

Organometallic Chemistry

30-Electron cationic iron- and cobalt-containing triple-decker complexes with a central cyclopentadienyl ligand. The first synthesis of the parent triple-decker iron complex with cyclopentadienyl ligands, $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$

A. R. Kudinov,* A. A. Fil'chikov, P. V. Petrovskii, and M. I. Rybinskaya

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: muratov@ineos.ac.ru

The parent 30-electron triple-decker iron complex with cyclopentadienyl ligands, $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ (**1**), was prepared for the first time by visible-light irradiation of ferrocene and $\{(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)\}\text{PF}_6$ in CH_2Cl_2 at 0 °C. An analogous reaction performed with the use of $(\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)$ (**2**) instead of ferrocene afforded the thermally labile 30-electron cationic iron-cobalt triple-decker complex $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)]\text{PF}_6$. The latter reacted with compound **2** at 20 °C to form the symmetrical 30-electron cationic dicobalt triple-decker complex $\{(\eta\text{-C}_4\text{Me}_4)\text{Co}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)\}\text{PF}_6$.

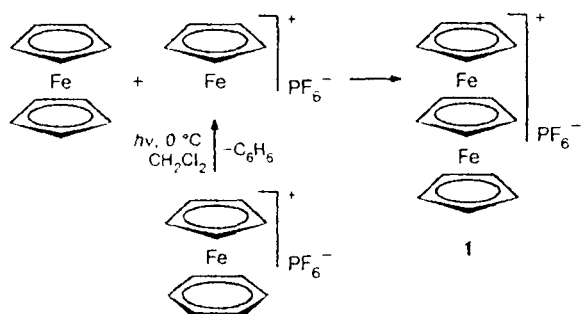
Key words: sandwich compounds, triple-decker complexes, iron, cobalt, ferrocene.

The first 34-electron triple-decker nickel complex with cyclopentadienyl ligands, viz., $[(\eta\text{-C}_5\text{H}_5)\text{Ni}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Ni}(\eta\text{-C}_5\text{H}_5)]\text{X}$ ($\text{X} = \text{BF}_4$ or PF_6), was synthesized by Werner and Salzer in 1972.^{1,2} In 1987, we described the synthesis of the first 30-electron triple-decker complexes of the iron-group metals with cyclopentadienyl ligands, $[(\eta\text{-C}_5\text{R}_5)\text{M}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{Me}_5)\text{M}'(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$,^{3–5} by the stacking reaction of the coordinatively unsaturated 12-electron fragments $\{(\eta\text{-C}_5\text{R}_5)\text{M}\}^+$ ($\text{M} = \text{Fe}$, $\text{R} = \text{H}$; $\text{M} = \text{Ru}$, $\text{R} = \text{H}$ or Me) with decamethylmetallocenes $\text{M}'(\eta\text{-C}_5\text{Me}_5)_2$ ($\text{M}' = \text{Fe}$, Ru , or Os). These compounds contain at least two pentamethylated cyclopentadienyl rings (the central ring and one terminal ring), like the analogous complexes $[(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{M}(\eta\text{-C}_5\text{Me}_5)]\text{CF}_3\text{SO}_3$ ($\text{M} = \text{Fe}$ or Ru) (terminal rings), which

have been prepared by Herberich and coworkers.⁶ The stability of the above-mentioned complexes of the iron-group metals is determined to a large extent by the presence of methyl substituents in the cyclopentadienyl rings. As for unsubstituted (parent) 30-electron triple-decker complexes of this type, the possibility of generation of the $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_5)]^+$ cation from ferrocene by electron impact has been demonstrated previously by mass spectrometry.⁷ At the same time, the problem of the chemical synthesis of the above-mentioned cation remained unresolved.

We found that the stacking reaction of the 12-electron cationic fragment $[(\eta\text{-C}_5\text{H}_5)\text{Fe}]^+$ with ferrocene in CH_2Cl_2 produced the parent 30-electron triple-decker iron compound **1** (Scheme 1).

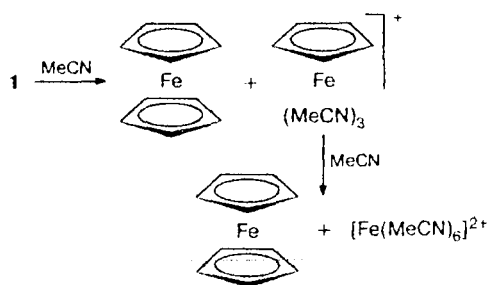
Scheme 1



The $[(\eta\text{-C}_5\text{H}_5)\text{Fe}]^+$ fragment was generated *in situ* under visible-light irradiation of the corresponding benzene complex at 0 °C. Low temperature is essential for the successful synthesis of complex **1** because the use of the same starting compounds even at 20 °C afforded the ferrocenium cation $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]^+$. It should be noted that the decamethylated derivative $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{Me}_5)\text{Fe}(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$ **4** can be synthesized at room temperature, which indicates that it is more stable than compound **1**.

Complex **1** is an air-unstable blue solid, which can be stored under an inert atmosphere at -78 °C. A solution of complex **1** in CH_2Cl_2 is stable at low temperature under an inert atmosphere but decomposes at room temperature in several hours to form paramagnetic products. More polar solvents rapidly decompose **1**. Thus, the addition of acetonitrile to a solution of **1** in CH_2Cl_2 or to a solid specimen leads to the disappearance of the characteristic blue color due to the nucleophilic replacement of ferrocene by solvent molecules (Scheme 2).

Scheme 2



In the course of addition of acetonitrile to a solution of complex **1** in CH_2Cl_2 at 0 °C, the solution may turn violet, which is typical of the trisacetonitrile cationic complex $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{MeCN})_3]^+$.⁸ However, the violet color rapidly disappears due to disproportionation of this complex to form ferrocene and $[\text{Fe}(\text{MeCN})_6]^{2+}$, which agrees with the proposed structure of **1** as a triple-decker complex. It should be noted that the ferrocenium cation

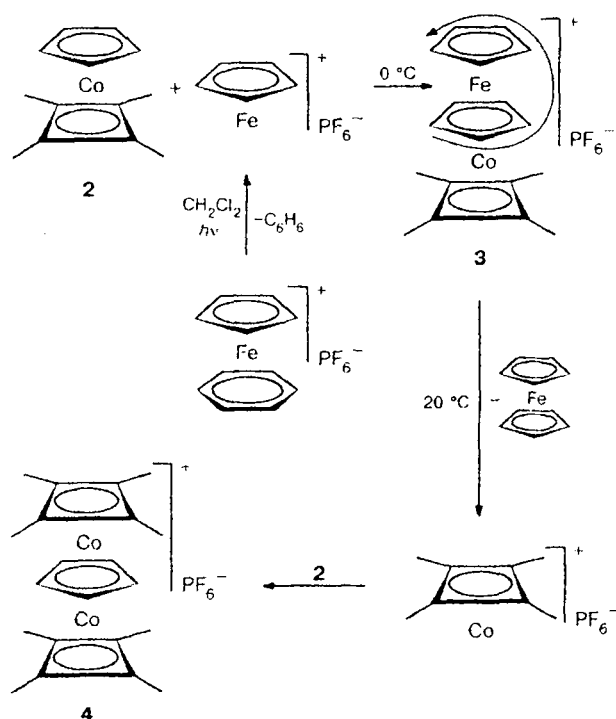
$[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]^+$, which is also blue, is rather stable in a MeCN solution. Therefore, the reaction with acetonitrile is a simple qualitative test for triple-decker complex **1**. This reaction can be also used in the case of other unstable cationic triple-decker complexes and, in particular, in the case of the iron-containing compounds $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{Me}_5)\text{M}(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$ ($\text{M} = \text{Fe}, \text{Ru}, \text{or Os}$), which we have prepared previously.⁴ The addition of acetonitrile to these compounds also results in the disappearance of the typical bright color. However, the Ru_2 - and RuOs -containing compounds $[(\eta\text{-C}_5\text{R}_5)\text{Ru}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{Me}_5)\text{M}(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$ ($\text{M} = \text{Ru}, \text{R} = \text{H or Me}; \text{M} = \text{Os}, \text{R} = \text{H}$) exhibit high stability⁴ and do not decompose under the action of acetonitrile.

Triple-decker complex **1** was also characterized by the data of elemental analysis as well as by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The data of elemental analysis indicate that compound **1** crystallizes with dichloromethane molecules. The ^1H NMR spectrum of this compound (in CD_2Cl_2) has the only singlet at δ 4.37 belonging to the C_5H_5 protons along with a signal of the protons of dichloromethane at δ 5.32. This suggests that the protons of the terminal and central cyclopentadienyl rings are equally shielded. This fact, while surprising, does not contradict the data for other iron-containing triple-decker complexes. For example, in $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$, $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Ru}(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$, and $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)]\text{PF}_6$ (see below), the signals of the protons of the terminal C_5H_5 rings are observed at δ 4.35, 4.52, and 4.53 and the signals of the protons of the central C_5H_5 rings are observed at δ 4.15, 4.22, and 4.39, respectively. In these compounds, the signal of the protons of one ring is only slightly shifted with respect to that of the second one (0.14–0.30 ppm). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1** (in CD_2Cl_2) has two singlets at δ 69.20 and 52.48 with an integrated intensity ratio of 2 : 1, belonging to the carbon atoms of the terminal and central rings, respectively, along with signals of dichloromethane. These data agree well with the spectral data for the related methylated triple-decker complexes of the iron-group metals, viz., $[(\eta\text{-C}_5\text{R}_5)\text{M}(\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{Me}_5)\text{M}'(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$ ($\text{M} = \text{Fe}, \text{R} = \text{H}; \text{M} = \text{Ru}, \text{R} = \text{H or Me}; \text{M}' = \text{Fe}, \text{Ru}, \text{or Os}$),^{3,4} whose structures were confirmed by the data of X-ray diffraction analysis of the Ru_2 - and RuOs -containing derivatives.^{4,5}

As part of continuing studies of the reactivity of the $[(\eta\text{-C}_5\text{H}_5)\text{Fe}]^+$ fragment with respect to sandwich compounds, we studied the reaction of this fragment with the cobalt complex $(\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)$ (**2**). It was demonstrated that the attack of the cationic species $[(\eta\text{-C}_5\text{H}_5)\text{Fe}]^+$ proceeds regioselectively on the five-membered ring of compound **2**. The 30-electron cationic iron-cobalt triple-decker complex **3** is formed as the primary reaction product (Scheme 3).

This compound can be isolated in the pure form if the reaction is carried out at 0 °C. At higher tempera-

Scheme 3



ture (20 °C), compound 3 decomposes with elimination of the stable ferrocene molecule and generation of the 12-electron $[(\eta\text{-C}_4\text{Me}_4)\text{Co}]^+$ cationic fragment. The latter fragment enters into the stacking reaction with compound 2, which is present in the reaction mixture, to form symmetrical 30-electron cationic triple-decker dicobalt complex 4 as the final product. To prepare complex 4 in the pure form, the initial compound 2 and $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ should be taken in a molar ratio of $\geq 2 : 1$. The reaction is accompanied by the transfer of the cyclopentadienyl ligand from cobalt to iron. This process occurs through intermediate formation of the thermally labile triple-decker complex 3, which is converted into complex 4 as a result of the exchange of ferrocene for 2. It should be noted that the ligand-exchange reactions play a significant role in the chemistry of π -complexes of transition metals. In the case under consideration, the molecules of the sandwich compounds (ferrocene and compound 2) act as ligands.

Triple-decker complexes 3 and 4 are brightly colored solid compounds. Compound 3 is stable (both in the solid state and in solutions in CH_2Cl_2) only at low temperature under an inert atmosphere. Compound 4 is more stable but it slowly decomposes in air. Triple-decker complexes 3 and 4 were characterized by the data of elemental analysis and ^1H NMR spectroscopy. The ^1H NMR spectrum of compound 3 has two singlets at δ 4.53 and 4.39 belonging to the protons of the terminal and central cyclopentadienyl rings, respectively, and a singlet of the protons of the methyl groups of the

C_4Me_4 ring at δ 1.31. The ^1H NMR spectrum of symmetrical compound 4 contains only two singlets, namely, a singlet of the protons of the central C_5H_5 ring at δ 4.44 and a singlet of the protons of the methyl groups of the C_4Me_4 ring at δ 1.47. The ^1H NMR spectral data for compounds 3 and 4 agree well with the data for other 30-electron triple-decker compounds containing the C_5H_5 ⁶ or C_5Me_5 ³⁻⁵ central ligands, which have been reported previously.

To summarize, in the present work we prepared new triple-decker iron and cobalt complexes with a central cyclopentadienyl ligand using the cationic fragment $[(\eta\text{-C}_5\text{H}_5)\text{Fe}]^+$ in stacking reactions with sandwich compounds.

Experimental

All operations were performed under an argon atmosphere with the use of anhydrous solvents freshly distilled under an inert atmosphere. The initial compounds $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ ⁹ and $(\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)$ ¹⁰ (2) were prepared according to known procedures. The reactions were carried out in 15-mm Schlenk tubes upon cooling with ice. Irradiation was performed with the use of a DRL-250 luminescent lamp (250 W).

The ^1H NMR spectra were recorded on a Bruker AMX-400 instrument.

($\mu\text{-}\eta\text{:}\eta\text{-Cyclopentadienyl}$)bis[($\eta\text{-cyclopentadienyl}$)iron] hexafluorophosphate, $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ (1). Dichloromethane (20 mL) was added to a mixture of $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ (86 mg, 0.25 mmol) and ferrocene (93 mg, 0.5 mmol). The reaction mixture was irradiated with visible light at 0 °C for 1 h with intense stirring using a magnetic stirrer. The blue solution was concentrated at 0 °C *in vacuo*. The residue was washed several times with petroleum ether to remove an excess of ferrocene and then dried *in vacuo*. Compound 1 was obtained as a blue solid in almost quantitative yield. The product can be reprecipitated with petroleum ether from CH_2Cl_2 . Found (%): C, 30.2; H, 2.83. $\text{C}_{18}\text{H}_{21}\text{Cl}_6\text{F}_6\text{Fe}_2\text{P}$ ($1 \cdot 3 \text{ CH}_2\text{Cl}_2$). Calculated (%): C, 30.59; H, 3.00. ^1H NMR (CD_2Cl_2), δ : 4.37 (s, $\eta\text{-C}_5\text{H}_5$, $\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2), δ : 69.20 (s, 10 C, $\eta\text{-C}_5\text{H}_5$); 52.48 (s, 5 C, $\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5$).

($\mu\text{-}\eta\text{:}\eta\text{-Cyclopentadienyl}$)[($\eta\text{-cyclopentadienyl}$)iron][($\eta\text{-tetramethylcyclobutadiene}$)cobalt] hexafluorophosphate, $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)]\text{PF}_6$ (3). Dichloromethane (20 mL) was added to a mixture of $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ (95 mg, 0.275 mmol) and compound 2 (58 mg, 0.25 mmol). The reaction mixture was irradiated at 0 °C for 2 h with intense stirring using a magnetic stirrer. The bright-red solution was concentrated to dryness, extracted with a 3/4 CH_2Cl_2 /hexane mixture, and filtered into an equal volume of hexane. The precipitate that formed was filtered off. All operations were carried out at 0 °C. Complex 3 was obtained in a yield of 95 mg (~70%) as a red solid. Found (%): C, 40.89; H, 4.40. $\text{C}_{18.5}\text{H}_{23}\text{ClCoF}_6\text{FeP}$ ($3 \cdot 0.5 \text{ CH}_2\text{Cl}_2$). Calculated (%): C, 41.10; H, 4.29. ^1H NMR (CD_2Cl_2), δ : 4.53 (s, 5 H, $\eta\text{-C}_5\text{H}_5$); 4.39 (s, 5 H, $\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5$); 1.31 (s, 12 H, C_4Me_4).

($\mu\text{-}\eta\text{:}\eta\text{-Cyclopentadienyl}$)bis[($\eta\text{-tetramethylcyclobutadiene}$)cobalt] hexafluorophosphate, $[(\eta\text{-C}_4\text{Me}_4)\text{Co}(\eta\text{-}\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-}\eta\text{-C}_4\text{Me}_4)]\text{PF}_6$ (4). A mixture of $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ (86 mg, 0.25 mmol) and compound 2 (128 mg,

0.55 mmol) in CH_2Cl_2 (20 mL) was irradiated at 20 °C for 2 h with intense stirring using a magnetic stirrer until the color of the solution changed from red to orange. The solution was filtered into hexane or ether (~100 mL) and the precipitate was reprecipitated with ether from CH_2Cl_2 . Yellow-orange complex **4** was obtained in a yield of 109 mg (80%). Found (%): C, 46.56; H, 5.54. $\text{C}_{21}\text{H}_{29}\text{Co}_2\text{F}_6\text{P}$. Calculated (%): C, 46.34; H, 5.37. ^1H NMR (CD_2Cl_2), δ : 4.44 (s, 5 H, μ - η - η - C_5H_5); 1.47 (s, 24 H, C_4Me_4).

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