-91-3; **10**, 127355-95-7; **11**, 65296-91-5; **12**, 127355-97-9; **13**, 127355-93-5; **14**, 127382-92-7; **15**, 125844-92-0; **16**, 127355-89-9; **17**, 127400-45-7; $[FeCp(C_6Me_6)]$, 70414-92-5; $[FeCp(C_6Me_6)]^+PF_6^-$, 53702-66-2.

Notes

Highly Specific, Interligand Triple Hydrogen Migrations Involved in the Formation of C_3H_6 from 1-Heptyne and Bare Iron(I) Cations. A Gas-Phase Analogue of the Crabtree–Felkin Type of CH Bond Activation[†]

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Summary: Fe^+-mediated formation of C_3H_6 from 1-heptyne constitutes a gas-phase analogue of the Crabtree–Felkin mechanism which accounts for the transition-metal-induced activation of alkanes. Extensive labeling studies in conjunction with tandem mass spectrometry and CIDI experiments demonstrate that the C_3H_6 neutral species originates >91% from the *unsaturated* C_3 part of 1-heptyne; in the course of the reaction three hydrogen atoms are transferred from the C_4H_9 alkyl ligand to the C_3H_3 fragment to generate a $Fe(C_3H_6)(C_4H_6)^+$ intermediate, which eventually dissociates to C_3H_6 and Fe(1,3-butadiene)$^+$.

There exists ample experimental as well as theoretical evidence that many unimolecular reactions of organic cations in the gas phase proceed via multistep processes involving ion/dipole complexes as central intermediates,[2] and in the last decade it became obvious that a similar principle is operative in the transition metal ion mediated activation of CH and CC bonds.[3] A typical, well-studied example from our own laboratory[4] is shown in Scheme I: Loss of C_2H_4 from 4-octyne was demonstrated to proceed via complex 3. While the metal ion M^+ (M = Cr, Fe, Co, Ni, Cu) exerts a pronounced effect in determining which of the steps depicted in Scheme I corresponds to the rate-determining step (RDS),[4,5] common to all the organometallic systems 1 studied is the fact that step **2** → 3 is irreversible. Obviously, olefin detachment from 3 is so fast that insertion of ethylene in the M^+–H bond, which would bring about H/D exchange in an isotopomer labeled in the ethyl group, cannot compete with the dissociation of 3. To put this finding in a different, more general, context, the ligands "anchored" at the metal centers of the intermediates 2 and 3 do not communicate with each other.

However, this situation is not always encountered. For example, Jacobson and Freiser[6] demonstrated that the bisligated complex formed in the ion/molecule reaction

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[†] In memoriam Professor J. Charles Morrow, Chapel Hill, NC.

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(2) For pertinent reviews and leading articles, see: (a) Morton, T. H. *Tetrahedron* **1982**, *38*, 3195. (b) McAdoo, D. J. *Mass Spectrom. Rev.* **1988**, *7*, 363. (c) Heinrich, N.; Schwarz, H. In *Ion and Cluster Ion Spectroscopy and Structure*; Maier, J. P., Ed.; Elsevier: Amsterdam, 1989; p 329. (d) Heinrich, N.; Louage, F.; Lifshitz, C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 8183. (e) Hammerum, S. *J. Chem. Soc., Chem. Commun.* **1988**, 858. (f) For an elegant and convincing study on the effects of ion/dipole complexes on the rates of unimolecular dissociation of cations, see: Shao, J.-D.; Baer, T.; Morrow, C. J.; Fraser-Monteiro, M. L. *J. Chem. Phys.* **1987**, *87*, 5242.

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(5) A recent, detailed study (Schulze, C.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.*, in press) reveals the following: For Co^+ and Cu^+ the RDS corresponds to the β-hydrogen transfer **2** → **3**; in distinct contrast, for Fe^+ it is the ligand detachment that is subject to an isotope effect, and for $M^+ = Co^+$ and Ni^+ either step **2** → 3 or **3** → C_2H_4 is associated with a kinetic isotope effect.

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