Inter-ring $\eta^6 \rightleftharpoons \eta^5$ haptotropic rearrangements of $18\bar{e}$ and $19\bar{e}$ (η^5-pentamethylcyclopentadienyl)(η^6-9-methylfluorenyl)iron complexes

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New cationic complexes $[(\eta^6\text{-}C_{13}H_{10})Fe(\eta^5\text{-}Cp^*)]PF_6$ and $[(\eta^6\text{-}9\text{-}CH_3\text{-}C_{13}H_9)Fe(\eta^5\text{-}Cp^*)]PF_6$ were obtained by the reaction of $Cp^*Fe(CO)_2Br$ with fluorene and 9-methylfluorene, respectively. Deprotonation of these complexes by *t*-BuOK in THF affords zwitter-ionic compounds $(\eta^6\text{-}C_{13}H_9)Fe(\eta^5\text{-}Cp^*)$ and $(\eta^6\text{-}9\text{-}CH_3\text{-}C_{13}H_8)Fe(\eta^5\text{-}Cp^*)$ (**A**). When **A** is heated in nonane at 150 °C it undergoes $\eta^6 \rightleftharpoons \eta^5$ inter-ring rearrangement with the formation of hexamethyldibenzoferrocene (**B**). The electrochemical behavior of **A** and **B** was studied by cyclic voltammetry. One-electron reduction of **A** and **B** to the corresponding radical anions induces inter-ring haptotropic rearrangement $\mathbf{A}^{\cdot-} \rightleftharpoons \mathbf{B}^{\cdot-}$. The equilibrium in the $19\bar{e}$ state is shifted to the η^6-isomeric radical anion $\mathbf{A}^{\cdot-}$, while in the $18\bar{e}$ precursors, it shifts to the η^5-isomer **B**.

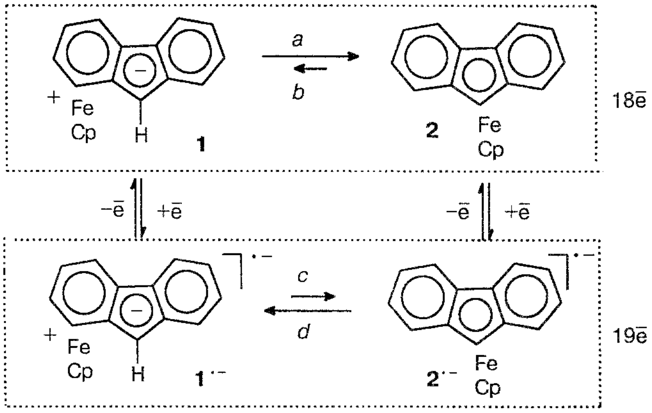
Key words: iron, π-complexes, haptotropic rearrangements, electron transfer-induced reaction, cyclic voltammetry.

At present, many examples of inter-ring haptotropic rearrangements are known.[1,2] The main characteristics, the kinetic and thermodynamic parameters of reversible $\eta^6 \rightleftharpoons \eta^6$ haptotropic isomerizations (for naphthalene complexes and similar systems) and $\eta^6 \rightleftharpoons \eta^5$ haptotropic isomerizations (for fluorenyl complexes and compounds similar in structure) of the series of $18\bar{e}$ π-complexes of transition metals with polyaromatic ligands have been determined, and the activation barriers have been obtained.[3,4] Inter-ring haptotropic rearrangements for the related $19\bar{e}$ complexes have not been studied until recently. The only example is $\eta^6 \rightleftharpoons \eta^5$-isomerization of the radical anions of η^6- and η^5-fluorenylcyclopentadienyl iron complexes $\mathbf{1}^{\cdot-} \rightleftharpoons \mathbf{2}^{\cdot-}$ found under conditions of electrochemical reduction (see Ref. 5) (Scheme 1). An important distinction from the similar process for $18\bar{e}$-precursors, *viz.*, **1** and **2**, is that in the case of the $19\bar{e}$-complexes $\eta^6 \rightleftharpoons \eta^5$-isomerization occurs under considerably milder conditions even at −60 °C, and the position of the equilibrium is strongly shifted to the isomeric η^6-radical anion. A decrease in temperature favors this shift of the equilibrium to a greater extent (see Scheme 1).

As follows from the results obtained, on going from the $18\bar{e}$ to the highly reactive $19\bar{e}$ state, the activation barrier to $\eta^6 \rightleftharpoons \eta^5$-rearrangement decreases substantially, the rate of haptotropic isomerization increases, and the relative quantitative composition of the isomers changes: the η^6-isomer predominates in the equilibrium mixture.

One example of the $\eta^6 \rightleftharpoons \eta^5$-rearrangement of $19\bar{e}$ fluorenyl complexes is insufficient to draw a conclusion about the factors governing these processes. Therefore, we have studied inter-ring haptotropic rearrangements in odd-electron ($17\bar{e}$, $19\bar{e}$) π-complexes of transition metals, their dependence on the nature of the metal atoms, and on the presence of substituents in the ligands.

Scheme 1



Cp = C_5H_5

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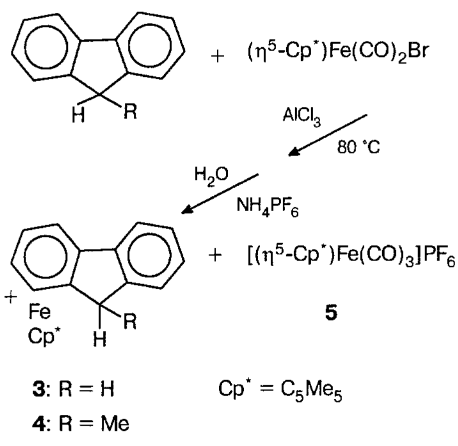
In the present work we report inter-ring haptotropic rearrangements in (η^5-pentamethylcyclopentadienyl)fluorenyl Fe^{II} complexes for both the $18\bar{e}$ and $19\bar{e}$ states. The results obtained together with the known data on analogous processes for structually related complexes **1** and **2** allow one to ascertain the effect of methyl groups on rearrangements of the (*a*—*d*)-type (see Scheme 1) and to evaluate the general character of the regularities previously found for inter-ring haptotropic isomerizations of $19\bar{e}$ fluorenyl complexes (*c* and *d*).

Results and Discussion

Previously unknown cationic pentamethylcyclopentadienyl iron complexes (**3** and **4**) with fluorene and 9-methylfluorene as ligands were synthsized by the method in Ref. 6 and used as the starting compounds. Complexes **3** and **4** were prepared by reacting (η^5-Cp*)Fe(CO)$_2$Br with fluorene (9-methylfluorene) in heptane at 80 °C in the presence of $AlCl_3$. In this reaction, tricarbonyl(η^5-pentamethylcyclopentadienyl)iron hexafluorophosphate **5** (up to 50 %) is formed as a by-product, which can be separated either by TLC or by its direct photodecomposition in a $CHCl_3$ solution over Al_2O_3 (Scheme 2).

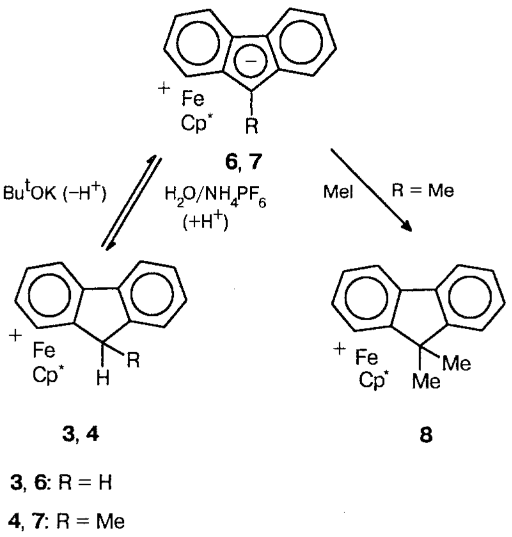
Scheme 2



3 And **4** can be also synthesized without a solvent, namely, in a melt according to a known procedure;[6] the yields of arene complexes **3** and **4** are not considerably higher, but complex **5** is formed in trace amounts.

The cationic complexes **3** and **4** are easily deprotonated under the action of Bu^{t}OK in THF to form the corresponding zwitter-ionic derivatives **6** and **7** (Scheme 3).

Scheme 3

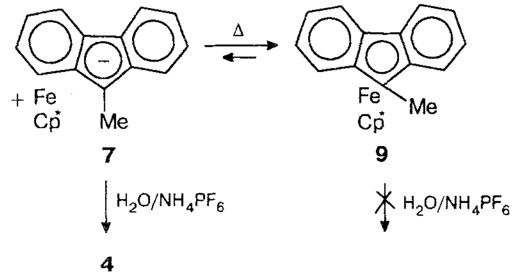


In solution protonation of **6** and **7** immediately after their formation results in the starting cations **3** and **4**. The zwitter-ionic complex **7** is stable in a THF solution for several hours and is smoothly alkylated by MeI to form the corresponding cationic complex **8**. Complex **6** is less stable in solution than **7**. Both neutral derivatives, **6** and **7**, were characterized by ^{1}H NMR spectroscopy after their generation in THF-d$_8$ in an evacuated and sealed system. Storage of their 0.05 *M* solutions in THF (**6**, for several hours; **7**, for 2—3 days) and increasing the solution concentration results in transformations of the zwitter-ionic complexes: the solutions become intensely bluish-violet, after which we failed to register the ^{1}H NMR spectrum, and the signals of **6** and **7** initially present in the spectra disappear completely. At the same time, intense absorption bands at λ ~600 nm are observed in the visible range of the electronic spectra of these solutions. The protonation and alkylation represented in Scheme 3 are impossible under the conditions mentioned. The structure of the transformation products of **6** and **7** is now under study and will be reported later. It should be mentioned that these transformations do not preclude the study of inter-ring haptotropic rearrangements of the (*a*—*d*)-type (see Scheme 1). Type (*a*) and (*b*) rearrangements of $18\bar{e}$-complexes occur in nonpolar (benzene, alkanes) solvents, in which **6** and **7** do not undergo the aforementioned transformations. Type (*c*) and (*d*) isomerizations of $19\bar{e}$-complexes (see Scheme 1) under conditions of cyclic voltammetry (CVA) have been studied, as a rule, in THF but at low concentrations ($5 \cdot 10^{-3}$ *M*) and occur with high rates. Therefore, the rate of the side transformation of **6** and **7** can be neglected. As **7** is more stable than **6**, it was used for studies of inter-ring haptotropic rearrangements of the (*a*—*d*)-type (see Scheme 1) both for the $18\bar{e}$- and $19\bar{e}$-states.

After the η^6-zwitter-ionic complex **7** was heated in nonane at 150 °C for 5 h, (η^5-9-methylfluorenyl)(η^5-pentamethylcyclopentadienyl)iron (**9**), hexamethyldibenzoferrocene, was isolated and fully characterized (Scheme 4).

When this thermal $\mathbf{7} \rightleftharpoons \mathbf{9}$ $\eta^6 \rightleftharpoons \eta^5$-isomerization is performed in an evacuated and sealed system at 150 °C, the $\mathbf{7} \rightleftharpoons \mathbf{9}$ equilibrium is established in 3 h. As in the

Scheme 4



case of the reversible haptotropic isomerization of the nonmethylated analogs (η^6-$C_{13}H_9$)Fe(η^5-Cp) (**1**) $\rightleftharpoons$ (η^5-$C_{13}H_9$)Fe(η^5-Cp) (**2**), the $\eta^6 \rightleftharpoons \eta^5$-equilibrium (see Scheme 4) is also shifted to the η^5-isomer (**9**). The ratio of isomers **7**:**9** in the equilibrium mixture determined after its treatment with H_2O/NH_4PF_6 (see Scheme 4) equals 1 : 6.

Thus, as follows from the results obtained, on going from cyclopentadienyl to pentamethylcyclopentadienyl derivatives of fluorenyliron, more drastic conditions are necessary for inter-ring $\eta^6 \rightleftharpoons \eta^5$-isomerization, and the activation barrier to the rearrangement increases, however, the position of the equilibrium is almost unchanged and, like in the case of **1** $\rightleftharpoons$ **2** isomerization (Ref. 7), the η^5-isomer predominates in the equilibrium mixture.

With the aim of studying the effect of the pentamethylcyclopentadienyl ligand on the course of the $\eta^6 \rightleftharpoons \eta^5$-rearrangement for fluorenyliron complexes in the 19$\bar{e}$-state, we examined the electrochemical behavior of **7** and **9** by CVA in a wide temperature range.

Previously we studied the redox properties of nonmethylated analogs of **7** and **9** (**1** and **2**) and showed that one-electron reversible reduction of **1** induces the inter-ring $\eta^6 \rightleftharpoons \eta^5$ haptotropic rearrangement **1** $\rightleftharpoons$ **2**; here, unlike the 18$\bar{e}$-precursors, the equilibrium is strongly shifted to the η^6-isomer.[5]

The electrochemical behavior of **7** and **9** is similar to that of their nonmethylated analogs **1** and **2** in many ways. The differences observed are related only to the stability of the electrogenerated radical anions and radical cations and the corresponding redox potentials. The introduction of donor methyl substituents into the cyclopentadienyl ring results in a negative shift of the oxidation potential of **9** (E^0 = 0.03 V, SCE) and **7** ($E_p{}^a$ = −0.37 V) (Fig. 1) as compared with those of **2** (E^0 = 0.28 V) and **1** ($E_p{}^a$ = −0.14 V). The electrogenerated radical cation **9**$^{\cdot+}$ is stable even at room temperature in the time scale of the CVA method, while the radical cation **2**$^{\cdot+}$ is stable only at $T < -70$ °C (see Ref. 5). The radical cation **7**$^{\cdot+}$, like **1**$^{\cdot+}$, is unstable even below −90 °C.

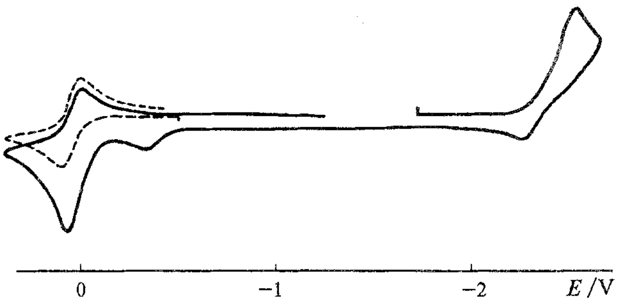


Fig. 1. Cyclic voltammograms of a 10^{-3} *M* solution of the η^5-isomer of (pentamethylcyclopentadienyl)(9-methylfluorenyl)iron (**9**) in THF/0.05 *M* Bu_4NPF_6 on a 1-mm Pt-electrode (v = 0.2 V s^{-1}) at 20 °C; the reference electrode is an aqueous saturated calomel electrode.

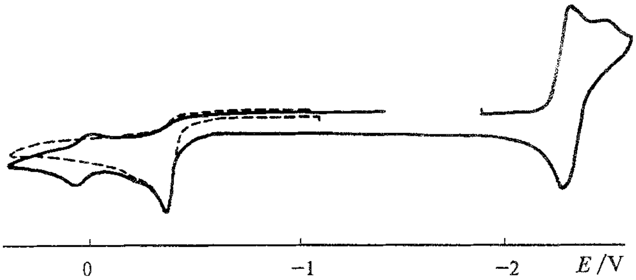
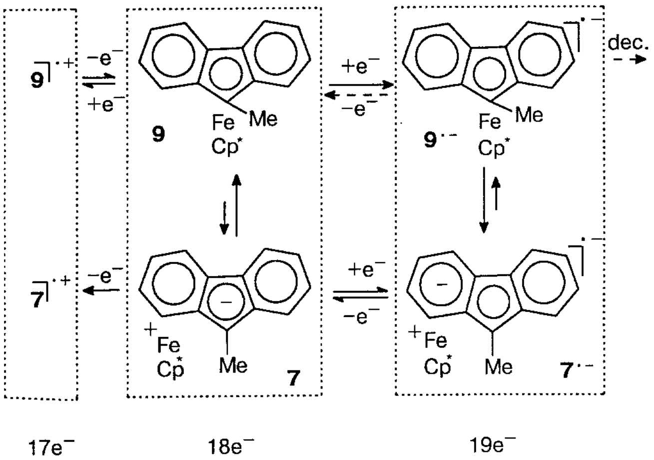


Fig. 2. Cyclic voltammograms of a 10^{-3} *M* solution of the η^6-isomer of (pentamethylcyclopentadienyl)(9-methylfluorenyl)iron (**7**) in THF/0.05 *M* Bu_4NPF_6 on a 1-mm Pt-electrode (v = 0.2 V s^{-1}) at 20 °C; the reference electrode is an aqueous saturated calomel electrode.

The reduction potentials of **7** (E^0 = −2.31 V) and **9** ($E_p{}^c$ = −2.51 V) (Fig. 2) are also shifted to the cathode region relative to the nonmethylated analogs (E^0 = −1.99 V for **1**; E^0 = −2.19 V for **2**). In the voltammograms of **7**, small reduction and oxidation peaks of **9** are observed in addition to the reversible one-electron reduction peak, which indicates the occurrence of $\eta^6 \rightarrow \eta^5$-isomerization at the stage of the electrogenerated radical anion **7**$^{\cdot-}$ (see Scheme 3). The small heights of the observed peaks of **9** and the reversible character of the reduction of **7** attest that the **7**$^{\cdot-} \rightleftharpoons$ **9**$^{\cdot-}$ $\eta^6 \rightleftharpoons \eta^5$-equilibrium is shifted to the radical anion of the η^6-isomer (**7**$^{\cdot-}$). Decreasing the temperature to −50 °C results in the complete suppression of $\eta^6 \rightarrow \eta^5$-isomerization, while in the case of the nonmethylated analogs even at −60 °C small peaks of the reduction and oxidation of **2** are observed in the voltammogram of the zwitter-ionic complex. Similarly to **2** (see Ref. 5), the reduction of **9** occurs irreversibly and is accompanied by $\eta^5 \rightarrow \eta^6$-isomerization (Scheme 5), as follows from the appearance of anodic peaks of the oxidation of **7**$^{\cdot-}$ and **7** on CVA. However, unlike **2**, whose irreversible reduction at $T < 0$ °C is caused exclusively by $\eta^5 \rightarrow \eta^6$-isomerization (see Ref. 5), the irreversibility of the reduction of **9** (up to −70 °C) is also related to the alternative channel of the decay of the electrogenerated radical anion **9**$^{\cdot-}$, because the heights of the anodic oxidation peaks of **7**$^{\cdot-}$ and **7** are essentially smaller than those of one-electron peaks. Detachment of the fluorenyl ligand to form

Scheme 5



decamethylferrocene can be suggested as an alternative channel of the decay of the radical anion $9^{\cdot -}$. This agrees with the considerable increase observed in the height of the oxidation peak of **9** on the anode branch of the CVA (with the change in the direction of potential scanning after the potentials of the generation of $9^{\cdot -}$), which can be related to the oxidation of Cp*Fe (E^0 = 0.0 V) at potentials of the oxidation of **9**.

Unfortunately, the dominant alternative channel of the decay of radical anion $9^{\cdot -}$ does not allow quantitative comparison of the kinetic and thermodynamic parameters of the $9^{\cdot -} \rightleftharpoons 7^{\cdot -}$ hapto-isomerization reactions.

Thus, while the activation barrier to the $\eta^6 \rightleftharpoons \eta^5$ inter-ring rearrangement of 18ē pentamethylcyclopentadienyl complexes of fluorenyliron **7** and **9** is considerably higher than that for their nonmethylated analogs, this distinction is almost absent for the 19ē-state of the complexes considered, and only slight increase in the rate of $\eta^6 \rightarrow \eta^5$-rearrangement is observed. On the whole, the characteristics found for the nonmethylated analogs hold, the activation barrier to the $\eta^6 \rightleftharpoons \eta^5$ inter-ring rearrangements is considerably lower than that for 18ē-complexes, and the position of the $\eta^6 \rightleftharpoons \eta^5$-equilibrium for the 19ē radical anions is shifted to the η^6-isomers.

Experimental

All of the reactions were performed in an atmosphere of dry purified argon. Benzene and THF were dried with benzophenone ketyl. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR—400 and Bruker WP—200SY spectrometers, FAB mass spectra were recorded on a Kratos Concept instrument, the energy of bombarding atoms (Cs) was 8 keV, 2-nitrobenzyl alcohol was used as the matrix. The melting points measured are uncorrected. (η^5-Cp*)Fe(CO)$_2$Br was prepared by the known procedure.[8]

Electrochemical measurements were performed in an atmosphere of dry argon. Abs. THF preliminarily purified by the "ketyl" procedure was distilled directly into the cell evacuated and filled with argon (see Ref. 9). A 0.05 *M* solution of Bu_4NPF_6 preliminarily dehydrated by melting *in vacuo* directly before the distillation of the solvent was used as the base electrolyte. The cell was kept at constant temperature with ethanol in a Dewar flask cooled with liquid nitrogen. All potentials were measured relative to an aqueous saturated calomel electrode (SCE) by referring the reference electrode potential (Ag/AgCl/4 *M* aqueous LiCl), which was separated from the solution studied by a bridge filled with a solution of the base electrolyte, to the potential of the redox transition bis(diphenyl)chromium$^{0/+}$ (E^0 = −0.68 V, SCE). A disk platinum electrode 1 mm in diameter sealed in glass and finished with a diamond paste (diameter of the grain was 1 mm) was used as the working electrode. Voltammograms were registered by a PAR 175 signal generator and a PAR 173 potentiostat with compensation of ohmic losses by the method of positive feedback.

Synthesis of (η^5-pentamethylcyclopentadienyl)(η^6-fluorenyl)iron hexafluorophosphate (3). A mixture of 2.00 g (0.062 mol) of (η^5-Cp*)Fe(CO)$_2$Br, 1.2 g (0.07 mol) of fluorene, and 3.5 g (0.27 mol) of $AlCl_3$ was heated for 4 h at 80 °C in heptane. After cooling, the reaction mixture was treated with water (50 mL) and filtered. The organic layer was separated, and the mixture was additionally washed with a small portion of water. A saturated aqueous solution of NH_4PF_6 was added to the combined aqueous extracts. The yellow precipitate was filtered off and dried on the filter. The thus obtained mixture of complexes **1** and **3** was separated by TLC on Al_2O_3 plates (Reanal, according to Brockmann activity II) in $CHCl_3$: C_2H_5OH = 19 : 1. From the band with R_f 0.65, 8.4 g (27 %) of [(η^6-$C_{13}H_{10}$)Fe(η^5-Cp*)]PF_6 (**3**) with m. p. 183—184 °C was isolated. Found (%): C, 54.06; H, 5.02. $C_{23}H_{25}F_6FeP$. Calculated (%): C, 54.97; H, 4.97. ^{1}H NMR ($(CD_3)_2CO$, TMS), δ: 1.68 (s, 15 H, CH_3); 4.04 (*AB*-system, *J* = 22.5 Hz, 2 H, CH_2); noncoordinated six-membered ring: 8.15 (m, 1 H); 7.82 (m, 1 H); 7.64 (m, 2 H); coordinated six-membered ring: 6.77 (d, *J* = 5.3, 1 H); 6.17 (m, 2 H). ^{13}C NMR ($(CD_3)_2CO$, TMS), δ: 9.32 (CH_3); 35.98 (C_9); 91.15 (C_5Me_5); noncoordinated six-membered ring: 124.04; 126.83; 129.07; 130.98; 137.25; 145.53; coordinated six-membered ring: 82.99; 87.75; 89.98; 90.22; 104.59; 105.96. MS, *m/z*: 1361 $[Q_3(PF_6)_2]^+$; 859 $[Q_2(PF_6)]^+$; 357 $[Q]^+$, where Q is the cationic part of molecule **3**, $[C_{23}H_{26}Fe]^+$.

Synthesis of [(η^5-pentamethylcyclopentadienyl)(η^6-9-methylfluorenyl)iron hexafluorophosphate (4). Complex **4** was prepared by the procedure described above for the synthesis of **3** from 4.0 g (12.7 mmol) of (η^5-Cp*)Fe(CO)$_2$Br, 2.6 g (0.14 mmol) of 9-methylfluorene, and 5.3 g (40 mmol) of $AlCl_3$. Complex **4** was obtained in 39 % yield with m. p. 191—194 °C (dec.). Found (%): C, 55.94; H, 5.28. $C_{24}H_{27}F_6FeP$. Calculated (%): C, 55.84; H, 5.27. ^{1}H NMR ($(CD_3)_2CO$, TMS), δ: noncoordinated six-membered ring: 8.07 (d, *J* = 7.2 Hz, 1 H); 7.79 (d, *J* = 7.2 Hz, 1 H); 7.6 (m, 2 H); coordinated six-membered ring: 6.7 (m, 1 H); 6.5 (m, 1 H); 6.1 (m, 2 H). Cp*-ring: 1.64 (s, 15 H); CH_3 in position 9 of the fluorenyl ligand 1.53 (d, *J* = 7.3 Hz, 3 H); H in position 9 of the fluorenyl ligand 4.25 (q, *J* = 7.3 Hz, 1 H). ^{13}C NMR ($(CD_3)_2CO$, TMS), δ: noncoordinated six-membered ring: 150.63; 136.824; 130.806; 128.081; 126.663; 123.596; coordinated six-membered ring: 110.973; 103.285; 91.004; 89.971; 86.79; 82.720; Cp*-ring: 9.012; (CH_3): 89.808; C_9 of the fluorenyl ligand: 41.972; CH_3 in position 9 of the fluorenyl ligand: 20.263. MS, *m/z*: 887 $[Q_2(PF_6)]^+$; 371 $[Q]^+$, where Q is the cationic part of molecule **4**, $[C_{24}H_{27}Fe]^+$.

Synthesis of (η^5-pentamethylcyclopentadienyl)(η^6-fluorenyl)iron (6). 2 mL of THF-d_8 and 0.05 g (0.1 mmol) of the cationic complex **3** were placed in a standard Schlenk vessel. The system was evacuated, degassed, and sealed off (vacuum $8 \cdot 10^{-2}$ Torr). Then 0.008 g (0.08 mmol) of Bu^{t}OK was added *in vacuo*, the system was stirred by brief shaking. The solution became intensely bluish-green almost immediately. After 2 h, the solution was filtered off *in vacuo* into an NMR tube that was then sealed. ^{1}H NMR (THF-d_8, TMS), δ: noncoordinated six-membered ring: 7.92 (d, J = 7.2 Hz, 1 H); 7.43 (d, J = 7.2 Hz, 1 H); 7.19 (t, J = 7.2 Hz, 1 H); 6.74 (t, J = 7.2 Hz, 1 H); coordinated six-membered ring: 6.16 (d, J = 6.2 Hz, 1 H); 5.48 (d, J = 6.2, 1 H); 4.92 (t, J = 6.2 Hz, 1 H); 4.79 (t, J = 6.2 Hz, 1 H); H in position 9 of the fluorenyl ligand: 5.63 (s, 1 H); Cp*-ring: 1.11 (s, 15 H). The signals for the protons of the starting cation **3** were also observed in the ^{1}H NMR spectrum. The sealed tube with the solution of **4** in THF-d_8 was kept for 7 days at 18 °C. After that the above signals for the protons completely disappeared and no new signals were observed.

Synthesis of (η^5-pentamethylcyclopentadienyl)(η^6-9-methylfluorenyl)iron (7). The zwitter-ionic complex **7** was prepared both *in vacuo* (similarly to the method described above) and under normal pressure. 0.03 g (0.28 mmol) of Bu^{t}OK was added to 0.120 g (0.24 mmol) of the cationic complex **4** in 50 mL THF. The mixture was magnetically stirred for 3 h, and the solution became deep-green. The reaction mixture was filtered, and the solvent was removed *in vacuo*. The solid residue was dissolved in benzene, the solution was filtered again, and benzene was removed *in vacuo*. **7** (0.035 g, 43 %) was obtained as a shiny blackish-green finely crystalline substance decomposing in air and in the light. ^{1}H NMR (C_6D_6, TMS), δ: noncoordinated six-membered ring: 8.12 (d, J = 7.5 Hz, 1 H); 7.91 (d, J = 7.5 Hz, 1 H); 7.76 (t, J = 7.5 Hz, 1 H); 7.26 (t, J = 7.5 Hz, 1 H); coordinated six-membered ring: 5.68 (d, J = 5.8 Hz, 1 H); 5.21 (d, J = 5.8 Hz, 1 H); 4.28 (m, 2 H); 2.76 (s, 3 H, CH_3); Cp*-ring: 1.11 (s, 15 H).

Interaction of 7 with methyl iodide. 0.5 mL (0.65 mmol) of methyl iodide was added to a solution of the zwitter-ionic complex **5** in THF that was obtained from 0.05 g (0.1 mmol) of cation **4** and 0.170 g (0.15 mmol) of Bu^{t}OK. The deep-green solution immediately became yellow, and 0.3 g NH_4PF_6 in 10 mL of water was added to the reaction mixture. THF was removed *in vacuo*, and the residue was treated with CH_2Cl_2. The solution obtained was dried with $MgSO_4$ and concentrated *in vacuo*. The product was precipitated from CH_2Cl_2 with ether. Complex **8** (0.03 g, 58 %) was obtained with m. p. 172 °C (dec.). ^{1}H NMR ($(CD_3)_2CO$, TMS), δ: noncoordinated six-membered ring: 8.06 (m, 1 H); 7.75 (m, 1 H); 7.61 (m, 1 H); 7.60 (m, 1 H); coordinated six-membered ring: 6.76 (d, J = 6.2 Hz, 1 H); 6.49 (d, J = 6.2 Hz, 1 H); 6.12 (t, J = 6.2 Hz, 1 H); 6.07 (t, J = 6.2 Hz, 1 H); 2.00 (s, 3 H, CH_3); 1.73 (s, 3 H, CH_3); 1.70 (s, 15 H, CH_3).

(η^5-Pentamethylcyclopentadienyl)(η^5-9-methylfluorenyl)iron (9). Thermal $\eta^6 \rightleftharpoons \eta^5$-rearrangement. 5 mL of THF and 0.25 g (0.48 mmol) of cationic complex **4** were placed in a standard Schlenk vessel. After evacuating and degassing, the system was sealed, then 0.1 g (0.99 mmol) of Bu^{t}OK was added to the solution of **4** in THF, and the mixture was magnetically stirred for 3 h. THF was removed *in vacuo* from the dark-green solution obtained, 12 mL of nonane were distilled to the solid residue, and the solution obtained was filtered *in vacuo* into another flask, which was sealed off. The solution was heated for 3.5 h at 150—160 °C. After cooling, the reaction vessel was opened and 0.05 g of NH_4PF_6 in 5 mL of H_2O was rapidly added. The mixture was vigorously shaken for 3 min, the organic layer was separated, and nonane was removed *in vacuo*. **9** was obtained in a yield of 0.09 g (55 %) as reddish-brown crystals, m. p. 140—143 °C (dec.), which are stable in air for several hours. ^{1}H NMR (C_6D_6, TMS), δ: noncoordinated six-membered rings: 7.70 (d, J = 7.0 Hz, 2 H); 7.26 (d, J = 7.0 Hz, 2 H); 7.08 (m, 2 H); 6.98 (m, 2 H); 2.33 (s, 3 H, CH_3); 1.27 (s, 15 H, CH_3). ^{13}C NMR (C_6D_6, TMS), δ: noncoordinated six-membered rings: 126.72; 125.95; 123.81; 121.87; 91.88; 83.01; C_5Me_5: 74.56; C_9 66.89; CH_3 in Cp*-ring: 8.44; CH_3 in position 9 of the fluorenyl ligand: 9.23. The mass spectrum contains an intense peak of the molecular ion $[M]^+$ 370.

After extraction with CH_2Cl_2 and precipitation with ether, 0.022 g (9 %) of cationic complex **4** was isolated from the aqueous layer.

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