Synthesis of the first unsymmetrical 34-electron cationic cobalt-nickel triple-decker complex with a central cyclopentadienyl ligand $[(\eta\text{-}C_6Me_6)Co(\mu\text{-}\eta{:}\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_5)]PF_6$

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The first unsymmetrical 34-electron cationic cobalt-nickel triple-decker complex with a central cyclopentadienyl ligand $[(\eta\text{-}C_6Me_6)Co(\mu\text{-}\eta{:}\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_5)]PF_6$ was prepared by the reaction of $[(\eta\text{-}C_6Me_6)_2Co]PF_6$ with nickelocene.

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

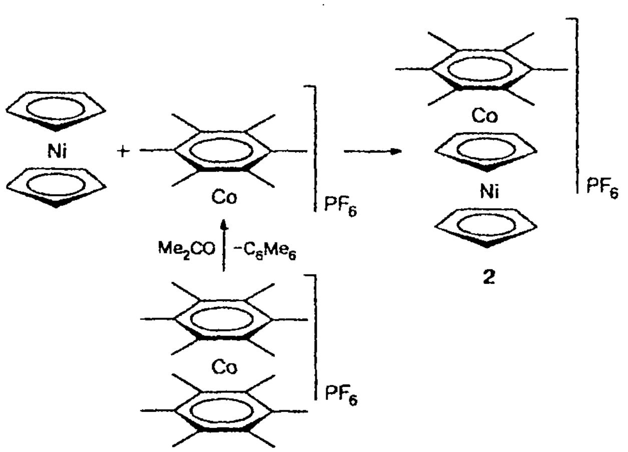
In 1972, Werner and Salzer synthesized[1,2] the first triple-decker compound, *viz.*, the 34-electron cationic nickel complex $[(\eta\text{-}C_5H_5)Ni(\mu\text{-}\eta{:}\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_5)]X$ ($X = BF_4$ or PF_6) (**1**), whose structure was confirmed by X-ray diffraction study.[3,4] Complex **1** was obtained as a result of an electrophilic attack of H^+ or Ph_3C^+ on nickelocene accompanied by the formation of intermediate labile cyclopentadiene cations $[(\eta\text{-}C_5H_5)Ni(\eta^4\text{-}C_5H_5R)]^+$ ($R = H$ or CPh_3), which serve as a source of the 14-electron cationic fragment $[(\eta\text{-}C_5H_5)Ni]^+$. The subsequent addition of this fragment to nickelocene afforded compound **1**.

Since the cationic 14-electron fragment $[(\eta\text{-}C_6Me_6)Co]^+$ is isolobal to the fragment $[(\eta\text{-}C_5H_5)Ni]^+$, its interaction with nickelocene would be expected to give an unsymmetrical cobalt-nickel triple-decker complex with a central cyclopentadienyl ligand. The 20-electron cobalt complex $[(\eta\text{-}C_6Me_6)_2Co]PF_6$ was used as the starting compound for generating the 14-electron fragment $[(\eta\text{-}C_6Me_6)Co]^+$. Previously,[5] it has been demonstrated that this compound reacts with dienes in the presence of acetone to form the 18-electron diene cationic complex $[(\eta\text{-}C_6Me_6)Co(\eta\text{-diene})]PF_6$. It can be assumed that the reaction proceeds through intermediate formation of the cationic fragment $[(\eta\text{-}C_6Me_6)Co]^+$ as a labile complex with acetone molecules.

We found that the reaction of $[(\eta\text{-}C_6Me_6)_2Co]PF_6$ with nickelocene in acetone actually yielded a 34-electron cationic cobalt-nickel triple-decker complex **2** (Scheme 1).*

Compound **2** was obtained as a blue solid, which is stable in an inert atmosphere but decomposes in air. This compound is soluble in dichloromethane and acetone but decomposes on storage in solutions.

Scheme 1



The structure of the triple-decker complex **2** was established based on the data of elemental analysis and ^1H NMR spectroscopy. The ^1H NMR spectrum (in acetone-d_6) has a singlet for the protons of the methyl groups at δ 2.45 and two singlets for the protons of the terminal (η-) and central (μ-η:η-) cyclopentadienyl rings at δ 5.23 and 4.02, respectively. These experimental results agree well with the ^1H NMR spectrum (in CD_3NO_2) of the related compound **1**, in which the protons of the terminal and central cyclopentadienyl rings manifest themselves[1,2] as singlets at δ 5.4 and 4.7, respectively.

The resulting compound **2** containing the cobalt and nickel atoms is the first example of an unsymmetrical 34-electron triple-decker complex with a central cyclopentadienyl ligand. In this work, we demonstrated for the first time that the 14-electron cationic fragment

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$[(\eta\text{-}C_6Me_6)Co]^+$ can be used successfully for preparing triple-decker complexes.

Experimental

All operations were carried out in an argon atmosphere with the use of anhydrous solvents which had been freshly distilled in an inert atmosphere. The compound $[(\eta\text{-}C_6Me_6)_2Co]PF_6$ was prepared according to a known procedure.[6]

The ^{1}H NMR spectra were recorded on a Brucker AMX-400 instrument.

$[(\eta\text{-}C_6Me_6)Co(\mu\text{-}\eta{:}\eta\text{-}C_5H_5)Ni(\eta\text{-}C_5H_5)]PF_6$ (2). Acetone (5 mL) was added to a mixture of $[(\eta\text{-}C_6Me_6)_2Co]PF_6$ (264 mg, 0.5 mmol) and nickelocene (118 mg, 0.625 mmol). The reaction mixture was stirred at 20 °C for 1 h. The resulting blue solution was filtered into pentane (20 mL). The precipitate that formed was reprecipitated with pentane from dichloromethane. Compound 2 was obtained as a blue solid in a yield of 225 mg (~70%). Found (%): C, 42.87; H, 4.68. $C_{22}H_{28}CoF_6NiP \cdot CH_2Cl_2$. Calculated (%): C, 43.16; H, 4.73. ^{1}H NMR (acetone-d_6), δ: 5.23 (s, 5 H, $\eta\text{-}C_5H_5$); 4.02 (s, 5 H, $\mu\text{-}\eta{:}\eta\text{-}C_5H_5$); 2.45 (s, 18 H, C_6Me_6).

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