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Abstract

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LIGAND EXCHANGE IN SUBSTITUTED FERROCENES

Earlier (1) we described the interaction of ferrocene with aromatic hydrocarbons, leading to arene-cyclopentadienyliron cations. In the present work it is shown that substituted ferrocenes are also capable of exchanging cyclopentadienyl rings for aromatic ligands. We have carried out the interaction of mono- and 1,1′-diethylferrocenes with benzene and mesitylene, mono- and 1,1′-diacetylferrocenes with mesitylene, and monocyanato-, monophenyl-, and 1,1′-diphenylferrocenes with benzene. As a result, the following arene-cyclopentadienyliron cations were obtained (see Table 1), isolated as tetraphenyl- and tetrafluoroborates and iodides. All decomposition and melting temperatures were determined in sealed capillaries and depended strongly on the heating rate.

Table 1

Salts of arene-cyclopentadienyliron with a substituent in the cyclopentadienyl ring $[RC_5H_4FeAren]X$

R	Arene	X	Reaction time, h	Reaction temp., °C	Decomp. temp., °C	Yield, %
C_2H_5	benzene	$[BF_4]^-$	8	80	91–93	20
C_2H_5	mesitylene	$[B(C_6H_5)_4]^-$	5	130	245.5–246.5	32
C_2H_5	mesitylene	J^-			~ 150	
C_2H_5	mesitylene	$[BF_4]^-$			136–138	•
CH_3CO	mesitylene	$[B(C_6H_5)_4]^-$ (1)	5	130	197–198	22
CN	benzene	$[BF_4]^-$			–	
CN	benzene	$[B(C_6H_5)_4]^-$	6	80	191–194	
C_6H_5	benzene	$[B(C_6H_5)_4]^-$	8	80	240–241	82
C_6H_5	benzene	$[BF_4]^-$			122–124	

The data obtained by us as a result of the work performed show that substituents in the ferrocene nucleus exert a substantial influence on ligand exchange.

At 90–100°, in the reaction with mesitylene, 1,1′-diethylferrocene forms 32% ethylcyclopentadienyl-mesityleneiron, ferrocene forms 20% cyclopentadienyl-mesityleneiron, and 1,1′-diacetylferrocene forms 4% acetylcyclopentadienyl-mesityleneiron. At 120–130°, respectively, diethylferrocene reacts to 39%, and diacetylferrocene to 22%. At 50°, diacetylferrocene does not react with mesitylene, while diethylferrocene forms 5% ethylcyclopentadienyl-mesityleneiron. Thus, the capacity for ligand exchange decreases in the series:

$$(C_2H_5C_5H_4)_2Fe > (C_5H_5)_2Fe > (CH_3COC_5H_4)_2Fe.$$

This is confirmed by the results obtained with monosubstituted ferrocenes. Reacting with benzene, ethylferrocene forms a mixture of 27% ethylcyclopentadienyl- and 73% cyclopentadienyl-benzeneiron:

$$(C_2H_5C_5H_4)(C_5H_5)Fe+C_6H_6 \xrightarrow[NaBF_4]{AlCl_3/Al} [(C_2H_5C_5H_4)(C_6H_6)Fe]\,BF_4+[(C_5H_5)(C_6H_6)Fe]\,BF_4$$

27% 73%

On interaction of acetylferrocene with mesitylene, a mixture of acetylcyclopentadienyl- and cyclopentadienyl-mesityleneiron is formed. It was not possible to separate this mixture chromatographically, since $[CH_3COC_5H_4FeC_6H_3 \cdot (CH_3)_3]BF_4$ decomposes appreciably on Al_2O_3. The results of fractional crystallization of the tetraphenylborates show that the cation mixture contains 80–90% acetylcyclopentadienyl-mesityleneiron.

Thus, in the case of monoalkylferrocene it is chiefly the substituted ring that undergoes exchange, whereas in the case of monoacetylferrocene it is the unsubstituted ring. The data obtained provide only a very rough estimate of the reactivity of the compounds studied, but nevertheless make it possible to draw the principal conclusion: electron-donating substituents in the ferrocene nucleus facilitate ligand exchange, while electron-accepting substituents hinder it. This applies both to the molecule as a whole and to an individual ring. Experiments with mono- and 1,1′-dicyanoferrocenes confirm this conclusion. 1,1′-Dicyanoferrocene does not react with benzene under the conditions (sixfold excess of $AlCl_3$, 80°) under which ferrocene and its alkyl derivatives react readily. Monocyanoferrocene interacts with benzene, forming a mixture of cyanocyclopentadienyl- and cyclopentadienyl-benzeneiron, with the former predominating.

Experimental Part

In the exchange reactions we carried out, the ratio of substituted ferrocene, Al powder, and $AlCl_3$ was 1 : 1 : 2. An excess of $AlCl_3$ (up to 8 moles) does not increase the yield. If the reacting substance contained substituents capable of complex formation with $AlCl_3$, the amount of the latter was increased accordingly (1 mole additionally for each CH_3CO group and 2 moles for each CN group). In the presence of groups capable of reduction (CH_3CO- and $CN-$), Al powder was not added to the reaction mixture. The optimum temperatures and reaction times are given in Table 1.

Almost all of the tetraphluoroborates and iodides of arene-cyclopentadienyliron cations obtained in this work are yellow. They are all readily soluble in water, C_2H_5OH, and CH_3OH, moderately soluble in isopropyl alcohol, dichloroethane, and acetone, and insoluble in benzene, petroleum ether, and diethyl ether. Almost all tetraphluoroborates were purified by reprecipitation with ether from dichloroethane and by recrystallization from isopropyl alcohol (exceptions are noted).

Below are given two standard procedures that were used for all the substances obtained.

Interaction of 1,1′-diethylferrocene with mesitylene.

a) **Isolation of the tetraphenylborate.** A mixture of 5.65 g (0.0233 mole) of 1,1′-diethylferrocene, 6.20 g (0.0466 mole) of $AlCl_3$, 0.63 g (0.0233 g-atom) of Al powder, and 88 ml of absolute mesitylene was stirred in a stream of nitrogen at 120–130° for 5 h. It was then decomposed at 0–5° with 300 ml of water. From the aqueous layer was precipitated a pale-yellow tetraphenylborate of ethylcyclopentadienyl-mesityleneiron; it was reprecipitated with water from acetone and recrystallized from acetone. The product yield was 5.35 g (39% of theory), mp 245.5–246.5° with decomposition.

Found, %:	C 81.69, 81.55; H 7.10, 6.93; Fe 9.82, 9.24
$C_{40}H_{41}BFe$. Calculated, %:	C 81.65; H 7.02; Fe 9.49

b) **Isolation of the tetraphluoroborate.** The experiment was carried out by the method described above. After heating had ended, the reaction mixture was decomposed at 0–5° with 75 ml of water; the aqueous layer was separated, and from it, by addition of 25% NH_4OH, aluminum was removed in the form of Al^{3+} hydroxide. Then 3.9 g (0.0355 mole) of $NaBF_4$ was added to the aqueous layer, and the water was removed under reduced pressure in a stream of N_2 (bath temperature not above 40–50°). Tetraphluoroborate

ethylcyclopentadienylmesityleneiron was extracted from the residue with hot dichloroethane and precipitated with ether.

Found, %: C 53.81, 53.89; H 5.99, 5.92; F 21.20, 21.31
$C_{16}H_{21}BF_4Fe$. Calculated, %: C 53.98; H 5.94; F 21.35

In one of the experiments, instead of $NaBF_4$, NaJ was added to the aqueous layer. Thus iodide ethylcyclopentadienylmesityleneiron, with decomposition temperature about 150° after recrystallization from tetrahydrofuran with $CHCl_3$ (2 : 1), was obtained.

Found, %: C 48.37, 48.43; H 5.34, 5.37; J 32.25, 32.18; Fe 13.91, 13.87
$C_{16}H_{21}JFe$. Calculated, %: C 48.51; H 5.35; J 32.04; Fe 14.10

The following were obtained by the methods described above:
From benzene and diethylferrocene—tetrafluoroborate of ethylcyclopentadienylbenzeneiron,

Found, %: C 50.01, 49.69; H 4.89, 4.76; F 24.10, 24.37
$C_{13}H_{15}BF_4Fe$. Calculated, %: C 49.73; H 4.81; F 24.21

From mesitylene and diacetylferrocene—pale-orange tetrafluoroborate of acetylcyclopentadienylmesityleneiron, recrystallized from alcohol with $CHCl_3$,

Found, %: C 52.21, 52.17; H 5.10, 5.21; F 20.40, 20.47
$C_{16}H_{19}OBF_4Fe$. Calculated, %: C 51.94; H 5.17; F 20.54

From benzene and 1,1′-diphenylferrocene—tetraphenylborate of phenylcyclopentadienylbenzeneiron, recrystallized from acetone,

Found, %: C 82.23, 82.51; H 6.10, 6.17; Fe 9.54, 9.59
$C_{41}H_{35}BFe$. Calculated, %: C 82.87; H 5.93; Fe 9.40

and tetrafluoroborate of phenylcyclopentadienylbenzeneiron, purified chromatographically on Al_2O_3,

Found, %: C 56.25, 56.00; H 4.20, 4.27; F 20.70, 20.49
$C_{17}H_{15}BF_4Fe$. Calculated, %: C 56.37; H 4.18; F 20.99

From an experiment with phenylferrocene (boiling for 15 h), a mixture of tetrafluoroborates of phenylcyclopentadienyl- and cyclopentadienylbenzeneiron was obtained. The mixture was separated by triple chromatography on Al_2O_3 (eluent—dichloroethane with 5-15% abs. alcohol).

Interaction of ethylferrocene with mesitylene and benzene

a) **Interaction with mesitylene.** From 5 g (0.0233 mole) of ethylferrocene, 12.56 g (0.0940 mole) of $AlCl_3$, 0.62 g (0.0229 g-at) of Al dust, and 88 ml of mesitylene (heating at 70-80°, 5 h), a mixture of ethylcyclopentadienyl- and cyclopentadienylmesityleneiron was obtained, precipitated in the form of tetraphenylborates. The total yield of products was 4 g. By extraction with acetone at various temperatures and fractional crystallization from dichloroethane with alcohol (2 : 1) and from acetonitrile, the mixture was partially separated, giving 2.3 g of tetraphenylborate of cyclopentadienylmesityleneiron, m.p. 256-258° with decomposition.

Found, %: C 81.25, 81.48; H 6.60, 6.51
$C_{38}H_{37}BFe$. Calculated, %: C 81.44; H 6.65

and 0.31 g of tetraphenylborate of ethylcyclopentadienylmesityleneiron, m.p. 245–246.5° with decomposition.

Found, %: C 81.64, 81.73; H 7.08, 7.13
$C_{40}H_{41}BFe$. Calculated, %: C 81.65; H 7.02

b) **Interaction with benzene.** As a result of the interaction of 13.92 g (0.0650 mole) of ethylferrocene, 34.8 g (0.2616 mole) of $AlCl_3$, 1.76 g

(0.0650 mole) of Al powder and 237 ml of benzene (boiling for 8 h), 3.7 g of a mixture of the tetrafluoroborates of ethylcyclopentadienyl- and cyclopentadienylbenzeneiron was obtained. This mixture was reprecipitated with ether from dichloroethane and then chromatographed several times on columns and on plates with Al_2O_3 (eluents: dichloroethane; dichloroethane with acetone (1 : 1)). As a result, 0.95 g (27% of the initial mixture) of ethylcyclopentadienylbenzeneiron tetrafluoroborate was obtained, m.p. 91–92.5°, with decomposition.

Found, %:	C 49.61, 49.67;	H 4.70, 4.67;	F 24.32, 24.25
$C_{13}H_{15}BF_4Fe$. Calculated, %:	C 49.73;	H 4.81;	F 24.21

and 2.61 g (~73% of the initial mixture) of cyclopentadienylbenzeneiron tetrafluoroborate

Found, %:	C 46.58, 46.49;	H 3.84, 3.82;	F 26.91, 26.16
$C_{11}H_{11}BF_4Fe$. Calculated, %:	C 46.49;	H 3.88;	F 26.87

Cyclopentadienylbenzeneiron tetrafluoroborate has no definite melting or decomposition point. In a sealed capillary it gradually becomes charred.

Reaction of acetylferrocene with mesitylene. As a result of the reaction of 1.21 g (0.0053 mole) of acetylferrocene, 2.84 g (0.0212 mole) of $AlCl_3$, and 30 ml of mesitylene (heating at 90–100° for 4 h), 2.84 g of a mixture of the tetraphenylborates of acetylcyclopentadienyl- and cyclopentadienylmesityleneiron was obtained. By extracting the mixture first with dichloroethane and then with alcohol at different temperatures, and crystallizing the substituted product from alcohol and the unsubstituted one from a mixture of acetonitrile with acetone, it was possible to establish that the product consisted approximately 83% of acetylcyclopentadienylmesityleneiron tetraphenylborate, m.p. 197–198°, with decomposition.

Found, %:	Fe 9.47, 9.19
$C_{40}H_{39}OBFe$. Calculated, %:	Fe 9.27

The isolated cyclopentadienylmesityleneiron tetraphenylborate had decomp. p. 257–258°.

Found, %:	Fe 9.74, 9.63
$C_{38}H_{37}BFe$. Calculated, %:	Fe 9.96

Reaction of cyanoferrocene with benzene. From 0.46 g (0.0022 mole) of cyanoferrocene, 1.76 g (0.0132 mole) of $AlCl_3$, and 20 ml of benzene (boiling for 6 h), a mixture of the tetraphenylborates of cyanocyclopentadienyl- and cyclopentadienylbenzeneiron was obtained (total yield 0.89 g, i.e., 75%, calculated for $[CNC_5H_4FeC_6H_6][B(C_6H_5)_4]$). By successive crystallizations from acetonitrile and acetone, 0.47 g of cyanocyclopentadienylbenzeneiron tetraphenylborate was isolated, m.p. 191–194°, with decomposition. The substance is yellow-orange in color.

Found, %:	C 79.83, 79.63;	H 5.74, 5.78;	N 2.73, 2.47
$C_{36}H_{30}BNFe$. Calculated, %:	C 79.58;	H 5.57;	N 2.58

In addition, 0.31 g of an inseparable mixture of tetraphenylborates with a constant decomp. p. 233–234° was obtained. A known mixture of the tetraphenylborates of cyanocyclopentadienyl- and cyclopentadienylbenzeneiron had decomp. p. 232–233°. Thus, in this experiment, a mixture of two substances was probably obtained.

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Note: Figure translations are in progress. See original paper for figures.

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