

## 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, $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$

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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  $\text{CH}_2\text{Cl}_2$  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  $[(\eta\text{-C}_4\text{Me}_4)\text{Co}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)]\text{PF}_6$ .

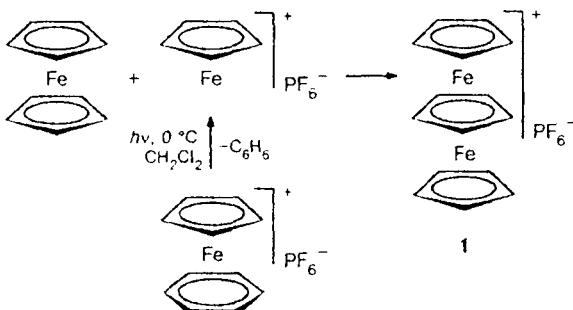
**Key words:** sandwich compounds, triple-decker complexes, iron, cobalt, ferrocene.

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  $\text{PF}_6$ ), was synthesized by Werner and Salzer in 1972.<sup>1,2</sup> In 1987, we described the synthesis of the first 30-electron triple-decker complexes of the iron-group metals with cyclopentadienyl ligands,  $[(\eta\text{-C}_5\text{R}_5)\text{M}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{Me}_5)\text{M}'(\eta\text{-C}_5\text{Me}_5)]\text{PF}_6$ ,<sup>3–5</sup> 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  $\text{Me}$ ) with decamethylmetallocenes  $\text{M}'(\eta\text{-C}_5\text{Me}_5)_2$  ( $\text{M}' = \text{Fe}$ ,  $\text{Ru}$ , or  $\text{Os}$ ). 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  $\text{Ru}$ ) (terminal rings), which

have been prepared by Herberich and coworkers.<sup>6</sup> 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.<sup>7</sup> 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  $\text{CH}_2\text{Cl}_2$  produced the parent 30-electron triple-decker iron compound 1 (Scheme 1).

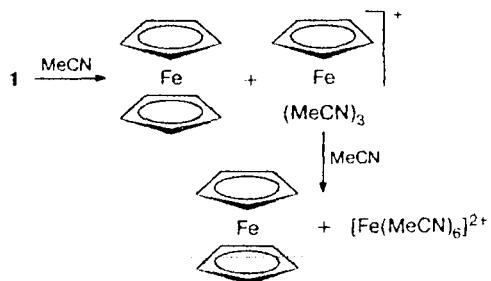
Scheme 1



The  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  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  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{Me}_5)_2\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]\text{PF}_6$ <sup>4</sup> 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  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  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  $\text{CH}_2\text{Cl}_2$  at 0 °C, the solution may turn violet, which is typical of the trisacetonitrile cationic complex  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}(\text{MeCN})_3]^+$ .<sup>8</sup> 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

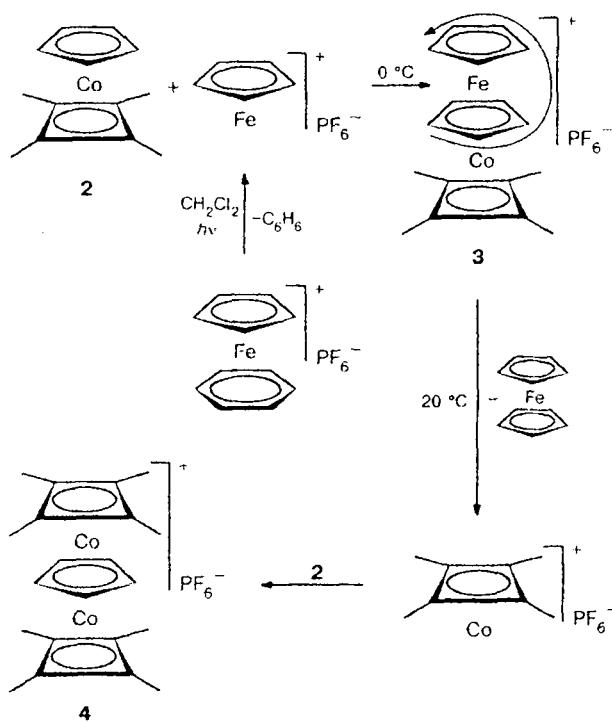
$[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]^+$ , which is also blue, is rather stable in a MeCN solution. Therefore, the reaction with acetonitrile is a simple qualitative test for triple-decker complex **1**. This reaction can be also used in the case of other unstable cationic triple-decker complexes and, in particular, in the case of the iron-containing compounds  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{Me}_5)_2\text{M}(\eta\text{-C}_5\text{Me}_5)_2]\text{PF}_6$  ( $\text{M} = \text{Fe}$ ,  $\text{Ru}$ , or  $\text{Os}$ ), which we have prepared previously.<sup>4</sup> The addition of acetonitrile to these compounds also results in the disappearance of the typical bright color. However, the  $\text{Ru}_{2-}$  and  $\text{RuOs}$ -containing compounds  $[(\eta\text{-C}_5\text{R}_5)_2\text{Ru}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{Me}_5)_2\text{M}(\eta\text{-C}_5\text{Me}_5)_2]\text{PF}_6$  ( $\text{M} = \text{Ru}$ ,  $\text{R} = \text{H}$  or  $\text{Me}$ ;  $\text{M} = \text{Os}$ ,  $\text{R} = \text{H}$ ) exhibit high stability<sup>4</sup> 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  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy. The data of elemental analysis indicate that compound **1** crystallizes with dichloromethane molecules. The  $^1\text{H}$  NMR spectrum of this compound (in  $\text{CD}_2\text{Cl}_2$ ) has the only singlet at  $\delta$  4.37 belonging to the  $\text{C}_5\text{H}_5$  protons along with a signal of the protons of dichloromethane at  $\delta$  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  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)_2\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]\text{PF}_6$ ,  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)_2\text{Ru}(\eta\text{-C}_5\text{Me}_5)_2]\text{PF}_6$ , and  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)_2\text{Co}(\eta\text{-C}_4\text{Me}_4)_2]\text{PF}_6$  (see below), the signals of the protons of the terminal  $\text{C}_5\text{H}_5$  rings are observed at  $\delta$  4.35, 4.52, and 4.53 and the signals of the protons of the central  $\text{C}_5\text{H}_5$  rings are observed at  $\delta$  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  $\text{CD}_2\text{Cl}_2$ ) has two singlets at  $\delta$  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.*,  $[(\eta\text{-C}_5\text{R}_5)_2\text{M}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{Me}_5)_2\text{M}'(\eta\text{-C}_5\text{Me}_5)_2]\text{PF}_6$  ( $\text{M} = \text{Fe}$ ,  $\text{R} = \text{H}$ ;  $\text{M} = \text{Ru}$ ,  $\text{R} = \text{H}$  or  $\text{Me}$ ;  $\text{M}' = \text{Fe}$ ,  $\text{Ru}$ , or  $\text{Os}$ ),<sup>3,4</sup> whose structures were confirmed by the data of X-ray diffraction analysis of the  $\text{Ru}_{2-}$  and  $\text{RuOs}$ -containing derivatives.<sup>4,5</sup>

As part of continuing studies of the reactivity of the  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  fragment with respect to sandwich compounds, we studied the reaction of this fragment with the cobalt complex  $(\eta\text{-C}_5\text{H}_5)_2\text{Co}(\eta\text{-C}_4\text{Me}_4)$  (**2**). It was demonstrated that the attack of the cationic species  $[(\eta\text{-C}_5\text{H}_5)_2\text{Fe}]^+$  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 ( $20^\circ\text{C}$ ), 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  $\pi$ -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  $\text{CH}_2\text{Cl}_2$ ) 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  $^1\text{H}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of compound 3 has two singlets at  $\delta$  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

$\text{C}_4\text{Me}_4$  ring at  $\delta$  1.31. The  $^1\text{H}$  NMR spectrum of symmetrical compound 4 contains only two singlets, namely, a singlet of the protons of the central  $\text{C}_5\text{H}_5$  ring at  $\delta$  4.44 and a singlet of the protons of the methyl groups of the  $\text{C}_4\text{Me}_4$  ring at  $\delta$  1.47. The  $^1\text{H}$  NMR spectral data for compounds 3 and 4 agree well with the data for other 30-electron triple-decker compounds containing the  $\text{C}_5\text{H}_5^6$  or  $\text{C}_5\text{Me}_5^{3-5}$  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  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_6\text{H}_6)]\text{PF}_6$ <sup>9</sup> and  $(\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)$ <sup>10</sup> (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  $^1\text{H}$  NMR spectra were recorded on a Bruker AMX-400 instrument.

**( $\mu\text{-}\eta\text{:}\eta\text{-Cyclopentadienyl})\text{bis}[(\eta\text{-cyclopentadienyl})\text{iron}]\text{hexafluorophosphate}$** ,  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)\text{Fe}(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$  (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  $0^\circ\text{C}$  for 1 h with intense stirring using a magnetic stirrer. The blue solution was concentrated at  $0^\circ\text{C}$  *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  $\text{CH}_2\text{Cl}_2$ . Found (%): C, 30.2; H, 2.83.  $\text{C}_{18}\text{H}_{21}\text{Cl}_6\text{Fe}_2\text{P}$  ( $1 \cdot 3 \text{ CH}_2\text{Cl}_2$ ). Calculated (%): C, 30.59; H, 3.00.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$ : 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 ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$ : 69.20 (s, 10 C,  $\eta\text{-C}_5\text{H}_5$ ); 52.48 (s, 5 C,  $\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5$ ).

**( $\mu\text{-}\eta\text{:}\eta\text{-Cyclopentadienyl})[(\eta\text{-cyclopentadienyl})\text{iron}]\text{[(}\eta\text{-tetramethylcyclobutadiene)\text{cobalt] hexafluorophosphate}$** ,  $[(\eta\text{-C}_5\text{H}_5)\text{Fe}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)]\text{PF}_6$  (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  $0^\circ\text{C}$  for 2 h with intense stirring using a magnetic stirrer. The bright-red solution was concentrated to dryness, extracted with a 3/4  $\text{CH}_2\text{Cl}_2$ /hexane mixture, and filtered into an equal volume of hexane. The precipitate that formed was filtered off. All operations were carried out at  $0^\circ\text{C}$ . 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.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$ : 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,  $\text{C}_4\text{Me}_4$ ).

**( $\mu\text{-}\eta\text{:}\eta\text{-Cyclopentadienyl})\text{bis}[(\eta\text{-tetramethylcyclobutadiene)\text{cobalt] hexafluorophosphate}$** ,  $[(\eta\text{-C}_4\text{Me}_4)\text{Co}(\mu\text{-}\eta\text{:}\eta\text{-C}_5\text{H}_5)\text{Co}(\eta\text{-C}_4\text{Me}_4)]\text{PF}_6$  (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  $\text{CH}_2\text{Cl}_2$  (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  $\text{CH}_2\text{Cl}_2$ . 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.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ),  $\delta$ : 4.44 (s, 5 H,  $\mu\text{-}\eta\text{-}\eta\text{-C}_5\text{H}_5$ ); 1.47 (s, 24 H,  $\text{C}_4\text{Me}_4$ ).

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