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Influence of Steric Bulk on Fischer-Type Syntheses of Peralkylated Electron Reservoir Sandwiches [FeCp*(arene)]$^+$: Cleavage of Alkyl Groups and Mechanistic Implications[1]

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The reaction of [FeCp*(CO)$_2$Br] (**1**, Cp* = η^5-C$_5$Me$_5$) with C$_6$Et$_6$ in the presence of Al$_2$Cl$_6$ leads only to the pure pentaethylbenzene complex [FeCp*(C$_6$Et$_5$H)]$^+$ (**2**) when the reaction is carried out below 100 °C (yields 28% at 80 °C and 3% at 50 °C). At 200 °C, this reaction gives a mixture of the tris-, tetra-, and pentaethylbenzene complexes. Similarly [FeCp′(CO)$_2$Br] (**3**, Cp′ = η^5-C$_5$Me$_4$Et) gives [FeCp′(C$_6$Et$_5$H)]$^+$ (**4**). Deuterium-labeling experiments indicate that the H atom replacing the cleaved Et group comes from a protic source in the medium not from Cp* or from an Et group. Although the pure complexes [FeCp(C$_6$Et$_6$)]$^+$ (**5**) and [FeCp*(C$_6$Me$_6$)]$^+$ (**6**) can both be made at reduced temperatures, loss of alkyl groups is also observed at higher reaction temperatures. Attempts to prepare the previously reported complex [Re(η^6-C$_6$Me$_6$)$_2$]$^+$ (**9**) yielded only dealkylation products. The loss of alkyl groups is interpreted in terms of competition between the retro-Friedel–Crafts mechanism and complexation. The latter is considerably slowed down when, simultaneously, the Cp ligand is permethylated and the arene ligand bears six Et substituents. A mechanism involving σ complexation of CpFe$^+$ to the arene ligand is proposed.

Introduction

The localization of an electron inside a three-dimensional molecular framework is a key property of electron reservoir complexes.[2] In order to stabilize a 19e radical form, it is necessary to protect the metal center bearing the extra electron by steric bulk. Indeed, in the Fe^{I}Cp(arene) series, the parent benzene complex is not stable at room temperature. Peralkylation of the benzene ligand is necessary in order to stabilize the Fe^{I} radical.[3] The need to modulate the redox properties of this Fe^{II}/Fe^{I} system also led to the use of Cp* instead of Cp, which produces a negative shift of 0.3 V in the redox potential in addition to steric bulk.[3] However, our first attempts to make these peralkylated mixed [FeCp*(C$_6$R$_6$)]$^+$ sandwiches were frustrated by the cleavage of alkyl groups, limiting the purity of the desired complexes. In the extreme case of [FeCp*(C$_6$Et$_6$)], the synthesis cannot be accomplished without the loss of an Et group. [Throughout this paper, Cp = η^5-C$_5$H$_5$, Cp* = η^5-C$_5$Me$_5$, Cp′ = η^5-C$_5$Me$_4$Et, and Fp* = Fe(η^5-C$_5$Me$_5$)(CO)$_2$.] In this paper we detail these studies on the loss of alkyl groups from the arene ligand, its consequences and implications for the ligand exchange mechanism.

FpCp*(Co)$_2$Br **1**
FeCp*(C$_6$Et$_5$H)$^+$ **2**
FeCp′(CO)$_2$Br **3**
FeCp′(C$_6$Et$_5$H)$^+$ **4**
FeCp(C$_6$Et$_6$)$^+$ **5**
FeCp*(C$_6$Me$_6$)$^+$ **6**
Re(C$_6$Me$_6$)$_2$$^+$ **9**
Fe^{I}Cp*C$_6$Et$_5$H **7**
FeCp*(C$_6$Me$_5$H)$^+$ **8**
Fe^{I}Cp*(C$_6$Me$_5$H) **10**

Experimental Section

General Data. All manipulations were carried out under argon or a nitrogen atmosphere using Schlenk techniques or in a glovebag. Reagent grade 1,2-dimethoxyethane (DME), diethyl ether, and pentane were predried and distilled over sodium benzophenone ketyl prior to use. Other chemicals were used as received. For reactions performed in sealed tubes, the glassware was flamed out under vacuum immediately prior to putting in the glovebag to minimize adsorbed moisture. ^{1}H NMR spectra were obtained with a Varian EM 360 or a Brucker WP80 or AM 300WB instrument. ^{13}C NMR spectra were recorded with a Brucker WP80 FT (20.115 MHz) or AM 300WB (75.469 MHz) spectrometer. Chemical shifts are reported in parts per million (δ, ppm) with reference to tetramethylsilane as an internal standard. Infrared spectra were recorded with a Pye-SP1100 Unicam spectrophotometer and calibrated with polystyrene film. Samples were prepared by using Nujol mulls on KBr plates or pentane solution in 0.10-mm KBr cells. Mass spectra were recorded on a Varian MAT 311 spectrometer at the Centre de Mesures Physiques pour la Chimie de Rennes. Elemental analyses were provided by the Centre de Microanalyses du CNRS at Lyon-Villeurbanne. Pentamethylcyclopentadiene was prepared according to the literature procedure.[5b]

1. Synthesis of [FeCp*(C$_6$Et$_5$H)]$^+$[PF$_6$]$^-$ (2). In a glovebag under argon, 9.81 g (30 mmol) of [Fe(C$_5$Me$_5$)(CO)$_2$Br][3] (**1**), 20 g (81.3 mmol) of C$_6$ (C$_2$H$_5$)$_6$, and 10.9 g (40.6 mmol) of Al$_2$Cl$_6$ were carefully mixed, and the solid reaction mixture was melted at 80 °C for 12 h. After the solution was cooled to 0 °C, the black residue was hydrolyzed with 300 g of ice water. The aqueous phase was washed three times with 50 mL of ether. Al ions were removed after addition of NH$_3$ (to pH 9) and filtration of Al(OH)$_3$. Addition of an aqueous solution of HPF$_6$ (30 mmol) to the filtrate precipitated a yellow solid. Then the solid was filtered, dissolved in acetone, and dried over MgSO$_4$. Filtration, concentration, and precipitation in ether gave 4.37 g (28%) (the yield was 3% when the reaction was carried out at 50 °C) of yellow powder. Recrystallization from hot ethanol provided 4.2 g (25%) of canary yellow plates.

^{1}H NMR (CD$_3$COCD$_3$): 5.84 (s, C$_6$ *H*, 1 H); 2.90 (m, CH$_2$, 10 H); 1.63 (s, 15 H, C$_5$(CH$_3$)$_5$); 1.38 (m CH$_3$, 15 H). ^{13}C NMR (CD$_3$CN): 106.2, 103.3, 89.7 (C$_6$(C$_2$H$_5$)$_5$); 103.4 (C$_6$H); 88.8 (C$_5$ ring);

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24.6, 22.4, 21.8 (CH_2); 16.7, 16.0, 15.7, (CH_3); 9.1 $C_5(CH_3)_5$. Mössbauer data (300 K, mm s^{-1}): IS, 0.48: QS, 1.70. Anal. Calcd for $C_{26}H_{41}F_6FeP$: C, 56.33, H, 7.45; Fe, 10.07. Found: C, 56.37; H, 7.44; Fe, 10.05.

When the above reaction was carried out at 200 °C, a mixture of three complexes ($([FeCp^*(C_6Et_{6-n}H_n)]^+[PF_6]^-)$) was recovered after workup. ^1H NMR (CD_3COCD_3): 5.62 (b s, C_6H_n); 3.54 (m, CH_2); 1.82, 1.76, 1.71 (s, $C_5(CH_3)_5$); 1.24 (m, CH_3).

In order to provide absolutely anhydrous conditions, complex 1 was recrystallized and dried at 40 °C in vacuo; C_6Et_6 was sublimed and Al_2Cl_6 doubly sublimed prior to use. The reaction was carried out on a 1-mmol scale. The three compounds were carefully mixed in a glovebag under argon and placed in a previously flamed glass tube. The tube was then sealed in vacuo and heated 12 h. No ionic complexes were isolated after workup.

In a 25 mL-flask equipped with a reflux condenser, 0.277 g (0.5 mmol) of 2 and 0.2 g (0.75 mmol) of Al_2Cl_6 were suspended in 10 mL of Decalin. The reaction mixture was heated 18 h at 200 °C. After hydrolysis, the yellow solid was filtered and dried over $MgSO_4$ in acetone and addition of excess diethyl ether provided 0.25 g of 2 identified by its ^1H NMR spectrum.

In a Schlenk tube under argon, 0.082 g (0.25 mmol) of 1, 0.062 g (0.25 mmol) of C_6Et_6, and 0.133 g (0.5 mmol) of Al_2Cl_6 were mixed and heated under low pressure at 80 °C for 12 h. The gas evolved during the reaction was analyzed by mass spectrometry. The spectrum showed peaks for C_2H_4 (calcd 28.0313, found 28.031), C_4H_{10} (calcd 58.0782, found 58.078), $Et^{35}Cl$ (calcd 64.0079, found 64.007), and $Et^{81}Br$ (calcd 109.9554, found 109.955). The peaks were assigned by using high-resolution measurements.

2. **Preparation of $[Fe^ICp^*(C_6Et_5H)]$ (7).** The yellow salt 2 (1.38 g, 2.5 mmol) prepared as above was stirred with 29 g (12.5 mmol) of Na/Hg in 10 mL of DME at 0 °C for 1 h. The solvent was removed in vacuo and the residue extracted with 3 × 20 mL of pentane. Recrystallization at −40 °C from a concentrated solution of pentane provided 0.46 g (25%) of 7 as large dark green crystals. MS: calcd 409.2257, found 409.2526. Mössbauer data (mm s^{-1}, 4.2 K): IS, 0.82; QS, 1.39. Mössbauer data (mm s^{-1}, 290 K): IS, 0.73; QS, 0.47. Anal. Calcd for $C_{26}H_{41}Fe$: C, 76.46; H, 9.87. Found: C, 76.02; H, 10.22.

3. **Dealkylation during the Synthesis of $[FeCp(C_6Et_6)]^+[PF_6]^-$ (5).** In a three-necked round-bottomed flask equipped with a reflux condenser, were successively added 7.8 g (42 mmol) of ferrocene, 15 g (62 mmol) of hexaethylbenzene, 1.3 g (42 mmol) of aluminum powder, 17 g (63 mmol) of Al_2Cl_6, and 0.758 mL of water under N_2 in 150 mL of degased Decalin. The reaction mixture was stirred 12 h at 135 °C and then cooled to 0 °C before the workup which proceeded as in 1. Recrystallization from hot ethanol gave 5.35 g of canary yellow plates. ^1H NMR (CD_3COCD_3 at 60 MHZ): 6.35 (s, $C_6(C_2H_5)_5H$]; 4.94 and 4.88 (2 singlets of equal intensity, C_5H_5); 3.13 and 3.10 (m, CH_2); 1.41 and 1.38 (m, CH_3). This spectrum corresponds to the 1:1 mixture of 5 and $[FeCp(C_6Et_5H)]^+[PF_6]^-$.

4. **Dealkylation during the Synthesis of $[FeCp^*(C_6Me_6)]^+[PF_6]^-$ (6).** In a glovebag under argon 32.7 g (100 mmol) of 1, 64.8 g (400 mmol) of hexamethylbenzene, and 40 g (150 mmol) of Al_2Cl_6 were carefully mixed. The black solid mixture was stirred 12 h at 170 °C. After the mixture was cooled to 0 °C, the work up proceeded as in 1, giving 36.55 g of yellow powder. Recrystallization from hot ethanol provided 29.5 g (61%) of microcrystals.

^1H NMR (CD_3CN): 5.47 (s, C_6H, 1 H); 2.24, 2.19, 2.16 (s, m, p, o CH_3, 15 H); 1.69 (s, $C_5(CH_3)_5$, 15 H). ^{13}C NMR (CD_3CN): 105.3, 100.2, 98.7 (m, p, o C_6 ring); 99.4 (C_6H); 88.2 (C_5 ring); 18.1, 15.0, 14.4 (CH_3); 10.1 ($C_5(CH_3)_5$). These spectra correspond to those of 8, as synthesized from 1 and C_5Me_5H. Anal. Calcd for $C_{21}H_{31}F_6FeP$: C, 52.08; H, 6.45; Fe, 11.53. Found: C, 51.77; H, 6.46; Fe, 11.18.

5. **Synthesis of $[Fe^ICp^*(C_6Me_5H)]$ (10).** The above synthesized yellow salt 8 (4.0 g, 8.26 mmol) was stirred with 95 g (41 mmol) of Na/Hg in DME at −20 °C for 1 h. The solvent was removed in vacuo at this temperature and the black residue extracted with 3 × 20 mL of cold pentane. Concentration and precipitation from pentane at −80 °C provided 1.43 g (51%) of an olive-green powder. Anal. Calcd for $C_{21}H_{31}Fe$: C, 74.33; H, 9.21; Fe, 16.46. Found: C, 73.92; H, 9.06; Fe, 17.01. MS: calcd 339.1775, found 339.1176. (Note that these analyses do not differentiate 10 from its dimer.)

6. **Attempt To Prepare $[Re(C_6Me_6)_2]^+$ $[PF_6]^-$ (9).** Following the published procedure,[4] 1 g (2.75 mmol) of $ReCl_3$, 3.12 g (19 mmol) of hexamethylbenzene, 3.70 g (7 mmol) of Al_2Br_6, 3.4 g (12.5 mmol) of Al_2Cl_6, and 0.126 g (4.67 mmol) of aluminum powder were carefully mixed under argon in a glovebag. The reaction mixture was stirred 12 h at 147 °C and then cooled to −80 °C for hydrolysis. At room temperature the dark aqueous solution was filtered and 3 mmol of aqueous HPF_6 was added to the dark red filtrate. The resultant pale yellow precipitate was collected, redissolved in acetone, dried over $MgSO_4$, and precipitated by addition of excess ether, to give 0.585 g of a yellow powder. ^1H NMR (CD_3COCD_3): 5.96, 5.84, 5.78, 5.64 (b s, C_6H), 2.28, 2.24, 2.20, 2.18, (s, CH_3). This spectrum corresponds to $[Re(C_6Me_{6-n}H_n)_2]^+[PF_6]^-$ (n = 1.44). (The percentage of CH_3 groups lost was obtained from relative NMR intensities). At 100 °C the same reaction gave no cationic product.

7. **Deuterium-Labeling Experiments.** A. The three following experiments (a–c) were carried out in the same fashion. The reaction was performed on a 1-mmol scale. The three reagents 1, $C_6(C_2H_5)_6$, and Al_2Cl_6 were carefully mixed together in a glovebag under argon, placed in a glass tube, and sealed in vacuo. The reaction was heated 12 h at 80 °C. The workup proceeded as in 1, yielding 22–25% of yellow powder. ^1H NMR spectra were recorded in CD_3COCD_3 solution. (a) $FeC_5(CD_3)_5(CO)_2Br$ + $C_6(C_2H_5)_6$ + Al_2Cl_6: 1.33 (m, CH_3, 15 H); 1.76 (m, $CD_{3-n}H_n$); 2.95 (m, CH_2, 10 H); 5.92 (s, C_6H, 1 H). (b) 1 + $C_6(CD_2CH_3)_6$ + Al_2Cl_6: 1.26 (b s, CH_3, 15 H); 1.83 (s, $C_5(CH_3)_5$, 15 H); 5.80 (s, C_6H, 1 H). (c) 1 + $C_6(CH_2CD_3)_6$ + Al_2Cl_6: 1.83 (s, $C_5(CH_3)_5$, 15 H); 2.93 (b s, CH_2, 10 H); 5.77 (s, C_6H, 1 H).

B. Ligand exchange in the presence of D_2O: 0.02 mL (1 mmol) was added to 0.534 g (2 mmol) of Al_2Cl_6 in a glass tube cooled to −90 °C. At room temperature the mixture of 0.327 g (1 mmol) of 1 and 0.246 g (1 mmol) of hexaethylbenzene were placed in the tube before sealing. The tube was heated for 12 h at 80 °C, and then the workup proceeded as in 1 providing 0.122 g (22%) of a yellow powder. ^1H NMR (CD_3COCD_3): 1.34 (m, CH_3, 15 H); 1.81 (s, $C_5(CH_3)_5$, 15 H); 2.78 (m, CH_2, 10 H); 5.67 (b s, C_6H, 0.25 H).

8. **Synthesis of $[FeCp'(CO)_2Br]$ (3).** Following the published procedure, 0.51 mL (10 mmol) of Br_2 in CH_2Cl_2 was added dropwise to a solution of 5.22 g (10 mmol) of $[FeCp(CO)_2]_2$ in CH_2Cl_2 at 0 °C; 4.48 g (66%) of deep purple crystals of $Fe(C_5(CH_3)_4C_2H_5)(CO)_2Br$ were collected after recrystallization from diethyl ether at −20 °C.

^1H NMR ($CDCl_3$): 2.24 (q, CH_2, 2 H); 1.86, 1.84 (s, CH_3, 12 H); 1.06 (t, CH_3, 3 H). ^{13}C NMR ($CDCl_3$): 214.3 (CO); 99.8 ($C_5C_2H_5$); 97.5, 95.6 (C_5CH_3); 18.2 (CH_3CH_2); 14.1 (CH_3CH_2); 9.8, 9.6 (C_5CH_3). Anal. Calcd for $C_{13}H_{17}BrFeO_2$: C, 45.78; H, 5.02; Br, 23.43; Fe, 16.37. Found: C, 45.48; H, 4.98; Br, 23.70; Fe, 16.17.

9. **Synthesis of $[FeCp'(C_6Et_5H)]^+$ $[PF_6]^-$ (4).** As in 1, 1.02 g (3 mmol) of 3, 0.75 g (3 mmol) of C_6 $(C_2H_5)_6$, and 1.20 g (4.5 mmol) of Al_2Cl_6 were mixed under argon and heated in the melt at 80 °C for 12 h. Work up proceeded as in 1 giving 0.203 g (12%) of a yellow powder after recrystallization from acetone/ether.

^1H NMR (CD_3CN): 5.50 (s, C_6H, 1 H); 2.73 (m, CH_2, 10 H); 2.17 (q, CH_2, 2 H); 1.65, 1.64 (s, C_5CH_3, 12 H); 1.23 (dt, CH_3, 15 H); 0.85 (t, CH_3, 3 H). ^{13}C NMR (CD_3CN): 106.3, 103.5, 102.9 (m, p, o, C_6 ring); 89.2 (C_6H); 93.3 ($C_5C_2H_5$); 89.6, 88.1 (C_5CH_3); 24.7, 22.5, 21.9 (m, p, o CH_2); 18.1 ($C_5CH_2CH_3$); 16.7, 16.1, 15.7 (m, p, o CH_3); 13.6 ($C_5CH_2CH_3$); 9.2, 8.9 (C_5CH_3).

Results

Reactions of $[Fe(C_5Me_4R)(CO)_2Br]$ (R = Me or Et) with C_6Et_6: Cleavage of One Et Group. As already reported for arene = C_6R_6 and R = H or Me,[3] the reactions of Fp*Br (Fp* = $FeC_5Me_5(CO)_2$) with arenes in the presence of Al_2Cl_6 give $[FeCp^*(arene)]^+$. However for R = Et the reaction only proceeds with cleavage of one Et group from C_6Et_6 (eq 1). The reaction product is $[FeCp^*(C_6Et_5H)]^+$, which is isolated as its PF_6^- salt. The reaction of eq 1 was performed in heptane or (more generally) neat at 80 °C. The pentaethylbenzene complex 2

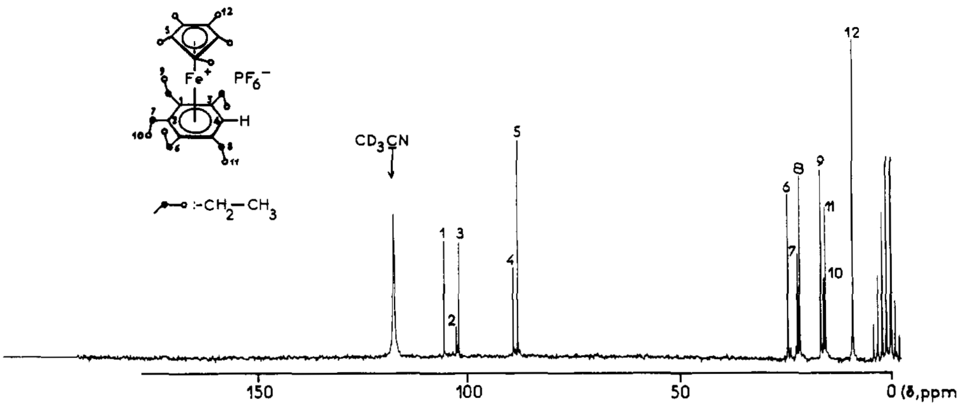
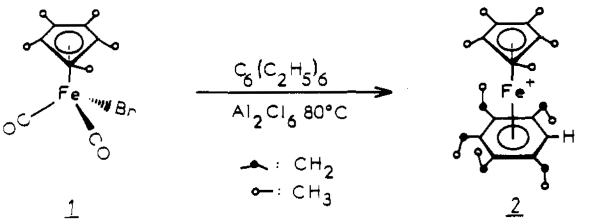


Figure 1. $[^1H]^{13}C$ NMR spectrum of **2** in CD_3CN.



(1)

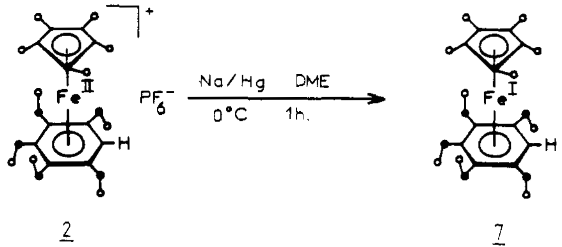
is the only salt thus isolated, as shown by the ^{13}C NMR spectrum (Figure 1).

The X-ray crystal structure of **2**, reported separately together with conformational studies on (hexaethylbenzene)iron complexes, indicates that the five ethyl groups are remote (distal) from iron.[6] We have attempted without success to make $[FeCp^*(C_6Et_6)]^+$. For instance, if one lowers the reaction temperature to 50 °C, a 3% yield of pure **2** is still obtained. On the other hand, if the ligand exchange reaction of eq 1 is performed at 200 °C, a mixture of three complexes is obtained. One of these is **2**, and, given the relative intensity of the aromatic protons observed by ^1H NMR, we assume that the two others are mixtures of isomers of $[FeCp^*(C_6Et_3H_3)]^+$ and $[FeCp^*(C_6Et_4H_2)]^+$. Furthermore, if **2** is heated with Al_2Cl_6 at 200 °C, it is entirely recovered without modification of structure. The reaction of eq 1 has usually been carried out without special care regarding the presence of traces of water. However, if extreme care is exercised (flamed glassware, doubly sublimed Al_2Cl_6, sublimed C_6Et_6, and dry Fp*Br), the reaction does not proceed at all. It is also possible to avoid this type of dealkylation of arenes by using $Al_2Cl_6 + Al_2Me_6$ in stoichiometric amount.[7] Ligand exchange reactions using this mixture generally work even better than with Al_2Cl_6 alone and also can be achieved at 50 °C. The reaction shown in eq 1 was effected with $Al_2Cl_6 + Al_2Me_6$ at 80 °C during 2 days, which did not give any of the expected sandwich complex.

The origin of the hydrogen atom that replaces the Et group was investigated by using deuterated complexes, the synthesis of which is reported elsewhere.[8] Thus the reaction of Fp*Br with $C_6(CD_2CH_3)_6$ or $C_6(CH_2CD_3)_6$ as well as the reaction of $[FeC_5(CD_3)_5(CO)_2Br]$ with C_6Et_6 gave nondeuterated **2**. On the other hand, when the reaction shown in eq 1 was performed in the presence of 1 equiv of D_2O, the monodeuterated complex $[FeCp^*(C_6Et_5D)]^+$ was obtained as the major product, and its $NaBH_4$ reduction product $[FeCp^*(\eta^5\text{-}C_6Et_5DH)]^8$ was characterized by mass spectrometry.

The reaction shown in eq 1 proceeds analogously with $[Fe(C_5Me_4Et)(CO)_2Br]$ instead of **1**.

Synthesis of $[Fe^ICp^*(C_6Et_5H)]$. The extremely electron-rich 19e complex $[Fe^ICp^*(C_6Et_5H)]$ (**7**) was synthesized by the classical Na/Hg reduction procedure (eq 2).



(2)

Complex **7** is extremely soluble in pentane and can be recrystallized at low temperature from this solvent. It is thermally stable at room temperature despite incomplete alkylation of the benzene ligand. It is slightly more electron-rich ($E°(Fe^{II}/Fe^I)$ = −1.88 V vs SCE, DMF, nBu_4NBF_4 0.1 M, Hg cathode) than the most electron-rich Fe^I complex $[FeCp^*(C_6Me_6)]$ found so far ($E°$ = −1.85 V; ionization potential = 4.1 eV).[9] It was also characterized by elemental analysis and Mössbauer spectroscopy. This latter technique shows that the Jahn–Teller active Fe^I sandwich exhibits a slow decrease of the quadrupole splitting as a function of temperature. This trend is typical of Fe^I sandwich complexes bearing a perethylated benzene ligand and results from coupling between the molecular electronic structure and the lattice.[10]

Loss of Alkyl Groups in Other Ligand Exchange Reactions. If the reaction is carried out below 125 °C, the reaction of $[FeCp^*(CO)_2Br]$ with C_6Me_6 in the presence of Al_2Cl_6 normally gives the expected permethylated complex $[FeCp^*(C_6Me_6)]^+[PF_6)]^-$.[3] (At this temperature, no trace of pentamethylbenzene complex is found and thus no dealkylation occurs). However, if this reaction is carried out at 170 °C, the pentamethylbenzene complex $[FeCp^*(C_6Me_5H)]^+[PF_6]^-$ (**8**) is formed, as identified by comparison with the reaction product of Fp*Br with C_6Me_5H at 80 °C. Similarly, if the temperature is kept below −100 °C, the reaction of ferrocene with C_6Et_6 in the presence of Al_2Cl_6 normally yields pure $[FeCp(C_6Et_6)]^+[PF_6]^-$ (**5**).[11]

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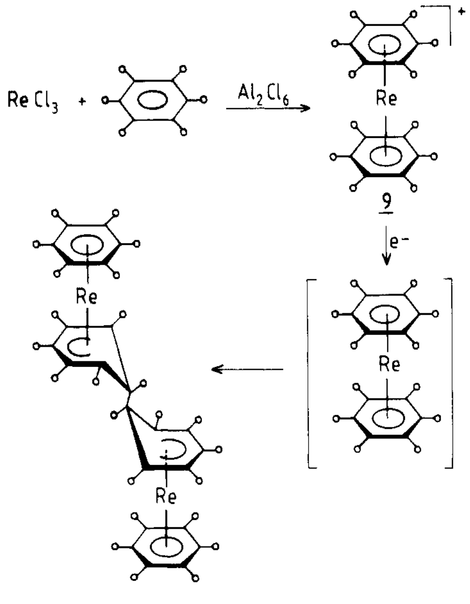
Scheme I



However, in an experiment carried out at 135 °C, a 1:1 mixture of **5** and $[FeCp(C_6Et_5H)]^+[PF_6]^-$ was formed, as determined from the ^1H NMR spectra.

The reaction of $ReCl_3$ with C_6Me_6 in the presence of Al_2Cl_6 was reported to give $[Re(C_6Me_6)_2]^+$ (**9**).[4] It was also mentioned that one-electron reduction of this 18e Re sandwich complex gives the product resulting from dimerization of the neutral 19e species (Scheme I). After the above finding for the peralkylated iron sandwich chemistry, we suspected that this complex is formed by dimerization through an arene carbon that does not bear a methyl group.[12]

Thus we attempted to prepare **9** by repeating its reported synthesis. We found that, at 147 °C, the reaction gives a mixture of $[Re[C_6(CH_3)_{6-n}H_n]_2]^+[PF_6]^-$ ($n = 1.44$). On the other hand, the reaction does not give any product when it is carried out at 100 °C. No reaction temperature could be found that would give the reported complex **9** without loss of methyl groups.

Discussion

The Fischer–Hafner complexation of aromatic ligands to a transition metal using transition-metal halides and aluminum chloride or aluminum bromide was pioneered by the synthesis of a bis(arene) chromium cation[13] (eq 3).

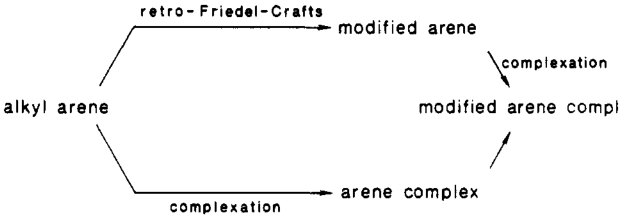
$$[CrCl_3] + \text{arene} + Al_2Cl_6 \rightarrow [Cr(C_6H_6)_2]^+ \qquad (3)$$

Fischer et al. synthesized a large number of transition-metal sandwiches using this general route[14] (eq 4). The role of Al_2Cl_6 in the reaction mechanism was also investigated in Fischer's group in the case of Cr.[15]

$$[MCl_n] + \text{arene} + Al_2Cl_6 \rightarrow [M(\text{arene})_2]^{m+} \qquad (4)$$

In the past, it has also been noted in a number of cases that aromatics are modified in the course of complexation. For instance bis(arene)chromium synthesized in this way was shown to contain bis(toluene)-, bis(xylene)-, and bis(diisopropylbenzene)chromium.[16] The ligand exchange reaction between ferrocene and tetramethylthiophene[17] was shown to lose Me groups at 135 °C (eq 5).[18] The

Scheme II



$$[FeCp_2] + C_4Me_4S + Al_2Cl_6 \rightarrow [FeCp(C_4Me_{4n}H_nS)]^+ \qquad (5)$$

ligand exchange reaction between ruthenocene and C_6Me_6 at 190 °C leads to the cleavage of several Me groups[19] (eq 6). Finally, loss and scrambling of Me groups were found

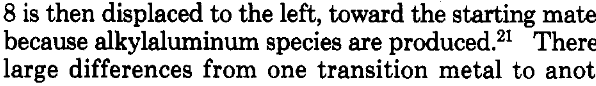
$$[RuCp_2] + C_6Me_6 + Al_2Cl_6 \rightarrow [RuCp(C_6Me_{6-n}H_n)]^+ \qquad (6)$$

in the syntheses of $Fe(\text{arene})_2{}^{2+}$ using the arene and Al_2Cl_6[20] (eq 7). These data may be compared with those

$$[FeCl_2] + C_6Me_nH_{6-n} + Al_2Cl_6 \rightarrow [Fe(C_6Me_nH_{6-n})]^{2+} \qquad (7)$$

described here concerning the reactions of ferrocene with C_6Et_6 and of **1** with C_6Me_6. In the case of C_6Et_6, what is interesting is the specificity obtained.

It appears that the general reason for the loss of alkyl substituents of the arene ligand is the retro-Friedel–Crafts reaction in the presence of traces of H^+ and of Al_2Cl_6[12b] (eq 8).



(8)

This process competes with the sandwich formation. Once the sandwich is formed, it is no longer sensitive to a Lewis acid, as confirmed by separate experiments. In the strict absence of a trace of H^+, loss of alkyl groups can be avoided. Also the use of a stoichiometric amount of Al_2Me_6 (in addition to Al_2Cl_6) is found to retard the loss of alkyl groups. It is possible that the equilibrium of eq 8 is then displaced to the left, toward the starting material, because alkylaluminum species are produced.[21] There are large differences from one transition metal to another, presumably because the rate of complexation varies with the transition metal used and the nature of their ligands (Scheme II). Interestingly, the ligand exchange reaction

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[12] (a) In the 19e Fe^{I}Cp(arene) series, permethylation of the arene inhibits the dimerization. The complex $[Fe^ICp(C_6Me_5H)]$ dimerizes readily whereas $[Fe^ICp(C_6Me_6)]$ is stable up to 100 °C.[3] (b) *Advanced Organic Chemistry*, 3rd ed.; March, J., Ed; Wiley: New York, 1985; p 105.

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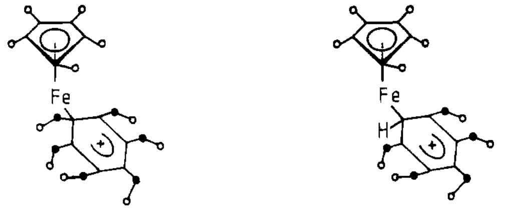
[21] (a) First report of the Friedel–Crafts reaction: Friedel, C., Crafts, J. M. *C. R. Hebd. Seances Acad. Sci.* **1877**, *84*, 1392. (b) For a recent paper on Al species and their role in Friedel–Crafts reactions. See: Olah, G. A.; Farooq, O.; Farnia, S. M. F.; Bruce, M. R.; Clouet, F. L.; Morton, P. R.; Prakash, G. K. S.; Stevens, R. C.; Ban, R.; Lammertsma, K.; Suzer, S.; Andrew, L. *J. Am. Chem. Soc.* **1988**, *110*, 3231. (c) Ethylene, butane, chloroethane, and bromoethane were found by mass spectral analysis of the gas phase of the reaction mixture before hydrolysis. Extrusion and insertion of ethylene can occur from ethylaluminum species formed in eq 8. Insertion of ethylene into the Al–Et bond gives Al–Bu species which can provide BuX after protonation of Bu–Al–halide. The reactions are classical in Al chemistry; see: Eisch, J. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: London, 1987; Vol. 1, Chapter 6, p 555.

Chart I. Proposed Complex as a Primary Fe–Arene Intermediate in the Reaction of Fp*Br and C_6Et_6



(a) C_6Et_6 (b) C_6Et_5H

[a] Only case b, C_6Et_5H, is tolerable; situation a is impeded by the bulk.

of ferrocene with an arene does not lead to cleavage of any alkyl group when the reactions are carried out at moderate temperatures (<100 °C).

One may compare the reactions in the same systems but using various arenes or various cyclopentadienyl ligands (Cp versus Cp*). Thus Fp*Br cannot react with C_6Et_6 without alkyl cleavage at this temperature. In contrast, $CpFe^+$ is complexed to C_6Et_6 in ferrocene without alkyl cleavage at 80 °C. This double comparison indicates that it is the cumulative steric bulk of Cp* and C_6Et_6 which leads to the observed reaction; neither Cp* nor C_6Et_6 alone leads to cleavage of an alkyl substituent of the arene below 100 °C.

One may then question the compatibility of two bulky ligands such as Cp* and C_6Et_6 in a sandwich compound. One notices the tremendous difference of reactivity between C_6Et_6 and C_6Et_5H in the Fp^*Br/Al_2Cl_6 system. Clearly C_6Et_6 cannot be complexed at all. It is thus reasonable to propose that, wherever retro-Friedel–Crafts can occur (with Al_2Cl_6 alone, not with Al_6Cl_6/Al_2Me_6), it produces C_6Et_5H if protic traces are present.

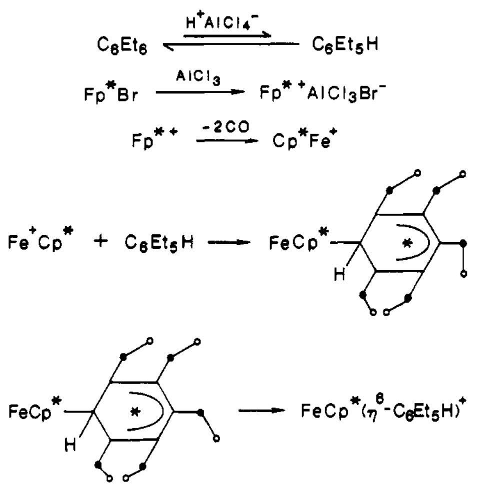
$$C_6Et_6 \xrightleftharpoons{H^+AlCl_4^-} C_6Et_5H$$

The arene C_6Et_5H is then readily complexed at 80 °C. That the sizes of both the Cp* and arene ligands are important suggests that ligand bulk prevents access to the transition state. The large difference in reactivity between C_6Et_6 and C_6Et_5H then can best be taken into account in terms of the formation of a σ complex between the arene and the Cp^*Fe^+ moiety. Direct formation of a π complex would not be much more inhibited by the C_6Et_6 bulk than by the C_6Et_5H bulk, but the σ complex is (Chart I). A possible overall mechanism is proposed in Scheme III.

Conclusion

1. The Fischer–Hafner synthesis of transition-metal sandwich complexes of alkyl-substituted arenes proceeds in most cases with cleavage of an alkyl substituent in the arene ligand.

Scheme III. Proposed Overall Mechanism for the Cleavage of an Et Group of C_6Et_6 in the Course of the Complexation by Cp^*Fe^+



2. The mechanism of this process can be suppressed by the rigorous exclusion of traces of water and by using of Al_2Cl_6/Al_2Me_6 (1/1). It involves a retro-Friedel–Crafts reaction as indicated by deuterium-labeling experiments.

3. The complexation and the retro-Friedel–Crafts cleavage of the alkyl group are in competition. It is found that the pentaalkylbenzene complex formed in situ is more reactive than the hexalkylbenzene precursor, especially in the case of hexaethylbenzene.

4. Since the cumulative bulk of both ligands of the sandwich is crucial, it is proposed that a σ complex between the Cp^*Fe^+ moiety and the arene forms before it forms the sandwich complex.

5. The 19e complex $[Fe^ICp^*(C_6Et_5H)]$, obtained by the reduction of its cationic precursor, is the most electron-rich Fe^I monomer and is thermally stable despite incomplete arene peralkylation.

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Registry No. **1**, 34808-38-3; **2**, 120854-25-3; **3**, 120854-26-4; **4**, 120854-28-6; **5**, 71713-63-8; **6**, 71713-57-0; **7**, 118301-39-6; **9**, 12099-86-4; **10**, 120881-30-3; $C_6(C_2H_5)_6$, 604-88-6; $FeCp_2$, 102-54-5; $[FeCp(C_6Et_5H)]^+[PF_6]^-$, 120854-30-0; C_6Me_6, 87-85-4; $ReCl_3$, 13569-63-6; $FeC_5(CD_3)_5(CO)_2Br$, 120854-31-1; $C_6(CD_2CH_3)_6$, 120854-32-2; $C_6(CH_2CD_3)_6$, 120854-33-3; $[FeCp^*(CO)_2]_2$, 112087-39-5.