Chemistry

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1963

SovietRxiv

Abstract

Full Text

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LIGAND EXCHANGE IN FERROCENE

Among the organic derivatives of transition metals constructed as π-complexes, ferrocene is distinguished by its stability. Until now, no cases have been described for it in which the cyclopentadienyl rings are replaced by other ligands.

In the present work we have for the first time succeeded in carrying out such an exchange reaction. When ferrocene is heated with aromatic hydrocarbons in the presence of aluminum chloride, one of the cyclopentadienyl rings of the ferrocene nucleus is replaced by an aromatic ring.

$$Fe(C_5H_5)_2 + C_6H_6 \xrightarrow{AlCl_3} [C_5H_5FeC_6H_6]^+ [AlCl_4]^-$$

In this process a singly charged arene-cyclopentadienyliron cation is formed. The fate of the eliminated cyclopentadienyl anion has not yet been investigated by us. An undesired side process is the oxidation of ferrocene to the ferricinium cation, apparently occurring under the action of $AlCl_3$. A similar phenomenon is known and was studied in detail by Hein (^{1}) for a series of diarenechromium compounds. In this connection, addition of a reducing agent (aluminum dust) promotes the successful course of the exchange reaction. We were unable to replace both cyclopentadienyl rings in ferrocene.

Thus we obtained the cations of benzene-, mesitylene-, and tetralin-cyclopentadienyliron, isolated as tetraphenylborates. The reaction with naphthalene proceeds analogously.

The cations of mesitylene- (^{2}) and benzene-cyclopentadienyliron (^{2}, ^{3}) had previously been obtained by interaction, respectively, of mesitylene and benzene with $(C_5H_5Fe(CO)_2)Cl$ in the presence of $AlCl_3$.

To prove the structure, we oxidized mesitylene-cyclopentadienyliron tetraphenylborate to trimesic acid, which confirmed the incorporation of mesitylene into the molecule of the π-complex.

Substituted ferrocenes are also capable of entering into the exchange reaction described above. Thus, when diacetylferrocene was heated with mesitylene in the presence of $AlCl_3$, we obtained the cation of mesitylene-acetylcyclopentadienyliron $(CH_3COC_5H_4FeC_6H_3(CH_3)_3)^+$. With diacetylferrocene the exchange reaction proceeds with more difficulty than with ferrocene itself. All the tetraphenylborates obtained by us are yellow crystalline substances, fairly readily soluble in acetone, dichloroethane, and acetonitrile, and insoluble in alcohol, ether, and benzene. Mesitylene-acetylcyclopentadienyliron tetraphenylborate is light orange in color and dissolves better than the other tetraphenylborates. All the substances obtained melt with decomposition and do not give melting-point depressions with one another. Solid tetraphenylborates are stable to atmospheric oxygen. In organic solvents, traces of decomposition appear rather quickly. Light accelerates decomposition. The cations of arene-cyclopentadienyliron are rather stabi-

resistant to the action of acids: they withstand heating with concentrated hydrochloric acid.

When an aqueous solution of the benzene-cyclopentadienyliron cation is treated with potassium triiodide (an aqueous solution of J_2 and KJ in a ratio of $1:5$), a dark-orange precipitate of the triiodide $(C_5H_5FeC_6H_6)(J_3)$ separates. After recrystallization this substance forms dark violet-red crystals. If the solution of the cation is treated with iodine and KJ in a ratio of $1:1$, a black polyiodide with an indefinite iodine content is formed. Such polyiodides were obtained for benzene-, mesitylene-, and tetralin-cyclopentadienyliron.

The polyiodide of benzene-cyclopentadienyliron was converted into the triiodide by the action of KJ in alcohol, and also by cautious reduction with a limited amount of Na_2SO_3. Vigorous reduction of the polyiodide (and also of the triiodide) with an excess of Na_2SO_3 led to iodobenzene-cyclopentadienyliron $(C_5H_5FeC_6H_6)J$—a yellow crystalline substance, extremely soluble in water and alcohol. Iodobenzene-cyclopentadienyliron can be converted again into the triiodide by the action of iodine.

On thermal decomposition in vacuum of the tetraphenylborates of benzene-, mesitylene-, tetralin-, and naphthalene-cyclopentadienyliron, as well as of $(C_5H_5FeC_6H_6)J$, we obtained ferrocene and a little iron. Evidently, cleavage of the aromatic hydrocarbon and disproportionation of the residue take place. From the naphthalene derivative naphthalene was also obtained.

Experimental Part

1. Synthesis of benzene-cyclopentadienyliron tetraphenylborate. Boiling and stirring for 6 hours in a stream of nitrogen of 2 g (0.0106 mole) of ferrocene, 2.84 g (0.0212 mole) of $AlCl_3$, 0.28 g (0.0106 g-atom) of Al powder, and 80 ml of benzene, after decomposition with 150 ml of water, gave a yellow aqueous solution of the benzene-cyclopentadienyliron cation. The latter was precipitated as the tetraphenylborate—a yellow crystalline substance with m.p. 250–251°* after reprecipitation with ether from acetone and recrystallization from acetonitrile.

$C_{35}H_{31}BFe$.	Found, %:	C 81.29;	81.29;	H 6.13;	6.06;	Fe 11.04;	10.5[[unclear]]
	Calculated, %:	C 81.10;		H 6.03;		Fe 10.77	

From the organic layer 1.33 g of ferrocene was isolated. Thus, the yield of benzene-cyclopentadienyliron tetraphenylborate was 20% of theoretical based on the ferrocene taken into the reaction, or 60.7% based on the ferrocene that entered into the reaction.

2. Synthesis of mesitylene-cyclopentadienyliron tetraphenylborate. The experiment was carried out as above. The mixture was boiled for 3 hours. From 1 g (0.0053 mole) of ferrocene, 1.42 g (0.00106 mole) of $AlCl_3$, 0.14 g (0.0053 g-atom) of Al powder, and 40 ml of mesitylene, 2 g (66% of theoretical) of mesitylene-cyclopentadienyliron tetraphenylborate was obtained, m.p. 257-258° with decomposition after reprecipitation with water from acetone and recrystallization from acetonitrile.

$C_{38}H_{37}BFe$.	Found, %:	C 81.04;	81.12;	H 6.65;	6.64;	Fe 9.98;	9.78;
	Calculated, %	C 81.44;		H 6.65;		Fe 9.96;	

3. Synthesis of tetralin-cyclopentadienyliron tetraphenylborate. From 2 g (0.0106 mole) of ferrocene, 2.84 g (0.0212 mole) of $AlCl_3$, 0.28 g (0.106 g-atom) of Al powder, and 70 ml of tetralin (heating for 3.5 hours at 160-165°), 2.9 g (48% of theoretical) of tetralin-cyclopentadienyliron tetraphenylborate was obtained, reprecipitated with water from acetone. After two recrystallizations from dichloroethane, the substance had m.p. 237.5-238.5° with decomposition.

$C_{39}H_{37}BFe$.	Found, %:	C 82.02;	81.75;	H 6.39;	6.62;	Fe 9.88;	9.66;
	Calculated, %:	C 81.84;		H 6.52;		Fe 9.76	

The substance is readily soluble in acetone, dichloroethane, and acetonitrile; moderately soluble in tetrahydrofuran.

4. **Synthesis of mesitylene-acetylcyclopentadienyliron tetraphenylborate.** A mixture of 1.43 g (0.0053 mole) of diacetylferrocene, 2.84 g (0.0212 mole) of $AlCl_3$, and 20 ml of mesitylene was heated for 4.5 hours at 120-130°, and, after decomposition and precipitation with sodium tetraphenylborate, 0.8 g (22% of theoretical) of mesitylene-acetylcyclopentadienyliron tetraphenylborate was obtained. The

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* All the substances described by us can be melted only in a sealed capillary, placing them in the apparatus no earlier than 30-40° below the decomposition temperature. Otherwise they decompose very gradually and imperceptibly.

substance is light orange in color. After reprecipitation with water from acetone and two recrystallizations from alcohol, it had m.p. 197-198° (decomp. temp. 199-200°). The substance is very soluble in acetone, dichloroethane, acetonitrile, and tetrahydrofuran, and moderately soluble in C_2H_5OH and CH_3OH.

$C_{40}H_{39}OBFe$. Found, %: C 79.90; 79.74; H 6.75; 6.70; Fe 9.41; 9.52
Calculated, %: C 79.75; H 6.52; Fe 9.27

In addition, from the aqueous layer there was obtained the tetraphenylborate of a cation not yet identified, with decomp. temp. 214-215° after recrystallization from dichloroethane. From the organic layer, 0.81 g of diacetylferrocene with m.p. 127-128° was isolated.

If this experiment is carried out at 90-100°, the yield of mesityleneacetylcyclopentadienyliron tetraphenylborate is only 4%.

5. **Oxidation of mesitylenecyclopentadienyliron tetraphenylborate.** A suspension of 1.19 g of mesitylenecyclopentadienyliron tetraphenylborate in 50 ml of water was heated to 95°. At this temperature and with vigorous stirring, $KMnO_4$ was gradually added to the suspension until decolorization ceased. Over 11 hours, 5.5 g of $KMnO_4$ was added. After the usual workup, 0.25 g (57% of theoretical) of trimesic acid with m.p. 351-352° was obtained, melting without depression with an authentic sample (m.p. 352-353°).

6. **Synthesis of benzene-cyclopentadienyliron iodides.** An aqueous solution of the benzene-cyclopentadienyliron cation, obtained under the conditions of the first experiment from 5 g (0.026 mole) of ferrocene, 7.1 g (0.053 mole) of $AlCl_3$, 0.7 g (0.026 g-at.) of Al dust, and 100 ml of benzene, was divided into two parts.

a) **Synthesis of triiodobenzene-cyclopentadienyliron.** To one half of the aqueous solution of the cation (25 ml) was added an excess of a solution of KI and I_2 (ratio 5 : 1) in a limited amount of water. The orange precipitate that separated was reprecipitated with ether from acetone and recrystallized from acetone. The resulting shiny violet-red crystals had decomp. temp. 226-227°.

$C_{11}H_{11}FeJ_3$. Found, %: C 23.17; 23.15; H 2.04; 1.97; J 65.50; 65.59; Fe 9.70; 9.81;
Calculated, %: C 22.81; H 1.91; J 65.67; Fe 9.63

The substance is soluble in acetone and acetonitrile, sparingly soluble in alcohol, water, dichloroethane, and tetrahydrofuran, and insoluble in benzene and ether.

b) **Synthesis of benzene-cyclopentadienyliron polyiodide.** To the second half of the aqueous solution of the benzene-cyclopentadienyliron cation was added an aqueous solution of KI and I_2 (1 : 1). Addition was continued until the precipitation of the black precipitate ceased and the solution above the precipitate turned red-brown. The brown-black precipitate of the polyiodide was washed with water and dried. The substance has no stable decomposition temperature; on storage it partially loses iodine.

soluble in acetone, alcohol, dichloroethane, poorly soluble in $CHCl_3$ and tetrahydrofuran, insoluble in water. If KI is added to a suspension of the polyiodide in alcohol, with stirring and heating of the mixture, the black precipitate of the polyiodide is converted into an orange precipitate of triiodo benzene-cyclopentadienyliron. Careful addition of Na_2SO_3 to a hot suspension of the polyiodide in alcohol leads to the same result.

c) Synthesis of iodo benzene-cyclopentadienyliron. 2 g of the polyiodide, suspended in 100 ml of boiling alcohol, were reduced with a large excess of sodium sulfate. The inorganic salts were filtered off; part of the alcohol was distilled off under nitrogen at reduced pressure. From the residue, ether precipitated shiny yellow crystals of iodo benzene-cyclopentadienyliron. After two recrystallizations from $CHCl_3$ the substance melted at 230–230.5° with decomposition.

Found, %: C 40.30; 40.29; H 3.46; 3.33; I 39.06; 38.86; Fe 17.17; 17.08
$C_{11}H_{11}FeI$. Calculated, %: 40.53; 3.40; I 38.93; Fe 17.13

Iodo benzene-cyclopentadienyliron is extremely soluble in water, C_2H_5OH, CH_3OH, readily soluble in acetone, moderately soluble in dichloroethane and $CHCl_3$, insoluble in benzene and tetrahydrofuran, and very sensitive to light, atmospheric oxygen, and peroxides in solvents. On addition of $Na(B(C_6H_5)_4)$ to an aqueous solution of iodo benzene-cyclopentadienyliron, the already known tetraphenylborate with decomp. temp. 250° is formed. Under the action of iodine in alcoholic solution, iodo benzene-cyclopentadienyliron is converted into the triiodo compound with decomp. temp. 225–227° (from acetone).

Iodo benzene-cyclopentadienyliron can also be obtained by reduction of triiodo benzene-cyclopentadienyliron under the same conditions as those described for the polyiodide.

7. Thermal decomposition of iodo benzene-cyclopentadienyliron. The decomposition was carried out in a sublimation apparatus at 230–240°/15 mm. The sublimed ferrocene had m.p. 171–172° after repeated sublimation and gave no depression with an authentic sample (m.p. 173–174°). A black charred residue remained in the apparatus, partially soluble in HCl. The hydrochloric acid solution gave a reaction for Fe^{3+}.

The investigated tetraphenylborates of arene-cyclopentadienyliron cations also form ferrocene on decomposition, but require a higher temperature (up to 300°)

and prolonged heating; first diphenyl sublimes, and then ferrocene.

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Received
18 II 1963

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