Activation of a Single Aromatic Ligand in $[Fe(\eta^6\text{-}C_6Me_6)_2]^{2+}(PF_6^-)_2$: Bifunctionalization via Protection by Hydride

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Although most carbanions react with $[Fe(\eta^6\text{-}C_6Me_6)_2]^{2+}(PF_6^-)_2$ (**1**) by electron transfer (ET) without C–C bond formation, functionalization of the C_6Me_6 ligand can proceed via protection by a hydride. Reactions of $PhCH_2MgBr$ and $Li\overline{\mathrm{CHS(CH_2)_3S}}$ with $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_6Me_6H)]^+PF_6^-$ (**2**) proceed smoothly without ET to give $[Fe(\eta^5\text{-}C_6Me_6H)(\eta^5\text{-}C_6Me_6R)]$, R = $PhCH_2$ (**3a**), $\overline{\mathrm{CHS(CH_2)_6S}}$ (**3b**). Deprotection easily proceeds by reaction with $Ph_3C^+PF_6^-$ by exergonic ET, giving the 17e species **3**$^+$ and $Ph_3C^\bullet$ followed by H atom transfer. This finally gives the complexes $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_6Me_6R)]^+PF_6^-$, (**4**; R = CH_2Ph (**4a**), $\overline{\mathrm{CHS(CH_2)_3S}}$ **4b**). Deprotonation of **4a** by KO-*t*-Bu and of **4b** by NaOMe gives the triene complexes $[Fe(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_5R(CH_2))]$ (**5a**,**b**). Benzoylation of **5a**,**b** with PhCOCl on the exocyclic methylene gives $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_6Me_5R(CH_2COPh))]^+PF_6^-$ (**6a**,**b**) after metathesis with $K^+PF_6^-$. Deprotonation of **6a** (R = $PhCH_2$) with use of KO-*t*-Bu gives the conjugated birefringent trienone complex $[Fe(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6Me_5(CH_2Ph)({=}CHCOPh))]$ (**7**), better represented by its zwitterionic mesomer $[Fe^+(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_6Me_5(CH_2Ph)(CH{=}C(O^-)Ph)]$, given the absence of C=O in the infrared spectra. The thermally fragile complex **7** can be benzoylated; it is also cleanly decomposed to the free ligands with use of $Al_2O_3 + O_2$ at 20 °C in ether, giving the pure trienone $[C_6Me_5(CH_2Ph)({=}CHCOPh)]$ (**9**) after chromatography.

Introduction

Activation of aromatics by transition-metal moieties is well-known for $Cr(CO)_3$ complexes.[1] More recently, other transition-metal groups have been used.[2-6] Among these, the dicationic complexes $[Fe(\eta^6\text{-arene})_2]^{2+}$ offer the possibility of double nucleophilic attack, which has indeed proved successful for the syntheses of functional cyclohexadienes.[5,10-12] A major problem in the chemistry of $[Fe(\eta^6\text{-arene})_2]^{2+}$ complexes is that nucleophilic attack by carbanions leads to the synthesis of C–C bonds for the mesitylene complex only.[6] Reactions of carbanions with $[Fe(\eta^6\text{-}C_6R_6)_2]^{2+}$ (R = H, Me) fail in most cases, often giving the electron-transfer (ET) products $[Fe(\eta^6\text{-}C_6R_6)]^{n+}$ (n = 0, 1).[7,8] On the other hand, all kinds of carbanions react with the complexes $[Fe(\eta^6\text{-arene})(\eta^5\text{-cyclohexadienyl})]^+$ to give the formation of C–C bonds.[5-13] Thus, a strategy has been developed to protect the dicationic sandwich complex by nucleophilic reaction with a hydride, which is removed after the nucleophilic attack of the carbanions.[5,11,12] This deprotection reactivates the ligands since the sandwich becomes cationic and a second nucleophilic attack is possible. This is true for the unsubstituted complex (arene = C_6H_6). When the arene is C_6Me_6, the bulk does not allow this second nucleophilic attack on the same ligand.[9,11] Instead, deprotonation of the functionalized ligand is observed, which can be followed by electrophilic functionalization.[9,11] The modified organic structure can be disengaged from the metal after deprotonation.[11] Here, we describe the details of this procedure with mechanistic emphasis on the deprotection, which involves an ET pathway.

Experimental Section

General Data. All reactions were performed under an argon atmosphere by Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere Dri-Lab. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under argon just before use. Aromatic impurities from pentane and hexane were removed by treatment with a sulfuric acid–nitric acid mixture; pentane and hexane were first distilled under argon over potassium hydroxide and then distilled over sodium benzophenone ketyl just before use. Benzene was distilled and stored under argon. Acetonitrile and dichloromethane were dried over P_2O_5, distilled from sodium carbonate, and stored under argon. Aluminum trichloride was sublimed three times. Sodium borohydride and potassium cyanide were dried by standing 15 h at 100 °C and stored under argon. All other chemicals were used as received. The complexes of the series $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-cyclohexadiene})]$ (**3**) were synthesized as previously described.[10] ^1H NMR spectra

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(13) (a) On the other hand, hydrides react with $[Fe(\eta^6\text{-}C_6Me_6)(\eta^5\text{-}C_6Me_6H)]^+$ by an ET pathway.[13b] (b) Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755.

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were obtained with a Varian 360 instrument (60 MHz, FT mode) or a Bruker WH 80 instrument (80 MHz, FT mode). ^{13}C spectra were recorded with a Bruker WP 80 spectrometer (20.115 MHz, FT mode) by Dr. S. Sinbandhit (Centre de Mesures Physiques de l'Ouest, Rennes, France). All chemical shifts are reported in parts per million (δ, ppm) with reference to tetramethylsilane (Me$_4$Si) and were measured relative to the solvent of Me$_4$Si. Mass spectra were recorded with use of a Varian MAT 311 (70 eV) instrument by Dr. P. Guénot (CMPO, Rennes, France). Gas chromatographic (GC) analyses were obtained with a Delsi GC 121 chromatograph equipped with a Hewlett-Packard 3390 integrator by using a glass column (length 1.4 m, i.d. 3 mm) packed with Apiezon L (15%) on Chromosorb WAW. Infrared spectra were recorded with a Pye-Unicam SP 1100 photospectrometer, which was calibrated with a polystyrene film. Elemental analysis were performed by the Centre of Microanalyses of the CNRS at Lyon-Villeurbanne, France. The $E^{1/2}$ potential of **3a**/**3a**$^+$ was recorded vs a SCE reference electrode equipped with a salt bridge (DMF, *n*-Bu$_4$N$^+$BF$_4^-$ 0.3 M) of composition identical with that of the investigated solution. The potential was calibrated vs the reduction wave of [FeCp(C$_6$Me$_6$)]$^+$PF$_6^-$[4b] with use of a Hg electrode.

Preparation of [Fe(η^5-C$_6$Me$_6$H)(η^5-C$_6$Me$_6$R)] (3). (a) 3a, R = CH$_2$Ph. To a cold (−80 °C) THF solution (20 mL) of the Grignard reagent PhCH$_2$MgBr (980 mg, 5 mmol) was added, under argon, the complex [Fe(η^6-C$_6$Me$_6$)(η^5-C$_6$Me$_6$H)]$^+$PF$_6^-$ (**2**; 1.052 g, 2 mmol). The mixture was slowly warmed up to 20 °C. After the solvent was removed in vacuo, the solid residue was dissolved in pentane and the solution was concentrated and cooled down to −30 °C; crystallization gave the orange complex **3a** (660 mg, 70% yield). ^{1}H NMR (C$_6$H$_6$): 1.20 (m, 19 H, *o,o'*-CH$_3$, endo CH$_3$, exo CH); 1.50 (s, 6 H, *m*-CH$_3$); 1.60 (s, 6 H, *m'*-CH$_3$); 1.71 (s, 2 H, CH$_2$); 1.75 (s, 3 H, *p*-CH$_3$); 7.10 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (C$_6$D$_6$): 14.4, 14.9, 15.1, 15.7, 16.3, 16.5, 17.1, 23.2 (*o,o'*-, *m,m'*-, *p,p'*-CH$_3$, endo CH$_3$); 38.1 (CH$_2$); 41.4, 47.3 (*o,o'*-diphenyl); 41.0, 46.6 (ipso, ipso'); 91.0, 93.4 (*m,m'*-dienyl); 91.5, 92.8 (*p,p'*-dienyl); 126.2, 127.6, 128.3, 130.6 (C$_6$H$_5$).

(b) 3b, R = $\overline{\mathrm{CHS(CH_2)_3S}}$. To a THF solution (15 mL) of dithiane (260 mg, 2.2 mmol) under argon at −80 °C was added a 1.6 M hexane solution of butyllithium (1.4 mL, 2.2 mmol). The solution was warmed up to −40 °C, purged three times and warmed up again to −10 °C. After this solution was stirred 0.5 h at −10 °C, it was cooled down to −80 °C[14] and the complex **2** (790 mg, 1.5 mmol) was added under argon. The reaction mixture was then warmed up to 20 °C in 5 h. After THF was removed in vacuo, the orange complex **3b** was recrystallized from pentane at −40 °C (450 mg, 60% yield of orange microcrystals). ^{1}H NMR (C$_6$D$_6$): 1.00 (m, 10 H, *o*-CH$_3$, endo CH$_3$, exo CH$_3$); 1.25 (m, 9 H, *o'*-CH$_3$, endo' CH$_3$); 1.53 (m, 12 H, *m,m'*-CH$_3$); 1.60 (m, 8 H, *p,p'*-CH$_3$, CH$_2$); 2.03 (m, 4 H, CH$_2$); 2.81 (s, 1 H, CH).

Reaction of Ph$_3$C$^+$PF$_6^-$ with [Fe(η^5-C$_6$Me$_6$H)(η^5-C$_6$Me$_6$R)] (3, R = CH$_2$Ph, $\overline{\mathrm{CHS(CH_2)_3S}}$). A CH$_2Cl_2$ solution (20 mL) of the complex **3** was cooled down to −80 °C under argon, and Ph$_3$C$^+$PF$_6^-$ (390 mg, 1 mmol) was added. The greenish stirred reaction mixture was warmed up slowly and turned carmine (the color of **4**) at −50 °C. Warming up to 20 °C was then achieved in 1 h. The solvent was then removed in vacuo, and the solid residue was dissolved in acetonitrile. After filtration and concentration, the cationic complex **4** was crystallized by addition of ether and dried in vacuo.

(a) 4a, R = CH$_2$Ph (550 mg, 90% yield). ^{1}H NMR (CD$_3$COCD$_3$): 1.08 (s, 6 H, *o*-CH$_3$); 1.55 (m, 5 H, endo CH$_3$, CH$_2$); 1.66 (s, 6 H, *m*-CH$_3$); 2.03 (s, 3 H, *p*-CH$_3$); 2.08 (s, 18 H, C$_6$Me$_6$); 6.46, 7.05 (m, 5 H, C$_6$H$_5$). Anal. Calcd for C$_{31}$H$_{43}$FePF$_6$: C, 60.3; H, 7.0. Found: C, 59.9; H, 6.8. The complex could also be made from [Fe(η^6-C$_6$Me$_6$)$_2$] and PhCH$_2$Br.[8]

(b) 4b, R = $\overline{\mathrm{CHS(CH_2)_3S}}$ (550 mg, 85% yield). ^{1}H NMR (CD$_3$COCD$_3$): 1.50 (m, 9 H, OCH$_3$, endo CH$_3$); 1.93 (m, 2 H, CH$_2$); 2.06 (m, solvent + *m*-CH$_3$); 2.26 (s, 18 H, C$_6$*Me*$_6$); 2.50 (m, 4 H, CH$_2$); 2.76 (s, 3 H, *p*-CH$_3$); 3.80 (s, 1 H, *H*CS$_2$). ^{13}C NMR (CD$_3$CN): 14.3 (*o*-CH$_3$); 18.8 (endo CH$_3$); 17.9 (*m*-CH$_3$); 19.5 (*p*-CH$_3$); 16.2 (C$_6$Me$_6$); 26.5 (CH$_2$); 31.5 (s, CH$_2$); 47.3 (*C*-Me ipso); 63.8 (HCS$_2$); 53.9 (*o*-dienyl); 92.3 (*m*-dienyl); 92.6 (*p*-dienyl); 101.9 (C$_6$Me$_6$). IR (KBr): $\nu_{\mathrm{C-S}}$ 905 cm^{-1}.

Preparation of the ESR Samples. [Fe(η^5-C$_6$Me$_6$H)(η^5-C$_6$Me$_6$R)] (1 mmol) was dissolved at −70 °C in CH$_2$Cl$_2$ (10 mL) and transferred to an ESR tube containing 30 mg of Ph$_3$C$^+$PF$_6^-$ (slight excess of the latter). The tube was warmed up to 0 °C with stirring; then, after a slight color change, it was cooled down in a liquid-nitrogen bath and stored until the ESR spectrum was recorded.

Deprotonation of [Fe(η^6-C$_6$Me$_6$)(η^5-C$_6$Me$_6$R)]$^+$ (4). KO-*t*-Bu (170 mg, 1.5 mmol) was added to a THF suspension (20 mL) of [Fe(η^6-C$_6$Me$_6$)(η^5-C$_6$Me$_6$CH$_2$Ph)]$^+$ (**4a**; 616 mg, 1 mmol) at −80 °C under argon and the mixture stirred. The reaction mixture was warmed up and, at −40 °C, the solution became transparent while turning red. The red solution was warmed up to 0 °C, THF was removed in vacuo, and the red solid was dissolved in pentane. After filtration and concentration, crystallization at −40 °C gave the red microcrystalline complex [Fe(η^6-C$_6$Me$_6$)(η^4-C$_6$Me$_5$-(CH$_2$Ph)(=CH$_2$))] (**5a**; 460 mg, 97% yield). ^{1}H NMR (C$_6$H$_6$): 0.84, 1.00, 1.38, 1.48, 1.56 (5 s, 5 × 3 H, CH$_3$, diene); 1.83 (s, 18 H, C$_6$Me$_6$); 2.29 (d, 1 H, $^2J_{\mathrm{H-H}}$ = 13 Hz, CH$_2$Ph); 2.62 (d, 1 H, $^2J_{\mathrm{H-H}}$ = 13 Hz, C*H*$_2$Ph); 4.36, 4.55 (2 s, 2 × 1 H, C=C*H*$_2$); 7.03 (m, 5 H, C$_6$H$_5$). ^{13}C NMR (C$_6$D$_6$): 14.3, 14.7, 17.6, 19.1, 28.5 (CH$_3$ diene); 46.4 (ipso C, diene); 47.3 (*C*H$_2$Ph); 55.7, 55.9 (α-C, diene); 82.0, 84.1 (β-C, diene); 91.1 (C$_6$Me$_6$); 91.5 (C=CH$_2$, exo); 125.5, 127.3, 130.8, 141.9 (*C*$_6$H$_5$); 15.9 (C$_6$*Me*$_6$). Anal. Calcd for C$_{31}$H$_{42}$Fe: C, 79.1; H, 8.9. Found: C, 78.7; H, 8.5. IR (Nujol): $\nu_{\mathrm{C=C}}$ = 1600 cm^{-1}, $\nu_{\mathrm{C-H(arom)}}$ = 3080 cm^{-1}.

The complexes **4b** was similarly deprotonated with use of NaOMe and subsequently benzoylated (vide infra), although it was not characterized otherwise.

Benzoylation of [Fe(η^6-C$_6$Me$_6$)(η^4-C$_6$Me$_5$R(CH$_2$))] (5). (a) R = CH$_2$Ph. PhCOCl (0.5 mL, excess) was added to a THF solution (20 mL) of **5a** (R = CH$_2$Ph; 470 mg, 1 mmol) at −80 °C. The mixture was stirred and warmed up; at −50 °C, a precipitate appeared and the solution turned light red. At 20 °C, THF was removed in vacuo and KPF$_6$ (190 mg, 1 mmol) and CH$_2$Cl$_2$ were added with vigorous stirring. The mixture was filtered, and ether was progressively added, which led to the crystallization of **6a** (700 mg, 97% of microcrystals after washing with ether and drying in vacuo). ^{1}H NMR (CD$_3$CN): 0.90 (s, 3 H, endo CH$_3$); 1.40, 1.64, 1.73, 2.02 (4 s, 4 × 3 H, CH$_3$ dienyl); 2.12 (m, 2 H, C*H*$_2$Ph); 2.19 (s, 18 H, C$_6$Me$_6$); 3.08 (d, 1 H, $^2J_{\mathrm{H-H}}$ = 17.6 Hz, CH$_2$CO); 4.24 (d, 1 H, $^2H_{\mathrm{H-H}}$ = 17.6 Hz, CH$_2$CO); 6.84 (m, 2 H, *o*-C$_6$*H*$_5$-CO); 7.13, 7.67 (2 m, 6 H, *m,p*-C$_6$H$_5$); 8.10 (m, 2 H, *o*-C$_5$*H*$_5$CH$_2$). ^{13}C NMR (CD$_3$CN): 14.2, 14.6, 15.0, 15.3, 25.9 (CH$_3$); 16.2 (C$_6$*Me*$_6$); 40.5 (CH$_2$Ph); 47.1 (ipso C); 49.5 (*C*H$_2$CO); 53.1, 55.6 (*o,o'*-dienyl); 92.9, 93.1 (*m,m'*-dienyl); 94.9 (*p*-dienyl); 101.3 (*C*$_6$Me$_6$); 126.9, 128.6, 129.1, 129.0, 131.2, 134.6, 137.5, 139.4 (*C*$_6$H$_5$); 197.4 (C=O). IR (KBr): $\nu_{\mathrm{C=O}}$ = 1700 cm^{-1}; $\nu_{\mathrm{C-H(arom)}}$ = 3080 cm^{-1}.

(b) R = $\overline{\mathrm{CHS(CH_2)_3S}}$. The same procedure as in (a) with 1 mmol of **5b** gave a 78% yield of **6b** as a BF$_4^-$ salt after metathesis with aqueous H$^+$BF$_4^-$ added to an acetone solution of [Fe(η^6-C$_6$Me$_6$)(η^5-C$_6$Me$_5$R(CH$_2$COPh)]$^+$Cl$^-$. ^{1}H NMR (CD$_3$COCD$_3$): 1.45 (s, 3 H, CH$_3$); 1.51 (s, 3 H, CH$_3$); 1.91 (m, 5 H, *p*-CH$_2$ dithiane, CH$_3$); 2.32 (s, 18 H, C$_6$Me$_6$); 2.35 (3 H, CH$_3$); 2.45 (m, 9 H, δ CH$_2$, CH$_3$, CH$_2$COPh); 3.71 (s, 1 H, CHS). ^{13}C NMR (CD$_3$CN): 14.4, 17.9, 18.8, 18.9 (CH$_3$); 16.6 (C$_6$*Me*$_6$); 26.6 (*C*H$_2$ dithiane); 31.6 (*C*H$_2$S); 40.0 (ipso *C*); 41.8 (*C*H$_2$CO); 63.8 (HCS$_2$); 54.1 (*o,o'*-dienyl); 92.2 (*m,m'*-dienyl); 92.6 (*p*-dienyl); 101.5 (*C*$_6$Me$_6$); 127.4, 128.9, 130.9, 147.9 (*C*$_6$H$_5$); 195.0 (C=O). Anal. Calcd for C$_{35}$C$_{47}$BF$_4$FeOS$_2$: C, 61.0, H, 6.82; S, 9.29. Found: C, 60.9; H, 6.85; S, 8.95. IR (KBr): $\nu_{\mathrm{C=O}}$ = 1700 cm^{-1}.

Deprotonation of [Fe(η^6-C$_6$Me$_6$)(η^5-C$_6$Me$_5$R-(CH$_2$COPh))]$^+$PF$_6^-$ (R = CH$_2$Ph, 6a). To a suspension of **6a** (360 mg, 0.5 mmol) in 20 mL of THF was added KO-*t*-Bu (70 mg, 0.6 mmol) under argon, and the mixture was stirred at −80 °C. The medium immediately became green. At −70 °C, the solution was dark green by reflection, whereas it was deep red by transmission (λ_{max} = 583 nm). The solution was warmed up to 20 °C, THF was removed in vacuo, the solid residue was dissolved in pentane, and the solution obtained was filtered, concentrated, and cooled down to −20 °C, which afforded the crystallization of a deep green microcrystalline solid. Yields varied from 50% to 90%, depending on the rapidity of this workup procedure when

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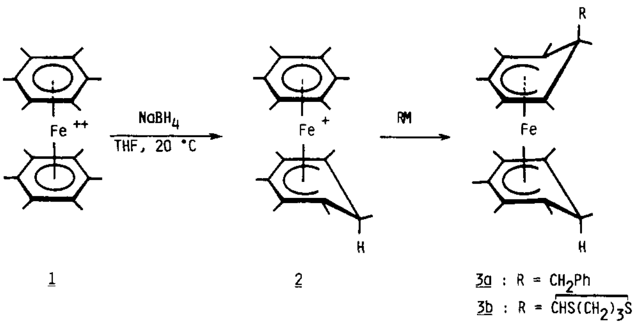
Scheme I



the latter was effected at 20 °C. The green complex 7 was washed with pentane at −50 °C and dried in vacuo. The thermal stability of 7 was weak at 20 °C. The ^{1}H NMR spectrum was recorded rapidly at 20 °C under argon in CH_3CN with use of a fresh sample. After 5 min, decomposition occurred and obtainment of the ^{13}C NMR spectrum failed with various solvents at low temperatures and finally succeeded with CD_2Cl_2 at −10 °C. After 4 h at −10 °C, the medium became paramagnetic, however. Before this ^{13}C spectrum was recorded, the solution was quickly filtrated on alumina at −10 °C for purification. ^{1}H NMR (CD_3CN): 0.87, 0.92, 1.17, 1.21, 1.31 (5 s, 5 × 3 H, CH_3 diene); 1.76 (s, 18 H, C_6Me_6); 2.46 (d, 1 H, $^2J_{\text{H-H}}$ = 12.4 Hz, CH_2Ph); 3.86 (d, 1 H, $^2J_{\text{H-H}}$ = 12.4 Hz, CH_2Ph); 6.18 (s, 1 H, C=CH); 6.98, 7.23 (2 m, 2 × 5 H, C_6H_5). ^{13}C NMR (CD_2Cl_2, −10 °C): 14.6, 15.1, 15.9, 18.1, 26.0 (CH_3, diene); 15.6 (C_6Me_6); 44.0 (CH_2Ph); 46.6 (ipso C, diene); 66.2, 68.9 (α-C diene); 85.8, 86.9 (β-C diene); 93.5 (C_6Me_6); 96.6 (C=CH_2, exo); 125.3, 127.1, 128.2, 128.9, 130.6, 141.9, 146.2 (C_6H_5); 142.8 (C=CH_2); 180.9 (C=O). Infrared spectra were recorded in ether, acetonitrile, and dichloromethane solutions, as a Nujol suspension, and in a KBr matrix. Between 1500 and 2900 cm^{-1}, only $\nu_{C=C}$ was observed at 1620 cm^{-1} (no ν_{O-H}). Mass spectrum: *m*/*e* 266 (($C_6Me_2CH_2COPh)^+$), 162 (($C_6Me_6)^+$), 91 (($C_6H_5CH_2)^+$) 56 ((Fe)$^+$).

Decomplexation of 7 and Preparation of 9. Photolysis of 7 for 20 min at 254 nm did not give any color change, and the reaction of 7 with O_2 at 20 °C did not have any significant effect. Prolabo alumina (5 g), predried at 150 °C overnight in vacuo, was added to an ether solution (400 mL) of **7** (290 mg, 0.5 mmol) under a pure O_2 atmosphere. The green solution immediately turned pale yellow, and the alumina took an orange color. The mixture was filtered, and the alumina was washed with ether. The solution obtained was then evaporated and the yellow residue extracted with pentane, while most white C_6Me_6 remained insoluble. The pentane solution was filtered and concentrated, and **9** was separated from residual C_6Me_6 by thin-layer chromatography on silica plates (1-mm thickness) with pentane as the eluent (R_f: **9**, 0.60; C_6Me_6, 1). Extraction of **9** from silica with use of ether, filtration, and removal of ether in vacuo gave yellow crystals of **9** (mp 28–30 °C; 140 mg, 80% yield). ^{1}H NMR (C_6D_6): 1.58 (m, 6 H, CH_3); 2.05 (s, 3 H, CH_3); 2.08 (s, 3 H, CH_3); 2.12 (s, 3 H, CH_3); 2.52 (d, 1 H, $^2J_{\text{H-H}}$ = 12.9 Hz, CH_2Ph); 2.85 (s, 1 H, $^2J_{\text{H-H}}$ = 12.9 Hz, CH_2Ph); 6.00 (s, 1 H, C=CH); 7.07, 7.70, 7.90 (3 m, 10 H, C_6H_5). ^{13}C NMR (C_6D_6): 20.6, 27.3, 28.9 (CH_3); 54.6 (CH_2Ph); 69.8 (ipso C, diene), 125.1 (C=CH); 123.9, 126.4, 127.6, 128.4, 128.5, 128.8, 129.9 (C_6H_5), diene); 155.9 (C=CH); 201.8 (C=O). IR (film): $\nu_{C=O}$ 1695 cm^{-1}; $\nu_{C=C}$ = 1595, 1610 cm^{-1}. Mass spectrum: *m*/E 356 ((M)$^+$), 265 ((M − CH_2Ph)$^+$), 251 ((M − COPh)$^+$), 91 ((PhCH_2)$^+$).

Benzoylation of [Fe(η^6-C_6Me_6)(η^4-C_6Me_5R(CH=COPh))] (7, R = CH_2Ph). PhCOCl (0.5 mL, excess) was progressively added to the complex 7 (R = CH_2Ph; 574 mg, 1 mmol) in THF at −80 °C with stirring. The reaction was immediate (precipitation), and the mixture was warmed up to 20 °C. After THF was removed in vacuo, 190 mg of KPF_6 and CH_2Cl_2 were added with stirring. The mixture was filtered, the solution was concentrated, and progressive addition of ether provided the crystallization of complex 8 (750 mg, 91% yield). ^{1}H NMR (CD_3CN): 0.91 (s, 3 H, endo CH_3); 1.62 (s, 6 H, CH_3 dienyl); 1.96 (s, 3 H, CH_3 dienyl); 2.10 (m, 5 H, CH_3 dienyl, CH_2Ph); 2.16 (s, 18 H, C_6Me_6); 5.95 (s, 1 H, OH); 6.57, 7.00, 7.42, 7.84 (4 m, 15 H, C_6H_5). ^{13}C NMR (CD_6CN): 14.6, 14.7, 15.9, 17.3, 25.3 (CH_3 dienyl); 16.2 (C_6Me_6); 49.1, 50.3 (ipso C, CH_2Ph); 54.6, 57.7 (*o*,*o*′-dienyl); 92.6, 93.9 (*m*,*m*′-dienyl); 94.6 (*p*-dienyl); 101.5 (C_6Me_6); 115.0 (C=CPh); 125.9, 127.3, 128.9, 130.0, 130.2, 131.1, 135.5, 138.4 (C_6H_5); 151.1 (=COH); 165.9 (C=O). Anal. Calcd for $C_{38}H_{45}F_6FeO_2P$: C, 62.1; H, 6.13. Found: C, 61.7; H, 6.04. IR (KBr): $\nu_{C=O}$ 1700 cm^{-1} (b); $\nu_{C=C}$ 1600 cm^{-1}.

Results and Discussion

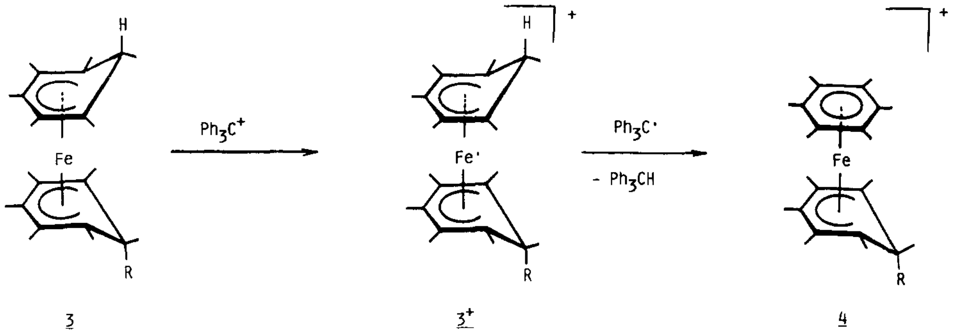
Addition of a Carbanion on 2. The complex [Fe(η^6-C_6Me_6)(η^5-C_6Me_6H)]$^+PF_6^-$ (**2**) is accessible from [Fe(η^6-$C_6Me_6)_2]^{2+}(PF_6^-)_2$ (**1**) and $NaBH_4$. It reacts with Grignard and lithium reagents without side ET; thus, the reaction with $PhCH_2MgBr$ and Li$\overline{\mathrm{CHS(CH_2)_3S}}$ gave dissymmetric bis(cyclohexadienyl) complexes in good yields. The complexes [Fe$^{\mathrm{II}}$(η^5-C_6Me_6H)(η^5-C_6Me_6R)], R = CH_2Ph (**3a**), $\overline{\mathrm{CHS(CH_2)_3S}}$ (**3b**), are thermally stable orange solids that are moderately air-sensitive (Scheme I). Addition of carbanions to 2 occurs on the arene ligand rather than on the cyclohexadienyl one. Addition of 2 equiv of hydride or of 2 equiv of methamide to 1 gives complexes of the type [Fe(η^6-C_6Me_6)(η^4-$C_6Me_6R_2$)], R = exo H or Me, resulting from the attack of the nucleophiles on the same ring[7] as in the parent series.[9,10] Thus, the addition of larger nucleophiles on the arene ring of complex 2 is due to the conjugated steric bulk of the nucleophile and of the methyl groups. Otherwise, the dominating orbital control is in favor of the attack on the same ring in most cases[10] (cited above). The influence of the bulk reverses the reactivity of the rings as in the mesitylene series.[6]

Hydride Transfer via an ET Pathway. Since the regioselectivity was oriented in this way, the strategy used in the parent benzene series, e.g. deprotection followed by attack of a second carbanion, would be of no interest because it would give bis(cyclohexadienyl) complexes. Instead we attempted to deprotonate the substituted cyclohexadienyl ligand in order to make substituted trienes.

The first step involves, as in the parent series, removal of a hydride from **3a,b** (Scheme II).

The *direct* removal of H$^-$ by Ph_3C^+ does not work in substituted cyclohexadienyl complexes, whereas it works in the nonsubstituted series.[15a] Steric arguments have

Scheme II



been invoked, but the problem can be circumvented first by removal of an electron followed by removal of a H atom. Permethylated neutral sandwiches are relatively electron-rich, although the valence shell of the metal bears only 18 valence electrons. Indeed, the thermodynamic redox potential $E°$ of the couple **3a**/**3a**$^+$ is -0.5 V vs SCE in DMF at a Hg cathode (0.1 V s^{-1}, $\Delta E_p = 0.12$ V, $i_a/i_c = 0.8$, 20 °C). Moreover, the reversibility of the system shows that **3**$^+$ is relatively stable. Since the redox potential of $Ph_3C^+/Ph_3C^•$ is +0.3 V vs SCE,[15b] ET between **3** and Ph_3C^+ is exergonic and thus fast. For the conditions under which the reaction occurs (THF), the decomposition of **3**$^+$ is even slower than in DMF, the solvent used in electrochemistry. In the parent series, the reaction between Ph_3C^+ and the neutral iron complex also proceeds by an ET pathway but the reaction medium had to be kept at -40 °C for 2 h in order to prevent the decomposition of the 17e radical cation before H atom transfer. In the present C_6Me_6 series, such care is not necessary, given the sufficient stability of the 17e species **3a,b**$^+$. Thus, reactions between **3a,b** and $Ph_3C^+PF_6^-$ proceed smoothly. When the reaction medium is warmed up from -80 to 20 °C in 40 min, a color change from dark brown to red occurs between -50 and -20 °C and the functional cationic complexes can be isolated in good yield. These complexes were thermally stable and not air-sensitive; they were characterized by using standard techniques, showing that only H is removed, not R. The mechanism of this reaction was investigated by using ESR spectroscopy; ESR spectra were recorded during the course of the reaction. When the reaction started, an ESR sample was taken and frozen down to -140 °C for recording. This spectrum showed the signals of both paramagnetic species (Figure 1), (i) the iron-centered and (ii) the carbon-centered radicals (**3a**$^+$, $g_\parallel = 2.130$, $g_\perp = 2.176$; Ph_3C^+, $g = 2.002$). When the spectrum was recorded at -50 °C, the iron radical predominated $g_{iso} = 2.100$), and at 20 °C, there was almost no iron radical left ($g_{iso} = 2.115$).

The radical $Ph_3C^•$ is also in equilibrium with its dimer, the monomeric form being favored as the temperature is raised (1% at 20 °C, eq 1).[15c]

$$2Ph_3C^• \rightleftharpoons (Ph_3C)_2 \qquad (1)$$

Deprotonation of Hexamethylcyclohexadienyl Complexes and Benzoylation of η^4-Triene Fe^0 Complexes. The deprotonation in exocyclic positions of alkyl substituents of polyhapto ligands in cationic complexes is a well-known consequence of the delocalization of the cationic charge in the β-position from the metal center.[16] The present case parallels the known precedent of the deprotonation in the isoelectronic [FeCp(arene)]$^+$ series.[17] In the latter series, single deprotonation gives a cyclohexadienyl ligand with an exocyclic methylene group[18] and double deprotonation from two other methyl groups gives the *o*-xylylene ligand (which has two exocyclic methylene groups[8]). These exocyclic methylene groups can be alkylated or acetylated either in situ or in steps, and multiple deprotonation-alkylation (or acylation) sequences are also known.[8,19] We took advantage of this property for the second functionalization of the C_6Me_6 ligand of **1**.

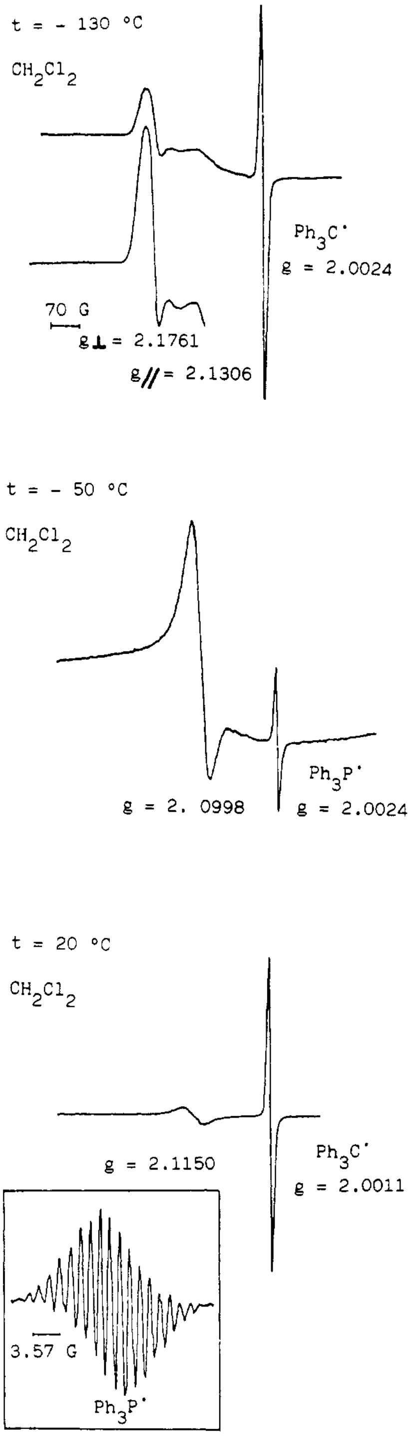


Figure 1. Monitoring of the reaction of $Ph_3C^•$ with [Fe(η^5-C_6Me_6H)(η^5-$C_6Me_6CH_2Ph$)] by ESR spectroscopy at different temperatures.

Complexes **4a,b** react with an alcoholate in THF suspension near -50 °C to give the blood red neutral complexes **5a,b** (eq 2).

Complex **5a** could be crystallized in high yield and was fully characterized by using standard techniques. The carbons of the exocyclic double bond are found at δ 159

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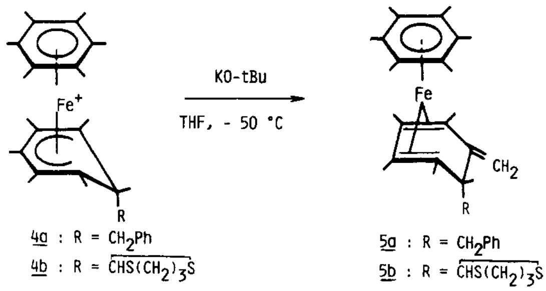
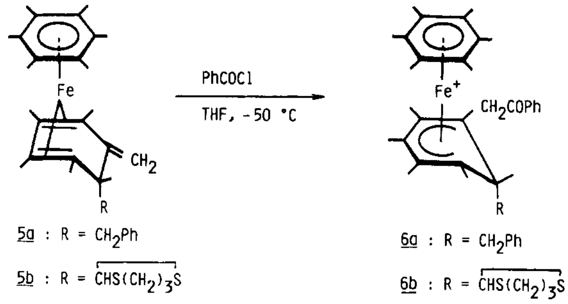


(2)

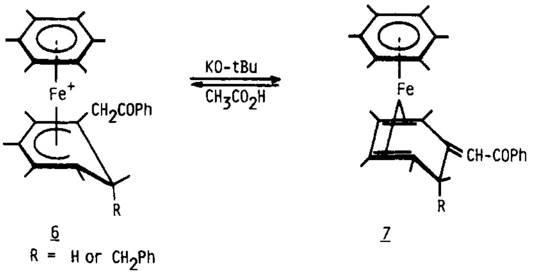
and 91 ppm (CH_2) in the ^{13}C NMR spectrum.

Complexes **5a,b** react with PhCOCl in THF near −50 °C to cleanly give the single benzoylation products **6a** and **6b**, which are crystallized as PF_6^- salts in high yields after metathesis with KPF_6 in CH_2Cl_2 (eq 3). The carmine complexes **6** are thermally stable and not air-sensitive. They show the characteristic trends of $[Fe(\eta^6\text{-arene})(\eta^5\text{-cyclohexadienyl})]^+$ complexes in ^1H NMR and ^{13}C NMR spectra, and the infrared spectra exhibit the expected carbonyl stretch at ν_{CO} = 1700 cm^{-1}.



(3)

Similarly, the complexes **6** (R = H, CH_2Ph) were deprotonated by reaction with 1 equiv of KO-*t*-Bu in THF at −80 °C. The reaction took only a few seconds at −80 °C and gave the birefringent complexes **7** (dark green by reflection and red by transmission: note the difference of color from that of **5** due to the conjugated carbonyl group). Thus, this deprotonation was faster than that of **5** because the exocyclic position was much more acidic due to the presence of the benzoyl group. The complexes **7** could be protonated in situ at −80 °C by reaction with CH_3CO_2H to give back **6** (eq 4).

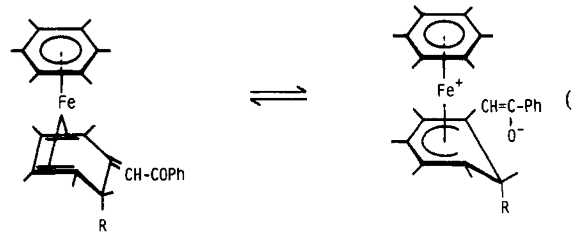


(4)

In contrast to the case for **5**, the complexes **7** were thermally labile. However, **7a** (R = CH_2Ph) could be crystallized at −20 °C to give dark green microcrystals, for which a ^{13}C NMR spectrum could be recorded in CD_2Cl_2 at −10 °C (Figure 2).

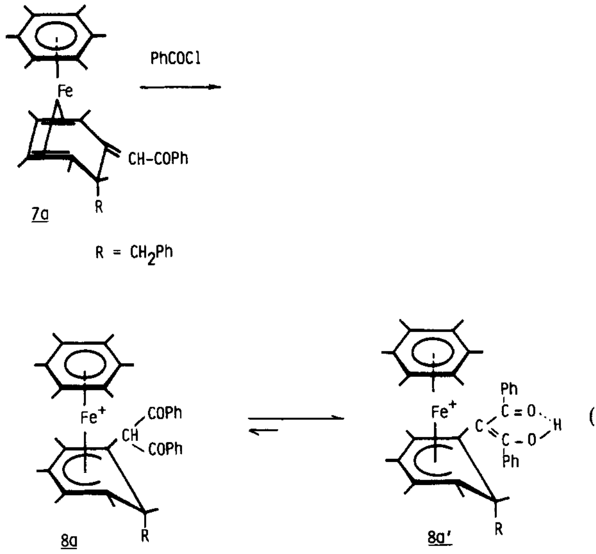
The CO stretch expected at 1700 cm^{-1} as in the other benzoylated compounds was never observed, whatever the nature of the sample. No OH stretch was observed as well. Thus, one must conclude that the zwitterionic enolate form predominates in **7** (eq 5).

In the mass spectrum of **7a**, the molecular peak was not obtained due to its thermal instability. However, the fragment at *m/e* 266 corresponding to $C_6Me_5CH_2COPh$ was observed.



(5)

The complex **7a**, as indicated by its protonation with CH_3CO_2H, was reactive toward electrophiles. Thus, reaction with PhCOCl in THF proceeded at −80 °C to give a second benzoylation of the exocyclic double bond (eq 6).



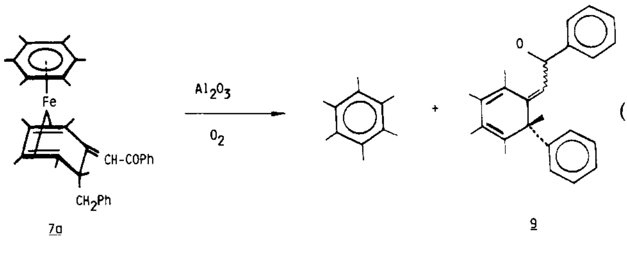
(6)

The red cation formed quantitatively was thermally stable and not air-sensitive. It was crystallized as the PF_6 salt **8a** after metathesis with KPF_6.

The infrared spectrum of **8a** ($\nu_{C=O}$ = 1700 cm^{-1} and $\nu_{C=O}$ = 1600 cm^{-1}) and its ^1H NMR and ^{13}C NMR spectra suggest that the enolic tautomer **8a′** predominates in the mixture **8a**/**8a′**. Indeed, the OH proton is located at 5.95 ppm in the ^1H NMR spectrum and the exocyclic carbon is located at 151 ppm in the ^{13}C NMR spectrum.

Thus, the three hydrogens are removed from the methyl group of the hexamethylcyclohexadienyl ligand of complex **2**. This transformation compares with the double benzoylation of the *o*-xylylene ligand obtained by double H atom abstraction by O_2 in the 20e complex $[Fe(\eta^6\text{-}C_6Me_6)_2]$.[8] The same substituents are obtained in both cases, but in the latter one, aromaticity and hexahapticity were recovered.

Decomplexation. The clean decomplexation of **7a** was attempted by various means in order to disengage the bifunctional ligand from the metal complex. Reactions with $FeCl_3$ or O_2 and UV photolysis did not give significant results. A clear reaction was obtained by mixing an ether solution of **7a** with activated Al_2O_3 under an O_2 atmosphere. This reaction was immediate and provided the desired free organic trienone **9** as light yellow crystals after chromatographic separation (eq 7).



(7)

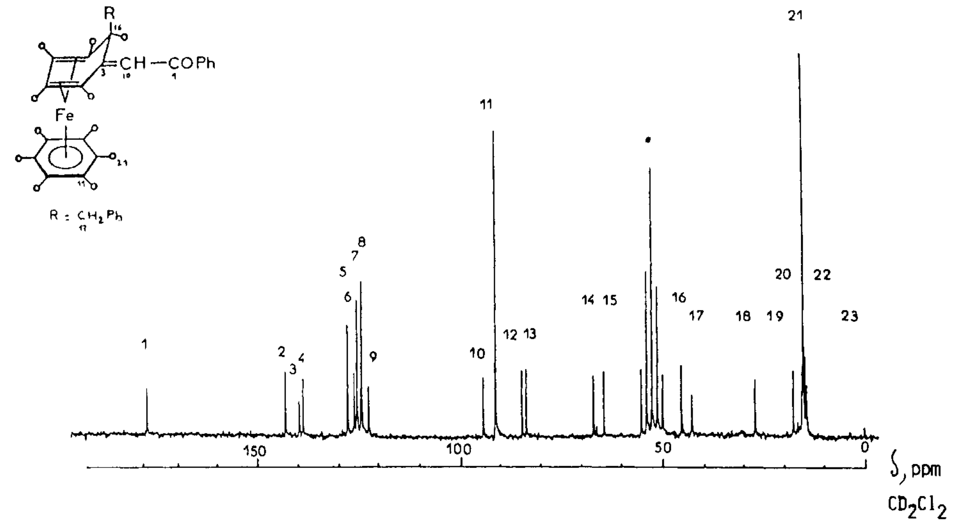
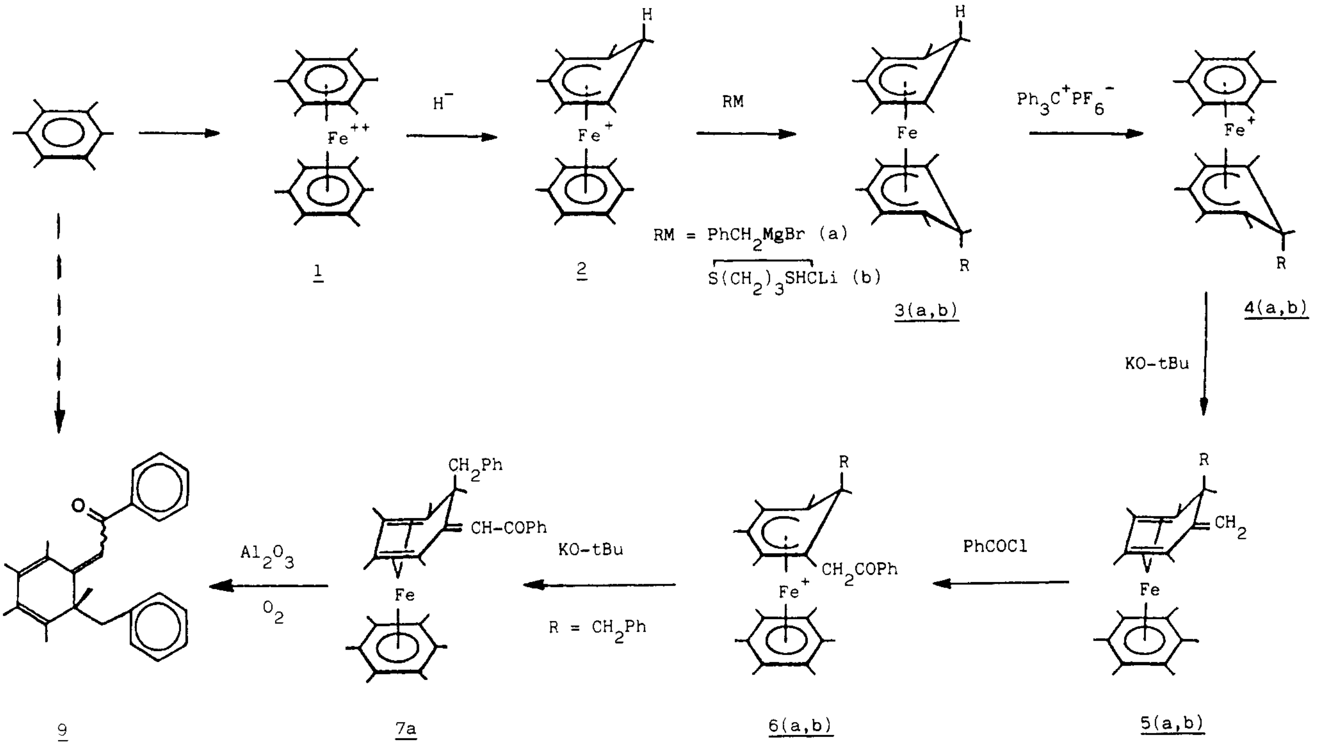


Figure 2. $^{13}C\{^1H\}$ NMR spectrum (20.115 MHz) of the thermally unstable complex **7a** in CD_2Cl_2 at -10 °C.

Scheme III



In contrast to the case for its precursor **7a**, the organic compound **9** shows an infrared absorption at $\nu_{C=O}$ = 1695 cm^{-1}. The conjugated double bonds are characterized by $\nu_{C=C}$ = 1600 cm^{-1} and by ^{13}C resonances near δ 130 ppm in the aromatic region. The exocyclic double bond carbons are found at δ 156 ppm (quaternary C) and δ 125 ppm (exocyclic C). The mass spectrum shows the molecular peak at *m/e* 356, confirming the structure of **9**.

Concluding Remarks

(i) The present study illustrates the reactivity of bulky complexes [Fe(η^6-arene)(η^5-cyclohexadienyl)]$^+$ toward hard nucleophiles.

(ii) It shows that the complexation of C_6Me_6 by Fe^{2+} makes it possible to functionalize the arene after using the hydride protection strategy.

(iii) It emphasizes the use of an ET pathway to remove a hydride from an electron-rich 18e complex. It shows that, when steric bulk is present, the 17e radical intermediate is well stabilized so that reaction conditions need not be so drastically controlled.

(iv) This activation of a C_6Me_6 ligand leads to Fe^0 complexes of trienes bearing a various number of benzoyl groups and to a new trienone. The overall transformation of C_6Me_6 is summarized in Scheme III. The eight steps proceed with an overall 32% yield.[20]

Acknowledgment. We are grateful to Drs. P. Guenot and S. Sinbandhit (Rennes, France) and F. Le Floch (Brest, France) for helpful experimental assistance. We also thank Dr. C. Lapinte for the synthesis of **5b** and for helpful discussions, Dr. J.-R. Hamon for helpful discussions, and the CNRS for a grant to D.M.

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[20] One step can be saved if one reacts [Fe(η^6-C_6Me_6)$_2$] with RX,[8] which gives the complexes **4** directly. The overall yield is not improved, however.