Synthesis of cationic complexes $[(C_4Me_4)CoL]^+$ (L is naphthalene, phenanthrene, and anthracene)*

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Cationic arene complexes $[Cb^*Co(naphthalene)]^+$ (**2**, $Cb^* = C_4Me_4$) and $[Cb^*Co(phenanthrene)]^+$ were synthesized by the reactions of $[Cb^*Co(MeCN)_3]^+$ with arenes. The $[Cb^*Co(anthracene)]^+$ complex was synthesized by the abstraction of the iodide ion from $[Cb^*CoI]_2$ by $TlBF_4$ in the presence of anthracene. Complex **2** exchanges the naphthalene ligand for other arenes at room temperature.

Key words: arene complexes, cobalt, sandwich compounds.

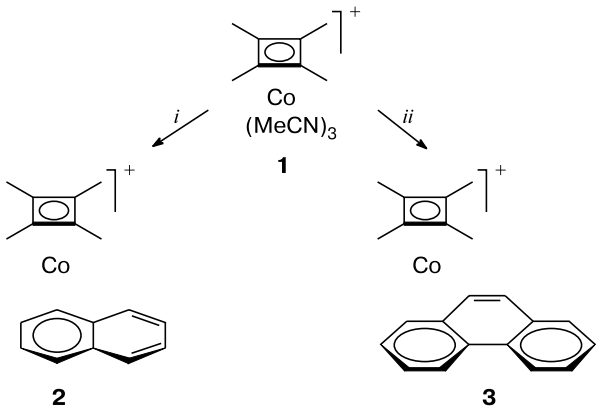
Complexes with condensed aromatic hydrocarbons $[L'M(polyarene)]^{n+}$ readily exchange the arene ligands, due to which they are convenient synthons of the $[L'M]^{n+}$ cationic fragments.[1—6] We have recently described the efficient methods for the syntheses of the cobalt tetramethylcyclobutadiene complexes with five-electron ligands of different types.[7—13] In this work, we synthesized the $[Cb^*CoL]^+$ complexes ($Cb^* = C_4Me_4$, L is polyarene).

Results and Discussion

We have previously[8,13] shown that the acetonitrile complex $[Cb^*Co(MeCN)_3]^+$ (**1**) can be used as a synthon for the $[Cb^*Co]^+$ cation under mild conditions due to lability of the acetonitrile ligands. In this work, the reactions of compound **1** with naphthalene and phenanthrene in nitromethane afforded the cationic complexes $[Cb^*Co(naphthalene)]^+$ (**2**) and $[Cb^*Co(phenanthrene)]^+$ (**3**) (Scheme 1).** These reactions are reversible, because cations **2** and **3** easily undergo nucleophilic substitution by MeCN. The increased reactivity of the anthracene derivative $[Cb^*Co(anthracene)]^+$ (**4**) toward acetonitrile prevents its formation from **1**.

This restriction can be avoided by the use of the procedure based on iodide ion abstraction from $[Cb^*CoI]_2$ by $TlBF_4$ in the presence of arene in THF (Scheme 2). The reaction proceeds, most likely, through the intermediate formation of the labile solvate complexes $[Cb^*Co(THF)_3]^+$. Substantially lower ability of THF to coordination compared to acetonitrile makes it possible to avoid nucleophilic substitution in cation **4**. Complexes **2** and **3** were also synthesized according to this method. However, the starting iodide $[Cb^*CoI]_2$ is formed upon heating of $[Cb^*Co(MeCN)_3]I$ *in vacuo* and, in addition, is highly sensitive to air. Therefore, it seems reasonable to use this protocol only when the direct synthesis from cation **1** is impossible.

Scheme 1



i. Naphthalene. *ii*. Phenanthrene.

Naphthalene and phenanthrene complexes **2** and **3** are stable in air in the solid state, and anthracene analog **4** decomposes rapidly. Cations **2** and **4** readily eliminate the arene ligand. In particular, they undergo nucleophilic substitution by coordinating solvents. The both complexes are immediately decomposed by acetonitrile to form complex **1**. Cation **4** is also decomposed immediately by

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** All synthesized cationic complexes were isolated as salts with the BF_4^- and PF_6^- anions (anions are omitted in the schemes).

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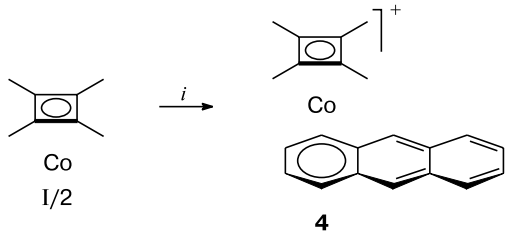
Scheme 2

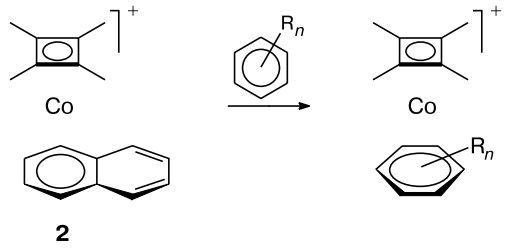


i. Anthracene.

acetone, whereas the conversion of **2** within 5 min is only ~25%.

Naphthalene complex **2** enters the arene exchange reaction at room temperature (Scheme 3). The reactions with benzene and mesitylene complete within 24 h in acetone. Arene exchange in the $[Cb^*Co(C_6H_6)]^+$ benzene complex occurs only under visible light irradiation or on heating.

Scheme 3



R_n = H; 1,3,5-Me_3

Thus, in this work the first Cb*Co complexes with condensed aromatic hydrocarbons were synthesized. Lability of the arene ligands in these compounds make it possible to use them as promising synthons of the $[Cb^*Co]^+$ cationic fragment.

Experimental

All reactions were carried out under argon using water-free solvents. The products, except for the anthracene complex [**4**]BF_4, were isolated in air. The starting compounds $[Cb^*Co(MeCN)_3]PF_6$ (see Ref. 8) and $[Cb^*Co(C_6H_6)]I$ (see Ref. 13) were synthesized according to known procedures. Irradiation was carried out in a Schlenk tube 15 mm in diameter using a 400-W mercury luminescent lamp. The Schlenk tube and lamp were placed in a vessel cooled with flowing water and covered inside with aluminum foil. ^{1}H NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz).

[(η-Tetramethylcyclobutadiene)(η-naphthalene)cobalt]hexafluorophosphate, $[Cb^*Co(\eta\text{-naphthalene})]PF_6$ ([2]PF_6). A mixture of $[Cb^*Co(MeCN)_3]PF_6$ (100 mg, 0.23 mmol) and naphthalene (100 mg, 0.78 mmol) in $MeNO_2$ (3 mL) was stirred for 24 h. The solvent was removed *in vacuo*. The brown residue was washed with ether (2×5 mL), dissolved in CH_2Cl_2, and filtered through a silica gel layer (1—2 cm). A yellow precipitate formed after the solvent was removed was reprecipitated with ether from CH_2Cl_2. The yield was 61 mg (60%). Found (%): C, 49.10; H, 4.75. $C_{18}H_{20}CoF_6P$. Calculated (%): C, 49.11; H, 4.58. ^{1}H NMR (nitromethane-d_3), δ: 7.88 (m, 4 H, H(5)—H(8)); 7.15 (m, 2 H, H(1), H(4)); 6.65 (m, 2 H, H(2), H(3)); 1.27 (s, 12 H, Cb*).

[(η-Tetramethylcyclobutadiene)(η-phenanthrene)cobalt]hexafluorophosphate, $[(\eta\text{-}C_4Me_4)Co(\eta\text{-phenanthrene})]PF_6$ ([3]PF_6) was synthesized analogously to [**2**]PF_6 by the reaction of [**1**]PF_6 (100 mg, 0.23 mmol) with phenanthrene (140 mg, 0.78 mmol). Yellow solid. The yield was 64 mg (57%). Found (%): C, 54.23; H, 4.60. $C_{22}H_{22}CoF_6P$. Calculated (%): C, 53.89; H, 4.52. ^{1}H NMR (acetone-d_6), δ: 8.84 (m, 1 H, H(5)); 8.20 (d, 1 H, H(8), J = 9.3 Hz); 8.16 (m, 1 H, H(6)); 8.10 (m, 1 H, H(7)); 7.91 (m, 2 H, H(9), H(10)); 7.80 (d, 1 H, H(4), J = 9.5 Hz); 7.37 (m, 1 H, H(1)); 6.97 (m, 2 H, H(2), H(3)); 1.22 (s, 12 H, Cb*).

[(η-Tetramethylcyclobutadiene)(η-anthracene)cobalt]tetrafluoroborate, $[(\eta\text{-}C_4Me_4)Co(\eta\text{-anthracene})]BF_4$ ([4]BF_4). A solution of $[Cb^*Co(C_6H_6)]I$ (100 mg, 0.27 mmol) in acetonitrile (3 mL) was irradiated for 4 h. The color of the reaction mixture turned red from yellow. After the solvent was removed *in vacuo*, a red finely crystalline complex of $[Cb^*Co(MeCN)_3]I$ was obtained, which then was heated *in vacuo* (~0.01 Torr) at 50—60 °C until the color turned dark green from red (10—15 min). Anthracene (73 mg, 0.41 mmol), $TlBF_4$ (79 mg, 0.27 mmol), and THF (5 mL) were added to thus synthesized $[Cb^*CoI]_2$ complex. The reaction mixture was stirred for 24 h. The yellow precipitate that formed was filtered off, washed with ether, and dissolved in a minimum amount of CH_2Cl_2. The solution was filtered off, and ether was added to the filtrate. Complex [**4**]BF_4 (67 mg, 57%) was obtained as an orange solid. All procedures on the synthesis and isolation of this compound were carried out under argon. Found (%): C, 58.33; H, 4.89. $C_{22}H_{22}CoBF_4 \cdot 0.33CH_2Cl_2$. Calculated (%): C, 58.25; H, 4.96. ^{1}H NMR (CD_2Cl_2), δ: 8.51 (s, 2 H, H(9), H(10)); 8.02 (m, 2 H, H(5), H(8)); 7.57 (m, 2 H, H(6), H(7)); 7.38 (m, 2 H, H(1), H(4)); 6.65 (m, 2 H, H(2), H(3)); 1.13 (s, 12 H, Cb*).

The [**2**]BF_4 (56%) and [**3**]BF_4 (57%) complexes were synthesized similarly.

Arene exchange in complex [2]PF_6. A solution of complex [**2**]PF_6 (50 mg, 0.1 mmol) and benzene or mesitylene (0.1 mL) in acetone (2 mL) was left for 24 h and then evaporated to a volume of ~0.5 mL. Ether (5 mL) was added, and the yellow precipitate that formed was reprecipitated with ether from acetone.

Complex $[Cb^*Co(C_6H_6)]PF_6$ was synthesized in a yield of 33 mg (85%). ^{1}H NMR, (acetone-d_6), δ: 6.72 (s, 6 H, C_6H_6); 1.70 (s, 12 H, Cb*) (*cf.* Ref. 10).

Complex $[Cb^*Co(1,3,5\text{-}C_6H_3Me_3)]PF_6$ was synthesized in a yield of 32 mg (75%). ^{1}H NMR (acetone-d_6), δ: 6.31 (s, 3 H, $C_6\underline{H}_3Me_3$); 2.39 (s, 9 H, $C_6H_3\underline{Me}_3$); 1.58 (s, 12 H, Cb*) (*cf.* Ref. 14).

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