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Synthesis of slipped μ-indenyl triple-decker complexes containing (C_4Me_4)Co and (C_5Me_5)Ru fragments

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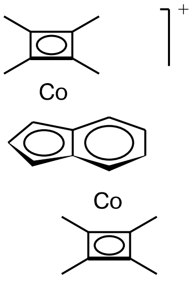
Slipped triple-decker complexes with the bridging indenyl ligand are represented only by the ruthenium complexes $[(C_5R_5)Ru(\mu,\eta^5:\eta^6\text{-}C_9H_7)Ru(C_5R'_5)]^+$,[1,2] which were prepared by the electrophilic stacking reaction of the indenyl complexes $(C_5R_5)Ru(\eta^5\text{-}C_9H_7)$ with the $[(C_5R_5)Ru]^+$ cations. The synthesis of cobalt-containing analogs was made possible with the use of the acetonitrile complex $[Cb^*Co(MeCN)_3]^+$ (Cb* = C_4Me_4) described recently.[3,4] The latter appears to be a convenient source of the Cb*Co fragment.

We prepared the η^5-indenyl complex $Cb^*Co(\eta^5\text{-}C_9H_7)$ (**1**) by the reaction of $[Cb^*Co(MeCN)_3]^+$ with lithium indenide.* The electrophilic stacking reaction of **1** with $[Cb^*Co(MeCN)_3]^+$ yielded the cationic triple-decker dicobalt complex $[Cb^*Co(\mu,\eta^5:\eta^6\text{-}C_9H_7)CoCb^*]^+$ (**2**). The cobalt ruthenium cation $[Cb^*Co(\mu,\eta^5:\eta^6\text{-}C_9H_7)RuCp^*]^+$ (**3**) was synthesized by the reaction of **1** with the acetonitrile complex $[Cp^*Ru(MeCN)_3]^+$.

The $[Cp^*Ru(\mu,\eta^5:\eta^6\text{-}C_9H_7)CoCb^*]^+$ cation (**4**) isomeric to cation **3** was prepared by the analogous reaction of the ruthenium indenyl complex $Cp^*Ru(\eta^5\text{-}C_9H_7)$ with $[Cb^*Co(MeCN)_3]^+$. In complex **3**, the cobalt atom is coordinated to the five-membered ring of the indenyl ligand, in contrast to **4**, where it is coordinated to the six-membered ring.

Triple-decker cations **2—4** were isolated as salts with the PF_6^- anion. These salts are air-stable for several hours. However, for prolonged storage, the salts should be kept under an inert atmosphere. The ^{1}H NMR spectra of cations **2—4** are similar to those of the diruthenium analogs $[(C_5R_5)Ru(\mu,\eta^5:\eta^6\text{-}C_9H_7)Ru(C_5R'_5)]^+$. The structure of one of diruthenium complexes has been established by X-ray diffraction.[2]

All reactions were carried out under argon using anhydrous solvents. The reaction products were isolated in air. The starting compounds **1**,* $Cp^*Ru(\eta^5\text{-}C_9H_7)$,[2] $[Cb^*Co(MeCN)_3]PF_6$,[3] and $[Cp^*Ru(MeCN)_3]PF_6$ [5] were prepared according to known procedures. The ^{1}H NMR spectra were recorded on a Bruker AMX-400 instrument (400.13 MHz).



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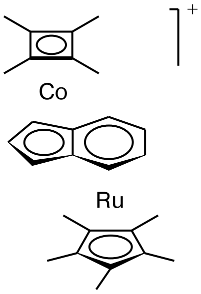

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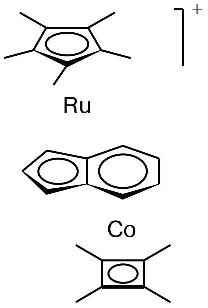

4

(μ,η^5:η^6-Indenyl)bis[(η-tetramethylcyclobutadiene)cobalt] hexafluorophosphate (2·PF$_6$). A mixture of compound **1** (56.5 mg, 0.2 mmol) and $[Cb^*Co(MeCN)_3]PF_6$ (69.6 mg, 0.16 mmol) in $MeNO_2$ (3 mL) was stirred for 24 h. The dark-red solution was concentrated to dryness. The residue was dissolved in CH_2Cl_2 (1 mL) and then diethyl ether (10 mL) was added. The dark-pink precipitate that formed was filtered off and twice reprecipitated with diethyl ether from CH_2Cl_2. The yield was 51.3 mg (54%). Found (%): C, 50.29; H, 5.18. $C_{25}H_{31}Co_2F_6P$. Calculated (%): C, 50.52; H, 5.26. ^{1}H NMR ($CDCl_3$), δ: 1.23 (s, 12 H, Cb*, η^5); 1.27 (s, 12 H, Cb*, η^6); 5.29 (d, 2 H, H(1), H(3), ^3J = 2.4 Hz); 5.32 (t, 1 H, H(2), ^3J = 2.4 Hz); 5.98 (m, 2 H, H(4), H(7)); 6.86 (m, 2 H, H(5), H(6)).**

(μ,η^5:η^6-Indenyl)[(η-tetramethylcyclobutadiene)cobalt][(η-pentamethylcyclopentadienyl)ruthenium] hexafluorophosphate (3·PF$_6$) was prepared analogously to **2**·PF$_6$ by the reaction of **1** (52.5 mg, 0.19 mmol) with $[Cp^*Ru(MeCN)_3]PF_6$ (85.7 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) as a red solid in a yield of

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* The results of this study will be published elsewhere.

** The H(4), H(7) and H(5), H(6) protons appear as multiplets characteristic of the A and B components of the AA´BB´ spin system.

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89.1 mg (79%). Found (%): C, 48.77; H, 5.17. $C_{27}H_{34}CoF_6PRu$. Calculated (%): C, 48.87; H, 5.16. ^{1}H NMR (CD_2Cl_2), δ: 1.27 (s, 12 H, Cb*, η^5); 1.65 (s, 15 H, Cp*, η^6); 5.04 (d, 2 H, H(1), H(3), ^3J = 2.4 Hz); 5.37 (m, 3 H, H(2), H(4), H(7)); 6.27 (m, 2 H, H(5), H(6)).*

(μ,η^5:η^6-Indenyl)][(η-pentamethylcyclopentadienyl)ruthenium][(η-tetramethylcyclobutadiene)cobalt] hexafluorophosphate (4 • PF_6) was prepared analogously to **2** • PF_6 by the reaction of Cp*Ru(η^5-C_9H_7) (56.2 mg, 0.16 mmol) with [Cb*Co(MeCN)$_3$]PF_6 (60.9 mg, 0.14 mmol) in $MeNO_2$ (3 mL) as a yellow solid in a yield of 50.1 mg (54%). Found (%): C, 48.93; H, 5.19. $C_{27}H_{34}CoF_6PRu$. Calculated (%): C, 48.87; H, 5.16. ^{1}H NMR (CD_2Cl_2), δ: 1.30 (s, 12 H, Cb*, η^6); 1.67 (s, 15 H, Cp*, η^5); 4.86 (t, 1 H, H(2), ^3J = 2.4 Hz); 5.00 (d, 2 H, H(1), H(3), ^3J = 2.4 Hz); 5.80 (m, 2 H, H(4), H(7)); 6.72 (m, 2 H, H(5), H(6)).*

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* The H(4), H(7) and H(5), H(6) protons appear as multiplets characteristic of the A and B components of the AA´BB´ spin system.

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