Synthesis of asymmetrical bis(arene) iron complexes*

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Visible light irradiation of the $[(\eta\text{-}C_6H_7)Fe(\eta\text{-}C_6H_6)]^+$ cation (**1**) in CH_2Cl_2 in the presence of alkyl-substituted benzenes results in arene exchange forming the $[(\eta^5\text{-}C_6H_7)Fe(\eta\text{-}C_6R_6)]^+$ cations (**2a—d**: C_6R_6 is toluene, *p*-xylene, mesitylene, and durene). The mixed bis(arene) $[(\eta\text{-}C_6H_6)Fe(\eta\text{-}C_6R_6)]^{2+}$ iron complexes (**3a—d**) were synthesized by hydride ion abstraction from **2a—d** by $[Ph_3C]^+$.

Key words: arene complexes, iron, sandwich compounds.

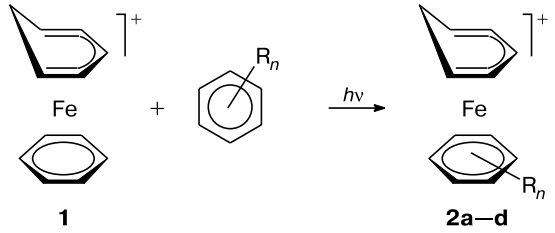
The first bis(arene) iron complex, *viz.*, $[Fe(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)_2]^{2+}$, was synthesized[1] by the reaction of $FeBr_2$ with mesitylene in the presence of $AlCl_3$. Further analogous complexes with other arenes were synthesized by this method.[2—5] However, this method is suitable only for the synthesis of symmetrical bis(arene) derivatives. Only one example of the mixed complex of this type is described[3]: the $[(\eta\text{-}C_6H_6)Fe(\eta\text{-}C_6Me_6)]^{2+}$ cation synthesized by the abstraction of two hydride ions from the cyclohexadiene $(\eta\text{-}C_6H_8)Fe(\eta\text{-}C_6Me_6)$ complex by $[Ph_3C]^+$. In this work, we proposed a general procedure for the synthesis of the asymmetrical iron bis(arene) complexes.

Results and Discussion

We have recently shown[6,7] that the visible light irradiation of the cyclohexadienyl complex $[(\eta\text{-}C_6H_7)Fe(\eta\text{-}C_6H_6)]^+$ (**1**) results in the substitution of benzene for MeCN, Bu^tNC, $Cp^*Fe(\eta\text{-}cyclo\text{-}P_5)$, and $[9\text{-}SMe_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$. In this work, we found that the benzene ligand in cation **1** also exchanges for other arenes (toluene, *p*-xylene, mesitylene, and durene) to form arene complexes **2a—d** (Scheme 1).** Similar photochemical exchange of arene has been observed earlier for the $[CpFe(\eta\text{-}C_6H_6)]^+$ (see Ref. 8) and $[(\eta\text{-}C_4Me_4)Co(\eta\text{-}C_6H_6)]^+$ (see Refs 9 and 10) cations. Unlike the reactions of these cations, arene exchange in **1** is incomplete because of the low reaction rate, and TLC should necessarily be used to isolate complexes **2a—d** in the individual state.

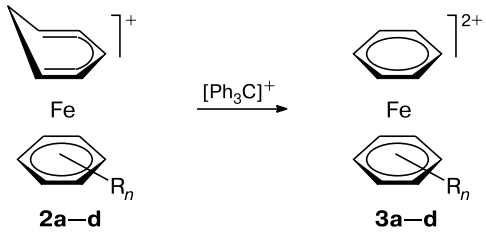
The subsequent reactions of **2a—d** with $[Ph_3C]^+$ afford asymmetrical dicationic bis(arene) complexes **3a—d** (Scheme 2). Unlike cyclohexadienyl derivatives **2a—d**, complexes **3a—d** are practically insoluble in CH_2Cl_2 but are well soluble in more polar solvents, such as Me_2CO, MeCN, and $MeNO_2$. The structures of the synthesized compounds were confirmed by the data of ^1H NMR spectra and elemental analysis.

Scheme 1



R_n = Me (**a**), 1,4-Me_2 (**b**), 1,3,5-Me_3 (**c**), 1,2,4,5-Me_4 (**d**)

Scheme 2



Thus, arene exchange in cation **1** followed by hydride ion abstraction is an efficient method for the synthesis of the asymmetrical iron bis(arene) complexes.

Taking into account that cation **1** is formed due to hydride ion addition to $[(\eta\text{-}C_6H_6)_2Fe]^{2+}$ (see Ref. 4), we can consider the sequence of reactions presented in Scheme 3 as the three-step exchange of arene in the latter. The direct exchange of arene in complexes of this type is unknown.

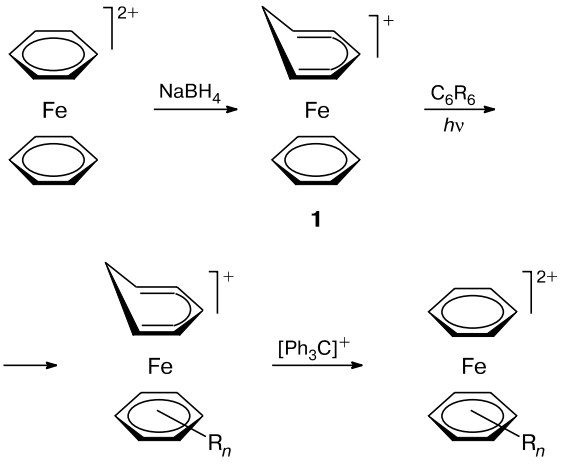
* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.

** All synthesized cationic complexes were isolated as salts with the PF_6^- anion (anions are omitted in the schemes).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1864—1865, September, 2007.

1066-5285/07/5609-1930

Scheme 3



Experimental

The reactions were carried out under argon using anhydrous solvents. Procedures associated with product isolation were carried out in air. The starting compounds [**1**]PF_6 (see Ref. 6) and $[Ph_3C]PF_6$ (see Ref. 11) were synthesized according to known procedures. Irradiation was carried out in a Schlenk tube 15 mm in diameter using mercury luminescent lamps with a total power of 650 W. The Schlenk tube and lamps were placed in a water-cooled vessel covered inside with aluminum foil. ^{1}H NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz).

[(η-Cyclohexadienyl)(η-arene)iron]hexafluorophosphate, [(η-C_6H_7)Fe(η-arene)]PF_6 ([2a—d]PF_6) (general procedure). A solution of complex [**1**]PF_6 (40 mg, 0.11 mmol) and excess arene (0.1 mL of C_6H_5Me, 1,4-$C_6H_4Me_2$, and 1,3,5-$C_6H_3Me_3$ or 150 mg of 1,2,4,5-$C_6H_2Me_4$) in CH_2Cl_2 (6 mL) was irradiated for 7 h. The solvent was removed *in vacuo*, and the residue was chromatographed on a silica gel plate using a CH_2Cl_2—acetone (10 : 1) mixture as eluent. The band closest to the front was collected. The product was eluted from silica gel with acetone and reprecipitated with ether from CH_2Cl_2. Orange solids were obtained.

Complex [2a]PF_6, arene C_6H_5Me, 14% yield. Found (%): C, 42.07; H, 4.05. $C_{13}H_{15}F_6FeP$. Calculated (%): C, 41.97; H, 4.06. ^{1}H NMR (acetone-d_6), δ: 1.09 (d, 1 H, C_6H_7); 2.48 (s, 3 H, $C_6H_5\underline{Me}$); 2.82 (m, 1 H, C_6H_7); 3.59 (m, 2 H, C_6H_7); 4.92 (m, 2 H, C_6H_7); 6.36 (m, 5 H, $C_6\underline{H}_5Me$); 7.06 (m, 1 H, C_6H_7).

Complex [2b]PF_6, arene 1,4-$C_6H_4Me_2$, 23% yield. Found (%): C, 43.49; H, 4.35. $C_{14}H_{17}F_6FeP$. Calculated (%): C, 43.55; H, 4.44. ^{1}H NMR (acetone-d_6), δ: 1.09 (d, 1 H, C_6H_7); 2.43 (s, 6 H, $C_6H_4\underline{Me}_2$); 2.80 (m, 1 H, C_6H_7); 3.33 (m, 2 H, C_6H_7); 4.85 (m, 2 H, C_6H_7); 6.28 (s, 4 H, $C_6\underline{H}_4Me_2$); 6.99 (m, 1 H, C_6H_7).

Complex [2c]PF_6, arene 1,3,5-$C_6H_3Me_3$, 49% yield. Found (%): C, 45.05; H, 4.69. $C_{15}H_{19}F_6FeP$. Calculated (%): C, 45.03; H, 4.79. ^{1}H NMR (acetone-d_6), δ: 1.07 (d, 1 H, C_6H_7); 2.42 (s, 9 H, $C_6H_3\underline{Me}_3$); 2.79 (m, 1 H, C_6H_7); 3.14 (m, 2 H, C_6H_7); 4.82 (m, 2 H, C_6H_7); 6.16 (s, 3 H, $C_6\underline{H}_3Me_3$); 6.84 (m, 1 H, C_6H_7).

Complex [2d]PF_6, arene 1,2,4,5-$C_6H_2Me_4$, 48% yield. Found (%): C, 46.39; H, 4.99. $C_{16}H_{21}F_6FeP$. Calculated (%): C, 46.40; H, 4.99. ^{1}H NMR (acetone-d_6), δ: 1.03 (d, 1 H, C_6H_7); 2.41 (s, 12 H, $C_6H_2\underline{Me}_4$); 2.74 (m, 1 H, C_6H_7); 3.02 (m, 2 H, C_6H_7); 4.69 (m, 2 H, C_6H_7); 6.12 (s, 2 H, $C_6\underline{H}_2Me_4$); 6.76 (m, 1 H, C_6H_7).

[(η-Benzene)(η-arene)iron]bis(hexafluorophosphate), [(η-C_6H_6)Fe(η-arene)]$(PF_6)_2$ ([3a—d]$(PF_6)_2$) (general procedure). Methylene chloride (2 mL) was added to a mixture of complex [**2**]PF_6 (0.04 mmol) and $[Ph_3C]PF_6$ (20 mg, 0.05 mmol), and the reaction mixture was stirred for 20 min. Ether (10 mL) was added, and the precipitate was filtered off and washed with ether. Light orange solids were obtained.

Complex [3a]$(PF_6)_2$, arene C_6H_5Me, 90% yield. Found (%): C, 28.79; H, 2.34. $C_{13}H_{14}F_{12}FeP_2\cdot 0.5CH_2Cl_2$. Calculated (%): C, 29.03; H, 2.71. ^{1}H NMR (acetone-d_6), δ: 2.87 (s, 3 H, $C_6H_5\underline{Me}$); 7.35 (m, 5 H, $C_6\underline{H}_5Me$); 7.42 (s, 6 H, C_6H_6).

Complex [3b]$(PF_6)_2$, arene 1,4-$C_6H_4Me_2$, 89% yield. Found (%): C, 30.10; H, 2.69. $C_{14}H_{16}F_{12}FeP_2\cdot 0.5CH_2Cl_2$. Calculated (%): C, 30.42; H, 2.99. ^{1}H NMR (acetone-d_6), δ: 2.83 (s, 6 H, $C_6H_4\underline{Me}_2$); 7.30 (s, 4 H, $C_6\underline{H}_4Me_2$); 7.40 (s, 6 H, C_6H_6).

Complex [3c]$(PF_6)_2$, arene 1,3,5-$C_6H_3Me_3$, 96% yield. Found (%): C, 32.35; H, 3.32. $C_{15}H_{18}F_{12}FeP_2\cdot 0.25CH_2Cl_2$. Calculated (%): C, 32.40; H, 3.30. ^{1}H NMR (acetone-d_6), δ: 2.80 (s, 9 H, $C_6H_3\underline{Me}_3$); 7.23 (s, 3 H, $C_6\underline{H}_3Me_3$); 7.34 (s, 6 H, C_6H_6).

Complex [3d]$(PF_6)_2$, arene 1,2,4,5-$C_6H_2Me_4$, 94% yield. Found (%): C, 33.82; H, 3.60. $C_{16}H_{20}F_{12}FeP_2\cdot 0.25CH_2Cl_2$. Calculated (%): C, 33.69; H, 3.57. ^{1}H NMR (acetone-d_6), δ: 2.77 (s, 12 H, $C_6H_2\underline{Me}_4$); 7.26 (s, 8 H, $C_6\underline{H}_2Me_4$ and C_6H_6).

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Received May 15, 2007