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Photochemical arene exchange in the (borole)cobalt complex [(η-C_4H_4BOH)Co(η-C_6H_6)]BF_4

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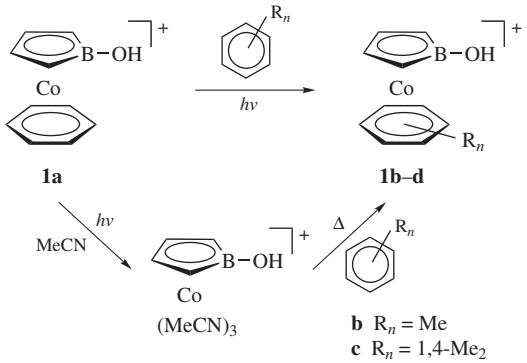
Visible-light irradiation of the cation [(η-C_4H_4BOH)Co(η-C_6H_6)]$^+$ in the presence of alkyl-substituted benzenes in CH_2Cl_2 results in arene exchange giving [(η-C_4H_4BOH)Co(η-C_6R_6)]$^+$ (C_6R_6 = toluene, *p*-xylene or mesitylene); the structure of [(η-C_4H_4BOH)Co(η-mesitylene)]BF_4 was confirmed by X-ray diffraction.

In 1980, Mann *et al.*[1] have found that the (cyclopentadienyl)iron complex [CpFe(η-C_6H_6)]$^+$ undergoes arene exchange under visible-light irradiation. It was a single example of photochemical arene exchange for a long time. Recently, we have demonstrated that other cationic arene complexes, [(η-cyclohexadienyl)Fe(η-C_6H_6)]$^+$,[2] [(η-1-Bu^{t}NH-1,8,10-$C_3B_8H_{10}$)Fe(η-C_6H_6)]$^+$,[3] [CpRu(η^6-$C_{10}H_8$)]$^+$,[4] and [(η-C_4Me_4)Co(η-C_6H_6)]$^+$,[5] react in a similar manner. In particular, easy replacement of benzene from the latter allowed us to synthesize various (tetramethylcyclobutadiene)cobalt complexes.[6] Cation [Co(η-C_4H_4BR)]$^+$ is isolobal with [Co(η-C_4Me_4)]$^+$, suggesting the ability of borole complexes [(η-C_4H_4BR)Co(η-C_6H_6)]$^+$ (ref. 7) to undergo photochemical arene exchange.

Indeed, visible-light irradiation of cation [(η-C_4H_4BOH)-Co(η-C_6H_6)]$^+$ **1a**† in the presence of toluene, *p*-xylene or mesitylene results in corresponding arene complexes **1b–d**‡ (Scheme 1). However, the rate of arene exchange is very low, and we were able to put it to the end only in the case of *p*-xylene.§ Analytically pure complexes **1b**,**d** were obtained by a two-step method, *viz.*, by irradiation of **1a** in acetonitrile with the subsequent reaction of the generated cation [(η-C_4H_4BOH)-Co(MeCN)$_3$]$^+$ with arenes.¶



Scheme 1

Arene exchange in the cyclobutadiene complex [(η-C_4Me_4)-Co(η-C_6H_6)]$^+$ can be induced both photochemically and thermally.[5(a)] However, borole analogue **1a** does not react with *p*-xylene in refluxing nitromethane.

Complexes [**1a–d**]BF_4 are yellow-orange air-stable solids. They were identified by ^{1}H and ^{11}B NMR spectroscopy. The structure of [**1d**]BF_4 was confirmed by X-ray diffraction (Figure 1).†† The borole ring is folded along the C(1)···C(4) line by 9.2°. This

† A solution of I_2 (127 mg, 0.5 mmol) in CH_2Cl_2 was added dropwise to a solution of complex [(η-C_4H_4BCy)Co(CO)$_2$]$_2$ (Cy = cyclohexyl) (261 mg, 0.5 mmol) in the same solvent (5 ml) cooled to –60 °C. The reaction mixture was allowed to warm to room temperature, and the solvent was removed *in vacuo*. The residue was extracted with light petroleum. The solvent was removed *in vacuo* giving complex (η-C_4H_4BCy)Co(CO)$_2$I as a black oil. Anhydrous $AlCl_3$ (1 g, 7.5 mmol) and benzene (10 ml) were added, and the reaction mixture was refluxed with vigorous stirring at 80 °C for 3 h, cooled to room temperature, and carefully hydrolyzed with ice water. The aqueous layer was separated and filtered. An aqueous $NaBF_4$ solution was added to the filtrate, and the product was extracted with $MeNO_2$ (3×3 ml). The solvent was removed *in vacuo*, and the residue was reprecipitated with diethyl ether from acetone. Complex [**1a**]BF_4 (122 mg, 40%) was obtained as an orange solid. ^{1}H NMR (acetone-d_6) δ: 7.09 (s, 1H, OH), 7.04 (s, 6H, C_6H_6), 6.11 (m, 2H, β-C_4H_4B), 4.17 (m, 2H, α-C_4H_4B). ^{11}B{^{1}H} NMR (acetone-d_6) δ: 27.47 (br. s, 1B, C_4H_4B), –0.81 (s, 1B, BF_4). Found (%): C, 39.31; H, 3.47. Calc. for $C_{10}H_{11}CoB_2F_4O$ (%): C, 39.54; H, 3.62.

‡ All the cationic complexes described here were isolated as salts with the BF_4^- anion.

§ *p*-Xylene (0.2 ml) was added to a solution of [**1a**]BF_4 (30 mg, 0.1 mmol) in CH_2Cl_2 (5 ml) in a Schlenk tube. The reaction mixture was irradiated using mercury luminescent lamps with a total power of 650 W for 35 h. Both the Schlenk tube and the lamps were placed into a vessel of an appropriate volume; cooling was accomplished by running water. The solvent was removed *in vacuo* and the residue was extracted with acetone. Precipitation with diethyl ether gives complex [**1c**]BF_4. Yield 27 mg (82%).

¶ A solution of [**1a**]BF_4 (30 mg, 0.1 mmol) in MeCN (3 ml) was irradiated for 5 h. The solvent was removed *in vacuo*, and an excess of toluene, *p*-xylene, or mesitylene (0.2 ml) in $MeNO_2$ (4 ml) was added. The reaction mixture was refluxed for 1 h. Then the solvent was removed *in vacuo*, and the residue was extracted with acetone. Precipitation with diethyl ether gives complexes [**1b–d**]BF_4 as yellow-orange solids.

[**1b**]BF_4: 65% yield. ^{1}H NMR (acetone-d_6) δ: 7.16 (s, 1H, OH), 6.93 (m, 5H, C_6H_5Me), 6.07 (m, 2H, β-C_4H_4B), 4.08 (m, 2H, α-C_4H_4B), 2.61 (s, 3H, C_6H_5Me). ^{11}B{^{1}H} NMR (acetone-d_6) δ: 26.87 (br. s, 1B, C_4H_4B), –0.95 (s, 1B, BF_4). Found (%): C, 41.11; H, 4.02. Calc. for $C_{11}H_{13}CoB_2F_4O$ (%): C, 41.57; H, 4.09.

[**1c**]BF_4: 70% yield. ^{1}H NMR (acetone-d_6) δ: 7.04 (s, 1H, OH), 6.83 (s, 4H, $C_6H_4Me_2$), 6.01 (m, 2H, β-C_4H_4B), 4.01 (m, 2H, α-C_4H_4B), 2.56 (s, 6H, $C_6H_4Me_2$). ^{11}B{^{1}H} NMR (acetone-d_6) δ: 26.91 (br. s, 1B, C_4H_4B), –0.91 (s, 1B, BF_4). Found (%): C, 43.01; H, 4.46. Calc. for $C_{12}H_{15}CoB_2F_4O$ (%): C, 43.44; H, 4.52.

[**1d**]BF_4: 75% yield. ^{1}H NMR (acetone-d_6) δ: 7.12 (s, 1H, OH), 6.69 (s, 3H, $C_6H_3Me_3$), 5.86 (m, 2H, β-C_4H_4B), 3.81 (m, 2H, α-C_4H_4B), 2.59 (s, 9H, $C_6H_3Me_3$). ^{11}B{^{1}H} NMR (acetone-d_6) δ: 26.95 (br. s, 1B, C_4H_4B), –0.87 (s, 1B, BF_4). Found (%): C, 44.93; H, 4.87. Calc. for $C_{13}H_{17}CoB_2F_4O$ (%): C, 45.15; H, 4.92.

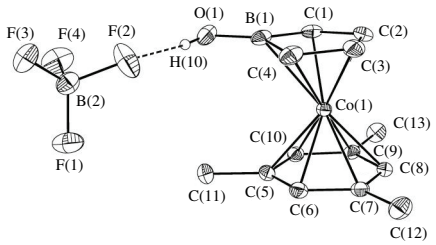


Figure 1 Structure of complex [**1d**]BF_4. Ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Co(1)–B(1) 2.263(2), Co(1)–C(1) 2.066(2), Co(1)–C(2) 2.007(2), Co(1)–C(3) 2.009(1), Co(1)–C(4) 2.077(2), Co(1)–C(5) 2.115(1), Co(1)–C(6) 2.082(1), Co(1)–C(7) 2.122(2), Co(1)–C(8) 2.126(1), Co(1)–C(9) 2.111(1), Co(1)–C(10) 2.093(1), C(1)–C(2) 1.419(2), C(2)–C(3) 1.424(2), C(3)–C(4) 1.417(2), C(1)–B(1) 1.547(2), C(4)–B(1) 1.552(2), B(1)–O(1) 1.363(2).

value is close to that for [**1a**]BPh_4 (10.3°).[7] The folding of the borole ring is a typical feature of the borole complexes.[8] For example, the folding angles for sandwich complexes with B-methyl and phenyl-substituted borole ligands are 2–6°,[9,10] while for compound $CpCo(\eta\text{-}C_4H_2Pr^i_2BNPr^i_2)$ this angle achieves 9.2° owing to B–N conjugation.[11] Similarly, the large angle for [**1d**]BF_4 is caused by B–O conjugation. There is a short distance between the hydrogen atom of the OH group and one fluorine atom of the anion BF_4^- [H(10)···F(2) 1.884, O(1)···F(2) 2.671 Å], suggesting the presence of hydrogen bond O(1)–H(10)···F(2). This is also confirmed by an IR low-frequency shift of the ν(O–H) band in [**1d**]BF_4 (3477 cm^{-1}) relative to that in the tetraphenylborate salt $[(\eta\text{-}C_4H_4BOH)Co(m\text{-xylene})]BPh_4$ (3548 cm^{-1}).

Thus, the benzene complex $[(\eta\text{-}C_4H_4BOH)Co(\eta\text{-}C_6H_6)]^+$ undergoes arene exchange under visible-light irradiation making it a convenient synthon of the cationic species $[Co(\eta\text{-}C_4H_4BOH)]^+$.

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†† Crystals of [**1d**]BF_4 were grown up by slow diffusion in two-layer system, light petroleum and a solution of the complex in CH_2Cl_2. Crystal data: $C_{13}H_{17}B_2CoF_4O$, orthorhombic, space group $P2_12_12_1$, a = 7.1374(5), b = 14.1202(11) and c = 14.1906(11) Å, V = 1430.15(19) Å^3, Z = 4, d_{calc} = 1.606 g cm^{-3}, μ = 1.237 mm^{-1}, crystal size 0.45×0.35×0.20 mm. X-ray diffraction experiment was carried out with a Bruker SMART APEX2 CCD area detector, using graphite monochromated MoKα radiation (λ = 0.71073 Å, $2\theta_{max}$ = 58°) at 100 K. The absorption correction was applied semi-empirically using SADABS program (T_{max}/T_{min} = 0.786/0.604). The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in anisotropic approximation for non-hydrogen atoms. All hydrogen atoms were refined in isotropic approximation in riding model with the U_{iso}(H) parameters equal to $1.2U_{eq}(C_i)$ or $1.5U_{eq}(C_{ii})$, where $U(C_i)$ and $U(C_{ii})$ are respectively the equivalent thermal parameters of the methyne and methyl carbon atoms to which the corresponding H atoms are bonded. The refinement converged to wR_2 = 0.0491 and GOF = 0.998 for all independent reflections [R_1 = 0.0215 was calculated against F for 3533 observed reflections with $I > 2\sigma(I)$].

CCDC 789929 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.