Reaction of Mercury(II) Trifluoroacetatewith Deprotonated (η⁶-Toluene)-, (η⁶-Diphenylmethane)-,and (η⁶-Triphenylmethane)(η⁵-cyclopentadienyl)iron(II)Complexes. Mercuration of Some Cationic (Arene)(cyclopenta-
dienyl)iron(II)Complexes

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Abstract — Treatment with mercury(II) trifluoroacetate of deprotonated (η^6 -toluene)- and (η^6 -diphenylmethane)(η^5 -cyclopentadienyl)iron(II) complexes gave mono-, di-, and trisubstituted [from (η^6 -toluene)-(η^5 -cyclopentadienyl)iron(II) cation] mercury-containing salts. The reaction of mercury(II) trifluoroacetate with deprotonated (η^6 -triphenylmethane)(η^5 -cyclopentadienyl)iron(II) afforded only the corresponding symmetric mercury derivative. The same product was obtained by direct mercuration with mercury(II) trifluoroacetate of (η^6 -triphenylmethane)(η^5 -cyclopentadienyl)iron(II) on heating the reactants in boiling unhydrous ethanol. Reactions of the resulting mercury-containing compounds with acids, symmetrizing bases, and acylating agents were studied.

In continuation of our studies on the synthesis of new mercury-containing cationic $(\eta^6\text{-arene})(\eta^5\text{-cyclopentadienyl})$ iron(II) complexes [1], in the present work we examined reactions of a series of deprotonat-

ed species **I–III** with mercury(II) trifluoroacetate. Complexes **I–III** were generated by the action of a small excess of potassium *tert*-butoxide on the corresponding salts containing (η^6 -toluene)- (**IV**, **V**),



IV, $X = BF_4$; V, $X = PF_6$.

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 $(\eta^6$ -diphenylmethane)- (VI) and $(\eta^6$ -triphenylmethane)(η^5 -cyclopentadienyl)iron(II) cations (VII) in a 1:1 mixture of anhydrous 1,2-dimethoxyethane and acetonitrile at 0°C under argon. Judging by the color change from yellow to deep red, deprotonation of the above salts occurred almost instantaneously to give the corresponding complexes I–III.

The resulting solution containing complexes I-III was filtered from excess deprotonating agent and

inorganic salt, and a required amount of electrophile, mercury(II) trifluoroacetate, was added. In all cases, the reaction readily occurred and was accompanied by change of the color.

Depending on the ratio of potassium *tert*-butoxide and mercury(II) trifluoroacetate, the reactions with salts IV and V gave mono- (VIII, IX), di- (X, XI), and trimercurated products (XII, XIII); from compound VI, mono- and dimercurated complexes XIV and XV were obtained.



VIII, X, XII, $X = BF_4$; IX, XI, XIII, $X = PF_6$; X, XI, n = 2; XII, XIII, n = 3.

However, the reaction with salt **VII** (through intermediate **III**), regardless of the ratio potassium tert-butoxide-mercury(II) trifluoroacetate afforded only symmetric product **XVI**. Its formation

can be interpreted in terms of greater CH acidity of salt **VII** due to effect of the two phenyl groups at the α -carbon atom of the coordinated arene ligand.



In fact, unlike salts **IV**–**VI**, we succeeded in effecting direct mercuration of **VII** with mercury(II) trifluoroacetate by heating equimolar amounts of the reactants for 3 h in boiling anhydrous ethanol. In this case we also isolated in 87% yield only symmetric mercuration product **XVI**. As in the above reaction, the result of the reaction almost did not depend on the reactant ratio, in particular when the amount of Hg(OCOCF₃)₂ was increased.

It should be noted that the structure of the mercurycontaining products is essentially influenced by both the reactant ratio and the experimental procedure. For example, deprotonation of salts **IV** and **V** with the use of 2.5 equiv of potassium *tert*-butoxide according to the procedures proposed previously [2, 3], i.e., without preliminary separation of excess deprotonating agent, the subsequent addition of an equimolar amount (with respect to **IV** or **V**) of mercury(**II**) trifluoroacetate led to formation of new compounds **XVII** and **XVIII** (Table 1) rather than mono- or dimercurated products **VIII–XI** (see above).

Mercury-containing compounds **VIII**–**XVIII** are as a rule yellow–brown fine crystalline powders which can be stored in the dark for a month without appreciable decomposition. On exposure to light, these products began to decompose fairly quickly with liberation of metallic mercury. This process is especially characteristic of compounds **XVII** and **XVIII**. Melting of complexes **VIII–XVIII** is also accompanied by their decomposition. The solubility of **VIII–XVIII** in ethanol, acetone, acetonitrile, dimethylformamide, and dimethyl sulfoxide sharply decreases as the percentage of mercury increases. For that reason we failed to record ¹H NMR spectra for some di- and trimercurated complexes. All the products are almost insoluble in water, diethyl ether, and benzene.

Study of the chemical properties of the prepared formed). Fina RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 73 No. 10 2003

complexes revealed that they are typical [4] organomercury compounds with a localized covalent C–Hg bond. This bond is fairly labile, and it readily undergoes dissociation by the action of acids, symmetrizing reagents, and acylating agents. Treatment of **VIII**– **XVIII** with hydrochloric acid resulted in protodemercuration and formation of initial compounds **IV**– **VII** which were isolated in high yields as known [5] tetraphenylborates and were identified by the melting points and IR spectra (by comparison with authentic samples).

Salts IX and XIV smoothly reacted with calcium chloride in a mixture of ethanol, ethylene glycol dimethyl ether, and acetonitrile at room temperature to give complexes XIX and XX via replacement of the OCOCF₃ group by chlorine. Special emphasis should be placed on the reaction of salts IX, XIV, **XVII**, and **XVIII** with ammonia. For example, treatment of compounds IX and XIV with ammonia in a mixture of acetonitrile and ethylene glycol dimethyl ether at room temperature led to symmetrization products XXI and XXII in high yields (Table 1) and with no liberation of metallic mercury. By contrast, analogous reactions of salts XVII and XVIII resulted in decomposition with liberation of a considerable amount of metallic mercury, and the yield of symmetric complex XXI was relatively low (40–42%).

These data unambiguously indicate the presence of univalent mercury in **XVII** and **XVIII**, for just the reaction with ammonia is used in analytical chemistry [6–8] as a qualitative test for univalent mercury salts (a fine black precipitate of metallic mercury is formed). Finally, mercury salt **IX** as an example was BOEV et al.



brought into reaction with acetyl bromide in the presence of a catalytic amount of anhydrous aluminum bromide in methylene chloride. The reaction gave known [9] complex **XXIII** via rupture of the C–Hg bond; the product was identified by the melting point and spectral parameters (Table 2).

Table 1. Yields, melting points, and elemental analyses of mercury-containing salts VIII-XXII

| Comp. no. | Yield, % | Decomp. point, °C | Found, % | | | | Esmuls | Calculated, % | | | |
|--------------|-------------|----------------------|----------|------|-------|-------|---|---------------|------|-------|-------|
| | | | С | Н | Fe | Hg | Formula | С | Н | Fe | Hg |
| VIII | 68 | 205–210 | 27.28 | 1.87 | 9.50 | 32.75 | C ₁₄ H ₁₂ BF ₇ FeHgO ₂ | 27.46 | 1.96 | 9.12 | 32.72 |
| IX | 73 | 195-200 | 24.93 | 1.68 | 8.10 | 29.87 | $C_{14}H_{12}F_{0}FeHgO_{2}P$ | 25.07 | 1.79 | 8.33 | 29.91 |
| Χ | 58 | 220-225 | 20.31 | 1.12 | 6.08 | 43.48 | $C_{16}H_{11}BF_{10}FeHg_2O_4$ | 20.78 | 1.19 | 6.04 | 43.37 |
| XI | 51 | 210-215 | 19.43 | 1.08 | 5.18 | 40.76 | $C_{16}H_{11}F_{12}FeHg_2O_4P$ | 19.55 | 1.12 | 5.68 | 40.81 |
| XII | 62 | 230-235 | 17.32 | 0.78 | 4.36 | 48.17 | $C_{18}H_{10}BF_{13}FeHg_3O_6$ | 17.47 | 0.81 | 4.51 | 48.63 |
| XIII | 54 | 200-205 | 16.38 | 0.85 | 4.50 | 45.65 | $C_{18}H_{10}F_{15}FeHg_3O_6P$ | 16.48 | 0.77 | 4.31 | 46.44 |
| XIV | 74 | 130-135 | 32.25 | 2.08 | 7.14 | 26.92 | C ₂₀ H ₁₆ F ₉ FeHgO ₂ P | 32.17 | 2.14 | 7.48 | 26.87 |
| XV | 70 | 185-190 | 24.67 | 1.36 | 4.72 | 37.96 | $C_{22}H_{15}F_{12}FeHg_2O_4P$ | 24.95 | 1.42 | 5.27 | 37.87 |
| XVI | 87 | 230-235 | 45.98 | 3.14 | 8.85 | 16.59 | $C_{46}H_{40}F_{12}Fe_2HgP_2$ | 46.24 | 3.35 | 9.35 | 16.79 |
| XVII | 78 | 245-250 | 21.43 | 1.57 | 6.56 | 49.66 | C ₁₄ H ₁₂ BF ₇ FeHg ₂ O ₂ | 20.68 | 1.48 | 6.87 | 49.35 |
| XVIII | 76 | 230-235 | 19.15 | 1.42 | 6.38 | 45.97 | C ₁₄ H ₁₂ F ₉ FeHg ₂ O ₂ P | 19.30 | 1.38 | 6.41 | 46.05 |
| XIX | 57 | 110-115 | 24.22 | 1.95 | 9.48 | 33.15 | C ₁₂ H ₁₂ ClF ₆ FeHgP | 24.30 | 2.02 | 9.42 | 33.82 |
| XX | 80 | 105-108 | 32.13 | 2.28 | 8.72 | 29.11 | C ₁₈ H ₁₆ ClF ₆ FeHgP | 32.31 | 2.39 | 8.35 | 29.98 |
| XXI | 72 | 235-237 | 31.46 | 2.53 | 12.25 | 20.65 | $C_{24}H_{24}F_{12}Fe_2HgP_2$ | 31.52 | 2.62 | 12.21 | 21.93 |
| XXII | 92 | 132–135 | 40.38 | 2.91 | 10.88 | 18.08 | $C_{36}H_{32}F_{12}Fe_2HgP_2$ | 40.54 | 3.00 | 10.47 | 18.81 |

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Table 2. IR and ¹H NMR spectra of mercury-containing salts VIII-XXII and compound XXIII

| Comp. no. | IR spectrum, v, cm^{-1} | ¹ H NMR spectrum, δ, ppm (² J _{HgH} , Hz) |
|--------------|--|---|
| VIII | 3120, 2965, 1695, 1508, 1465, 1428, 1288, 1204, 1160, 1078, 1039, 852, 745, 710, 628, 550, 468 | 6.68 s (5H, C ₆ H ₅ Fe), 5.38 s (5H, C ₅ H ₅), 2.83 s (2H, CH ₂ , J 184) |
| IX | 3125, 2950, 1700, 1506, 1470, 1430, 1278, 1200, 1162, 1081, 1042, 860, 741, 705, 622, 556, 460 | 6.67 s (5H, C_6H_5Fe), 5.40 s (5H, C_5H_5), 2.83 s (2H, CH_2 , J 185) |
| X | 3120, 2920, 1705, 1512, 1472, 1428, 1270, 1206, 1160, 1075, 1030, 1001, 832, 752, 706, 628, 552, 472 | 6.68 s (5H, C_6H_5Fe), 5.38 s (5H, C_5H_5), 3.24 s (1H, CH, J 125) |
| XI | 3140, 2960, 1700, 1506, 1483, 1430, 1268, 1200, 1158, 1080, 1042, 852, 745, 700, 628, 552, 468 | 6.65 s (5H, C_6H_5Fe), 5.38 s (5H, C_5H_5), 3.22 s (1H, CH, J 126) |
| XII | 1720, 1442, 1304, 1218, 1145, 1042, 843, 812, 730, 625, 530, 450 | _ |
| XIII | 2970, 1718, 1445, 1300, 1212, 1150, 1042, 850, 810, 732, 628, 542, 454 | _ |
| XIV | 3140, 2950, 1695, 1505, 1460, 1430, 1290, 1208, 1155, 1080, 1040, 848, 742, 715, 635, 560, 500, 464 | 7.50–7.63 m (5H, C_6H_5), 6.71 d (5H, C_6H_5Fe), 5.43 s (5H, C_5H_5), 4.46 s (1H, CH, J 110) |
| XV XVI | 3130, 1690, 1502, 1431, 1215, 1162 3140, 1505, 1460, 1428, 1330, 1090, 1040, 850, 726, | 7.43–7.66 m (20H, $4C_6H_5$), 6.78 s, 6.58 s, 6.15 s (10H, |
| XVII | 632, 576, 480 3122, 2960, 1700, 1512, 1460, 1430, 1288, 1200, 1162, 1040, 826, 755, 712, 620, 558, 462 | $2C_6H_5Fe)$, 5.31 s, 5.26 s (10H, $2C_5H_5$) 6.68 s (5H, $C_6H_5Fe)$, 5.37 s (5H, C_5H_5), 2.75 s (2H, CH2, |
| XVIII | 1040, 830, 753, 712, 020, 538, 402 3120, 2960, 1695, 1508, 1472, 1428, 1279, 1205, 1170, 1043, 853, 812, 763, 710, 625, 552, 471 | 6.68 s (5H, C_6H_5Fe), 5.36 s (5H, C_5H_5), 2.76 s (2H, CH_2 , J_1 76) |
| XIX | 3100, 2960, 1517, 1500, 1460, 1428, 1268, 1162, 1064, 1026, 850, 748, 633, 552, 468 | 6.68 s (5H, C_6H_5Fe), 5.36 s (5H, C_5H_5), 2.84 s (2H, CH_2 , J 178) |
| XX | 3150, 2965, 1510, 1462, 1426, 1287, 1162, 1082, 1039, 852, 743, 712, 642, 560, 510, 460 | 7.52–7.63 m (5H, C_6H_5), 6.72 d (5H, C_6H_5Fe), 5.43 s (5H, C_5H_5), 4.48 s (1H, CH, J 98) |
| XXI | 3100, 1465, 1421, 1160, 1015, 860, 512, 455 | 6.63 s (10H, $2C_6H_5Fe$), 5.45 s (10H, $2C_5H_5$), 2.79 s (4H, $2CH_2$, J 130) |
| XXII | 3152, 1502, 1460, 1420, 1175, 1018, 858, 528, 460 | 7.48–7.60 m (10H, $2C_6H_5$), 6.68 d (10H, $2C_6H_5Fe$), 5.36 s (10H, $2C_5H_5$), 4.42 s (2H, 2CH, J 68) |
| | 3120, 2920, 1705, 1508, 1470, 1420, 1325, 1285, 1167, 1069, 1033, 850, 786, 720, 634, 510, 465 | 6.42 s (5H, C ₆ H ₅), 5.22 s (5H, C ₅ H ₅), 4.21 s (2H, CH ₂), 2.26 s (3H, CH ₃) |

Apart from chemical transformations, the structure of compounds **VIII–XXIII** was confirmed by elemental analysis (Table 1) and ¹H NMR and IR spectroscopy (Table 2). All the products showed in the IR spectra absorption bands of various intensities in the regions 1420–1460, 1112–1125, 1005–1015,

850–860, and 712–730 cm⁻¹, which belong to vibrations of bonds in the $(\eta^6$ -arene) $(\eta^5$ -cyclopentadienyl)iron fragment [2, 10, 11]. In the IR spectra of compounds **VIII–XV**, **XVII**, and **XVIII** having a trifluoroacetate group we also observed strong absorption bands at 1690–1720 and 1200 cm⁻¹, which arise

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from stretching vibrations of the C=O and C-O bonds, respectively [12]. The lack of such bands in the spectra of **XIX–XXII** indicates complete replacement of the trifluoroacetate moiety by the corresponding group. Stretching vibrations of the anions, PF_6^- and BF_4^- give rise to strong bands in the regions 830–840 and 1085–1095 cm⁻¹, respectively [3]. In addition, the IR spectra contain bands at 540–560 cm⁻¹, which can be assigned to vibrations of the Hg–C bond [13].

The ¹H NMR spectra of **VIII–XI**, **XIV**, **XVI**, and **XVII** are consistent with the proposed sandwich-like cationic structures. In all cases, a peak corresponding to resonance of five cyclopentadienyl protons was present at δ 5.20–5.48 ppm [10]. Signals from protons of the coordinated aromatic fragments (δ 6.15–6.80 ppm) are displaced upfield relative to those belonging to the noncoordinated benzene ring (δ 7.43–7.65 ppm) in compounds **XIV** and **XVI** or to the initial ligand. In the ¹H NMR spectra of most compounds, signals appear as fairly narrow peaks, so that spin systems corresponding to coordinated and non-coordinated rings are clearly seen.

Signals from the methylene and methine protons in the spectra of VIII-XI, XIV, and XVII are located at δ 2.75–3.24 (cations VIII–XI and XVII and 4.46 ppm (XIV). This means that mercury-containing substituents deshield protons of the methylene and methine groups: The downfield shift of the corresponding signals relative to those of initial salts IV-VI [10, 14] ranges from 0.22 to 0.70 ppm. It is known [15] that such displacement may be caused by both the electron-acceptor effect of the mercury-containing substituent and its magnetic anisotropy. Taking into account the fairly similar electronegativities of the hydrogen (2.1) and mercury atoms (1.9) [16], we can conclude that the latter factor is more significant. In the case of salt **XVII**, its effect is the weakest. This also follows from comparison of the spin-spin coupling constants ${}^{2}J_{HgH}$. Its value for compound **XVII** is lower by a factor of 2.4 than those found for salts **VIII** and **IX**. Evidently, the mercury-containing substituents attached to the methylene carbon atom in compounds XVII and in VIII and IX have different natures. On the basis of our experimental results (Tables 1, 2) and published data [6] we propose the structure of XVII and XVIII shown below, where the cation contains two univalent mercury atoms linked through a Hg-Hg bond.

The ¹H NMR spectra of **XIX–XXII** are characterized by almost the same signal patterns as those observed for **VIII–XI** and **XIV** but different ${}^{2}J_{\text{HgH}}$ values. The difference in ${}^{2}J_{\text{HgH}}$ conforms to published data [6, 17].



XVII, $X = BF_4$, **XVIII**, $X = PF_6$.

Thus, the results of our study demonstrate a wide synthetic potential of mercury-containing salts derived from cationic (η^6 -arene)(η^5 -cyclopentadienyl)iron(II) complexes. The relatively easy replacement of mercury-containing substituents by a metal, halogen, or alkyl, acyl, and other groups [4] opens further prospects in using the prepared compounds in the synthesis of new functionally substituted salts from cationic (η^6 -arene)(η^5 -cyclopentadienyl)iron(II) complexes.

EXPERIMENTAL

The IR spectra were taken on UR-20 or IKS-29 spectrometer from samples pelleted with KBr or dispersed in mineral oil. The ¹H NMR spectra of solutions in DMSO- d_6 were recorded on a Bruker WP-200SY spectrometer at 200.13 MHz using HMDS as internal reference. Initial compounds **IV–VII** were synthesized by the procedures described in [2, 10, 18, 19]. All reactions with deprotonated complexes **IV–VII** were carried out under argon.

 $(\eta^{5}\text{-}Cyclopentadienyil)(\eta^{6}\text{-}trifluoroacetoxy\text{-}$ mercuriomethylbenzene)iron(II) hexafluorophos**phate(V) (IX).** To a solution of 0.36 g of $(\eta^{5}$ -cyclopentadienyl)(η^6 -toluene)iron(II) hexafluorophosphate(V) (V) in 12 ml of a 1:1 mixture of anhydrous acetonitrile and ethylene glycol dimethyl ether we added with stirring at 0°C 0.13 g of potassium tertbutoxide. After 20 min, the dark red solution containing compound I was filtered, and 0.43 g of mercury(II) trifluoroacetate was added to the filtrate under stirring. The mixture quickly changed from dark red to yellow-brown. It was stirred for 20 min at 20°C, the solvent was removed under reduced pressure at room temperature, and the residue was washed first with hexane and then with water and dried in air until constant weight. Yield 0.49 g.

Compound VIII was synthesized in a similar way.

 $[\eta^{6}$ -Bis(trifluoroacetoxymercurio)methylbenzene](η^{5} -cyclopentadienyl)iron(II) hexafluorophos-

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phate(V) (XI). To a solution of 0.36 g of complex V in 12 ml of a 1:1 mixture of acetonitrile and ethylene glycol dimethyl ether we added with stirring at 0°C 0.27 g of potassium *tert*-butoxide. After 20 min, the dark red solution containing compound I was filtered, and 0.85 g of mercury(II) trifluoroacetate was added under stirring. The mixture quickly changed from dark red to brown. It was stirred for 20 min at 20°C, the solvent was removed under reduced pressure at room temperature, and the precipitate was washed first with hexane and then with water and dried in air until constant weight. Yield 0.50 g.

Compound **X** was synthesized in a similar way.

 $(\eta^5$ -Cyclopentadienyl)[η^6 -tris(trifluoroacetoxymercurio)methylbenzene]iron(II) hexafluorophosphate(V) (XIII). To a solution of 0.36 g of compound V in 12 ml of a 1:1 mixture of acetonitrile and ethylene glycol dimethyl ether we added with stirring at 0°C 0.40 g of potassium *tert*-butoxide. After 20 min, the dark red solution containing compound I was filtered, and 1.28 g of mercury(II) trifluoroacetate was added under stirring. The mixture quickly changed from dark red to brown. It was stirred for 20 min at 20°C, the solvent was removed under reduced pressure at room temperature, and the precipitate was washed first with hexane and then with water and dried in air until constant weight. Yield 0.70 g.

Compound XII was synthesized in a similar way.

 $(\eta^{5}\text{-}Cyclopentadienyl)[\eta^{6}\text{-}diphenyl(trifluoro$ acetoxymercurio)methane]iron(II) hexafluorophos**phate(V) (XIV).** To a solution of 0.43 g of $(\eta^3$ -cyclopentadienyl)(η^{5} -diphenylmethane)iron(II) hexafluorophosphate(V) (VI) in 12 ml of a 1:1 mixture of anhydrous acetonitrile and ethylene glycol dimethyl ether we added with stirring at 0°C 0.13 g of potassium tert-butoxide. After 20 min, the dark red solution containing compound II was filtered, and 0.43 g of mercury(II) trifluoroacetate was added under stirring. The dark red mixture quickly turned red-brown and then green. It was stirred for 20 min at 20°C, the solvent was removed under reduced pressure at room temperature, and the residue was washed first with hexane and then with water and dried in air until constant weight. Yield 0.55 g.

 $(\eta^5$ -Cyclopentadienyl)[η^6 -diphenylbis(trifluoroacetoxymercurio)methane]iron(II) hexafluorophosphate(V) (XV). To a solution of 0.43 g of compound VI in 12 ml of a 1:1 mixture of acetonitrile and ethylene glycol dimethyl ether we added with stirring at 0°C 0.27 g of potassium *tert*-butoxide. After 20 min, the dark red solution containing compound **II** was filtered, and 0.85 g of mercury(II) trifluoroacetate was added under stirring. The mixture quickly changed from dark red to red–brown and then to blue– green. The mixture was stirred for 20 min at 20°C, the solvent was removed under reduced pressure at room temperature, and the residue was washed first with hexane and then with water and dried in air until constant weight. Yield 0.75 g.

 $Di(\eta^5$ -cyclohexadienyl)[bis(η^6 -triphenylmethyl)mercury]diiron(II) bis[hexafluorophosphate(V)] (XVI). a. To a solution of 0.51 g of $(\eta^{2}$ -cyclopentadienyl)(η^6 -triphenylmethane)iron(II) hexafluorophosphate(V) (VII) in 20 ml of a 3:1 mixture of anhydrous acetonitrile with ethylene glycol dimethyl ether we added with stirring at 0°C 0.13 g of potassium tert-butoxide. After 20 min, the crimson solution containing compound III was filtered, and 0.43 g of mercury(II) trifluoroacetate was added under stirring. The mixture quickly changed from crimson to light yellow and then greenish-yellow. It was stirred for 20 min at 20°C, the solvent was removed under reduced pressure at room temperature, and the residue was washed first with hexane and then with water and dried in air until constant weight. Yield 0.51 g.

b. To a solution of 0.51 g of compound **VII** in 24 ml of anhydrous ethanol we added 0.43 g of mercury(II) trifluoroacetate. The mixture was heated for 3 h under reflux, the solvent was removed under reduced pressure at room temperature, and the residue was washed with water and dried in air until constant weight. Yield 0.53 g.

 $(\eta^5$ -Cyclopentadienyl)(η^6 -trifluoroacetoxydimercuriomethylbenzene)iron(II) tetrafluoroborate (XVII). To a solution of 0.30 g of (η^5 -cyclopentadienyl)(η^6 -toluene)iron(II) tetrafluoroborate (IV) in 10 ml of anhydrous tetrahydrofuran we added with stirring at 0°C 0.27 g of potassium *tert*-butoxide. After 8 min, 0.43 g of mercury(II) trifluoroacetate was added to the resulting red-brown mixture which very quickly turned black with a gray-green tint. The mixture was stirred for 15 min at 20°C and filtered, the solvent was removed from the filtrate under reduced pressure at room temperature, and the residue was washed first with hexane and then with water and dried in the dark until constant weight. Yield 0.63 g.

Compound **XVIII** was synthesized in a similar way.

 $(\eta^{6}$ -Chloromercuriomethylbenzene) $(\eta^{5}$ -cyclopentadienyl)iron(II) hexafluorophosphate(V) (XIX). To a solution of monomercurated complex IX prepared as described above (without isolation) we added 0.22 g of calcium chloride in 5 ml of a 1:1

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mixture of ethanol with acetonitrile. A light brown solid immediately precipitated, and the color of the solution became much less intense. After 20 min, the solvent was removed under reduced pressure at room temperature, and the residue was washed first with hexane and then with 5 ml of cold water and dried in air until constant weight. Yield 0.34 g.

 $[\eta^6$ -Chloromercurio(diphenyl)methane](η^5 -cyclopentadienyl)iron(II) hexafluorophosphate(V) (XX). To a solution of monomercurate complex XIV prepared as described above (without isolation) we added 0.22 g of calcium chloride in 5 ml of a 1:1 mixture of ethanol with acetonitrile. A yellow–green solid immediately precipitated, and the color of the solution sharply decreased in intensity. After 20 min, the solvent was removed under reduced pressure at room temperature, and the residue was washed first with hexane and then with 5 ml of cold water and dried in air until constant weight. Yield 0.52 g.

(Di- η^6 -benzylmercury)di(η^5 -cyclopentadienyl)diiron(II) bis[hexafluorophosphate(V)] (XXII). *a.* To a solution of monomercurated complex IX prepared as described above (without isolation) we added 4 ml of a saturated solution of ammonia in acetonitrile. A small amount of a light yellow solid immediately precipitated, and the color of the solution became less intense. After 20 min, the solvent was removed under reduced pressure at room temperature, and the residue was washed first with hexane and then with 5 ml of cold water and dried in air until constant weight. Yield 0.33 g.

b. To a solution of 1 mmol of compound **XVII** or **XVIII** in 15 ml of acetonitrile we added 4 ml of a saturated solution of dry ammonia in acetonitrile. The originally yellow-brown solution immediately turned black, and (after 20 min) finely dispersed metallic mercury separated from the solution as a light gray precipitate. A saturated aqueous solution of NH_4PF_6 , 3 ml, was added, the mixture was filtered, the solvent was removed from the filtrate under reduced pressure at room temperature, and the residue was washed first with hexane and then with 5 ml of cold water, and dried in air until constant weight.

[Bis(η^6 -diphenylmethyl)mercury]di(η^5 -cyclopentadienyl)diiron(II) bis[hexafluorophosphate(V)] (XXII). To a solution of monomercurated derivative XIV prepared as described above (without isolation) we added 4 ml of a saturated solution of dry ammonia in acetonitrile. A small amount of a yellow–green solid immediately precipitated, and the mixture became less intensely colored. After 20 min, the solvent was removed under reduced pressure at room temperature, and the residue was washed first with hexane and then with 5 ml of cold water and dried in air until constant weight. Yield 0.49 g.

(η⁵-Cyclopentadienyl)(η⁶-1-phenyl-2-propanone)iron(II) hexafluorophosphate(V) (XXIII). To a mixture of 1 mmol of salt **IX** and 1.2 mmol of acetyl bromide in 10 ml of dry methylene chloride, protected from atmospheric moisture, we added 0.1 g of anhydrous AlBr₃. The mixture was stirred for 3 h at 20°C, 5 ml of 5% hydrochloric acid and 3 ml of a saturated solution of NH₄PF₆ were added, and the mixture was stirred for 0.5 h. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 $(3 \times 10 \text{ ml})$. The extracts were combined with the organic phase and dried over anhydrous Na_2SO_4 , the solvent was removed under reduced pressure at room temperature, and the residue was recrystallized from acetone-diethyl ether (1:1). Yield 0.18 g, mp 87-88°C [9].

REFERENCES

- Boev, V.I., Boev, A.M., Moskalenko, A.I., and Pil'ko, E.I., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 4, p. 637.
- Sutherland, R.G., Steele, B.R., Demchuk, R.J., and Lee, C.C., *J. Organomet. Chem.*, 1979, vol. 181, no. 3, p. 411.
- 3. Vol'kenau, N.A., Bolesova, I.N., Peregudov, A.S., and Kravtsov, D.N., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, no. 4, p. 933.
- Makarova, L.G. and Nesmeyanov, A.N., *Metody* elementoorganicheskoi khimii. Rtut' (Methods of Organometallic Chemistry. Mercury) Moscow: Nauka, 1965, pp. 353–390.
- 5. US Patent 3130214, *Chem. Abstr.*, 1964, vol. 61, p. 4397.
- 6. Boev, V.I. and Moskalenko, A.I., Zh. Obshch. Khim., 1994, vol. 64, no. 9, p. 1516.
- Nekrasov, B.V., Osnovy obshchei khimii (Principles of General Chemistry), Moscow: Khimiya, 1969, vol. 2, p. 360.
- Cotton, F.A. and Wilkinson, G., Advanced Inorganic Chemistry. A Comprehensive Text, New York: Wiley, 1966, 2nd ed. Translated under the title Sovremennaya neorganicheskaya khimiya, Moscow: Mir, 1969, part 2, p. 478.
- Gill, U.S. and Moriarti, R.M., Synth. React. Inorg. Met.-Org. Chem., 1986, vol. 16, no. 14, p. 485.
- 10. Helling, J.F. and Hendrickson, W.A., *J. Organomet. Chem.*, 1977, vol. 141, no. 1, p. 99.
- 11. Pavlik, J. and Kriz, P., *Collect. Czech. Chem. Commun.*, 1966, vol. 31, p. 4412.

- 12. Bellamy, L.J., *The Infra-red Spectra of Complex Molecules*, London: Methuen, 1958.
- 13. Gutowsky, H.S., J. Chem. Phys., 1949, vol. 17, no. 1, p. 128.
- 14. Moinet, C. and Raoult, E., J. Organomet. Chem., 1982, vol. 231, no. 2, p. 245.
- Silverstein, R.M., Bassler, G.C., and Morrill, T.C., Spectrometric Identification of Organic Compounds, New York: Wiley, 1974, 3rd ed. Translated under the title Spektrometricheskaya identifikatsiya organicheskikh soedinenii, Moscow: Mir, 1977, pp. 277– 407.
- Pauling, L. and Pauling, P., *Chemistry*, San Francisco: Freeman, 1975. Translated under the title *Khimiya*, Moscow: Mir, 1978, p. 156.
- 17. Boev, V.I. and Moskalenko, A.I., Zh. Obshch. Khim., 1994, vol. 64, no. 6, p. 1028.
- Nesmeyanov, A.N., Vol'kenau, N.A., and Bolesova, I.N., *Dokl. Akad. Nauk SSSR*, 1966, vol. 166, no. 4, p. 607.
- Shilovtseva, L.S., Vol'kenau, N.A., Peregudov, A.S., Petrovskii, P.V., and Kravtsov, D.N., *Metalloorg. Khim.*, 1988, vol. 1, no. 2, p. 441.