

Reactions of Cobaltocenes with Some Alkyldihaloboranes, Aryldihaloboranes and Alkylating Reagents

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A series of cobalt π -complexes containing borinato and boracyclohexa-2,4-diene ligands, viz. cyclopentadienyl[1-(2',4',6'-trimethylphenyl)borinato]cobalt (*1d*), bis(1-benzylborinato)cobalt (*2c*), cyclopentadienyl(1-benzylborinato)cobalticinium cation (*3c*), cyclopentadienyl[1-(2',4',6'-trimethylphenyl)borinato]cobalticinium cation (*3d*) and cyclopentadienyl[1-(2',4',6'-trimethylphenyl)boracyclohexa-2,4-diene]cobalt (*4d*) have been synthesized from benzylidibromoborane or dichloro(2,4,6-trimethylphenyl)borane and cobaltocene through a ring expansion reaction. In alkylation reactions 1,1'-dimethylcobaltocene was found to react stereoselectively with 2-cyanoazopropane and 2-bromo-2-phenylpropane to give (methylcyclopentadienyl)[2-methyl-5-exo(1'-cyano-1'-methyl)ethyl]cyclopentadiene]cobalt (*5e*) and (methylcyclopentadienyl)[2-methyl-5-exo(1'-methyl-1'-phenylethyl)cyclopentadiene]cobalt (*5f*), respectively. In the latter reaction 2,3-dimethyl-2,3-diphenylbutane was obtained as a by-product which supports a radical mechanism for the reaction.

Cobaltocene has been found^{1,2} to react with dihalomethyl- and dihalophenylboranes to give cobalt complexes of 1-methylborinate and 1-

phenylborinate ions (*1-3*, *a* and *b*) (Fig. 1). The reaction has now been extended to other alkyl- and aryldihaloboranes. Cobaltocene and benzylidibromoborane gave bis(1-benzylborinato)cobalt (*2c*) and cyclopentadienyl(1-benzylborinato)cobalticinium cation (*3c*) (Scheme 1) but dichloropentafluorophenylborane gave only decomposition products. Dichloro(2,4,6-trimethylphenyl)borane gave in addition to cyclopentadienyl[1-(2',4',6'-trimethylphenyl)borinato]cobalt (*1d*) also the diamagnetic cyclopentadienyl[1-(2',4',6'-trimethylphenyl)boracyclohexa-2,4-diene]cobalt (*4d*) (Scheme 2). The compound *4d* is probably formed by nucleophilic addition of a hydride ion to *3d* (cf. Ref. 2).

The ¹H NMR spectra of the compound *4d* are fully consistent with the proposed structure also in spin-spin decoupling experiments. The ¹¹B NMR spectrum verifies that the three-coordinated boron atom lies in the plane of the π electron system of the hetero ligand. In a structure with three-coordinated boron out of plane of the π electron system the empty *p*_z-orbital of the *sp*²-hybridized boron atom overlaps only to a limited extent with the π electron system, and a resonance at

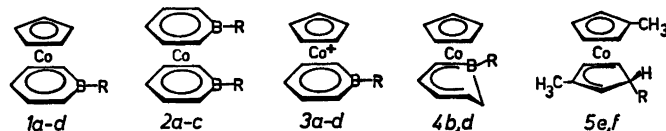
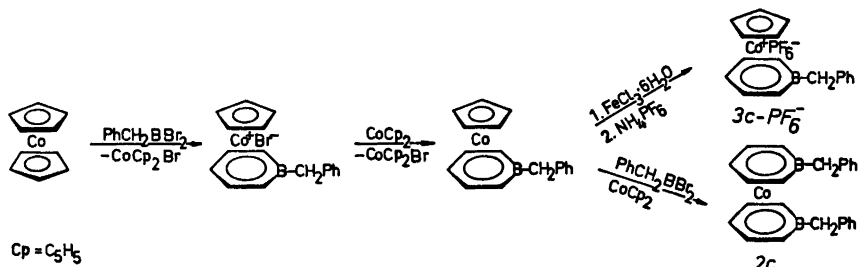
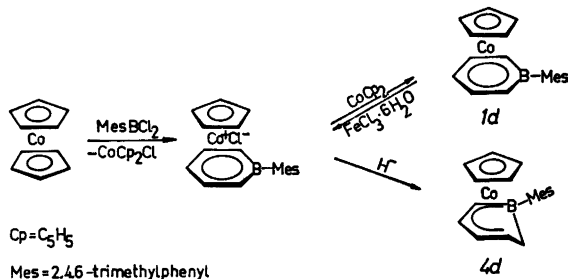


Fig. 1. *a*, R = CH₃; *b*, R = C₆H₅; *c*, R = C₆H₅CH₂; *d*, R = 2,4,6-trimethylphenyl; *e*, R = (CH₃)₂C—CN; *f*, R = (CH₃)₂C—C₆H₅.



Scheme 1.



Scheme 2.

$\delta = -50$ to -60 ppm (relative to external trifluoroborane etherate) would be expected^{1,2} which is not in agreement with the value $\delta = -33$ ppm obtained. Compound **4d** is unexpectedly stable towards heat and oxidation, in contrast to **4b** which is very thermolabile and air-sensitive.³ No decomposition was observed after exposing to air for even more than two days.

Reaction of bisindenylcobalt with dichlorophenylborane and dibromomethylborane gave not the desired boranaphthalene anion complexes but bisindenylcobalticenium cation and decomposition products.

1,1'-Dimethylcobaltocene reacted with 2-cyanoazopropane and 2-bromo-2-phenylpropane under strong steric control giving isomerically pure (methylcyclopentadienyl)(2-methyl-5-exo-alkylcyclopentadiene)cobalt compounds (**5e,f**). In the reaction with 2-bromo-2-phenylpropane, 2,3-dimethyl-2,3-diphenylbutane was obtained as a by-product, which supports a radical mechanism⁶ proposed for this type of reaction.

EXPERIMENTAL

Air and moisture were excluded rigorously by the use of Schlenk techniques, unless otherwise stated. Dry, oxygen-free nitrogen was used as a protective gas.

¹H NMR spectra were recorded at room temperature at 60, 100 or 270 MHz. ¹¹B NMR spectra were recorded at room temperature at 19 MHz with trifluoroborane etherate as an internal standard. The MS spectra were taken with a one-focusing Atlas-CH-5 mass spectrometer at 70 eV.

Bis(1-benzylborinato)cobalt (2c). A solution of 2.07 g (10.9 mmol) of benzyldibromoborane^{7,8} in ca. 10 ml of toluene was added to a solution of 3.28 g (12.5 mmol) of cobaltocene in 50 ml of toluene at room temperature during 15 min (cf. Ref 2). A yellow-green precipitate was formed immediately. After stirring at room temperature for 5 h the precipitate containing cobalticenium bromide and **3c-Br⁻** was filtered off and washed with two 10 ml portions of toluene. The dark red opaque solution was concentrated to 10 ml at 10 Pa without heating. Pentane (120 ml) was added to the remaining solution. After 1 h at -78°C the solvent was decanted off from the precipitate obtained. This was dissolved in 20 ml of toluene and the solution was filtered through a 1 cm thick layer of alumina (neutral, deactivated with 7% water). The deep red filtrate was evaporated to dryness without warming at 7 Pa, leaving 0.41 g of a deep brown solid. This residue was dissolved in 10 ml of toluene. After adding 30 ml of pentane and cooling to -30°C big dark red crystals and a small amount of light pale crystals were obtained. The latter was easily decanted off with the mother liquor. The dark red product was isolated after washing twice with cooled pentane and recrystallization from pentane. Yield 0.20 g. M.p. 150–150.5

°C (stable to at least 370 °C). Anal. $C_{22}H_{24}B_2Co$ (393.0): C, H. The product could also be purified by column chromatography on alumina (neutral, oxygen-free, deactivated with 4 % water) by eluting with increasing amounts of toluene in pentane followed by sublimation *in vacuo*.

MS [IP 70 eV; *m/e* (% rel. int.)]: 393 (100, M), 291 (6, $[C_5H_5CoC_5H_5BCH_2C_5H_5]$), 226 (28, $[CoC_5H_5BCH_2C_5H_5]$), 200 (5, $[C_5H_5BCoC_5H_5]$), 150 (10, $[CoC_5H_5BCH_3]$), 135 (14, $[C_5H_5BCo]$), 124 (9, $[C_5H_5Co]$), 91 (18, $[C_7H_7]$).

Cyclopentadienyl(1-benzylborinato)cobalticenium hexafluorophosphate ($3c-PF_6^-$). I. Water was added without exclusion of air to the yellow-green precipitate earlier obtained. A tarry product was filtered off and the filtrate was treated with an excess of ammonium phosphate in water (*cf.* Ref. 2). The product obtained (2.40 g) consisted of cobalticenium hexafluorophosphate and a small amount of $3c-PF_6^-$. The latter compound was concentrated to ca. 75 mol % by dredging the product in 5 ml of chloroform and then evaporating the solvent.

II. Cobaltocene (3.96 g, 20.9 mmol) and 2.19 g (83.7 mmol) of benzyltribromoborane were reacted as described earlier and the yellow-green precipitate filtered off. The red filtrate was oxidized with iron(III) chloride hexahydrate and the pale red solution obtained was treated with ammonium hexafluorophosphate (*cf.* Ref. 2). The product obtained (2.85 g) consisted of cobalticenium hexafluorophosphate and $3c-PF_6^-$ in the molar ratio of 3:1 according to 1H NMR analysis. The product was dissolved in 20 ml of acetone and 15 ml of water was added. A red-brown precipitate was obtained, which, after cooling to 0 °C, was filtered off and washed with pentane. Compound $3c-PF_6^-$ (0.39 g) free from cobalticenium hexafluorophosphate was isolated according to 1H NMR analysis. Another recrystallization was performed from acetone/diethyl ether. Anal. $C_{17}H_{17}BCoF_6P$ (463.03): C, H.

1H NMR (60 MHz, CD_3CN): δ 2.87 (2 H, s, $-CH_2-$), 5.53 (2 H, dd, H_2 and H_3 , $J_{H_2-H_3}$, 2 Hz, $J_{H_2-H_4}$, 9 Hz), 5.70 (5 H, s, C_5H_5), 6.7 (3 H, m, H_3-H_5), 7.36 (5 H, s, C_6H_5).

Cyclopentadienyl[1-(2',4',6'-trimethylphenyl)boracyclohexa-2,4-diene]cobalt (4d). A solution of 2.60 g (12.9 mmol) of dichloro(2,4,6-trimethylphenyl)borane⁹⁻¹⁰ in 45 ml of toluene was added to a solution of 1.71 g (9.0 mmol) of cobaltocene in 45 ml of toluene during half an hour at room temperature. A precipitate was obtained immediately and the solution became dark red. The mixture was stirred for a further 17 h at room temperature. The precipitate (2.39 g) was isolated and treated with ammonium hexafluorophosphate as described earlier giving 1.80 g of salt consisting of cobalticenium hexafluorophosphate containing ca. 2 mol % of cyclopentadienyl[1-(2',4',6'-trimethylphenyl)borinato]cobalticenium hexafluorophosphate ($3d-PF_6^-$) according to 1H NMR analysis.

The dark-red filtrate was cooled to 0 °C and extracted with three 10 ml portions of cooled water, two 5 ml portions of cooled 2 M sodium hydroxide and with water to neutral reaction. After filtering the solution through a 1 cm layer of alumina (neutral, oxygen-free, deactivated with 4 % water), the solvent was stripped off at 0.13 Pa without warming leaving 0.75 g of a dark red oil.

The product was chromatographed on a 67×1.6 cm column of alumina (neutral, oxygen-free, deactivated with 4 % of water) by eluting with pentane. Three distinct zones were obtained, a very faint yellow one at the top, a broad red one in the middle (zone II) and a broad brown-red one (zone I) at the bottom of the column. Zone I was eluted with 1500 ml of pentane leaving 0.15 g of a dark red crystalline product with m.p. 70 °C after evaporating the solvent. Crystallization from 4 ml of pentane at -80 °C gave 0.13 g of 4d with m.p. 92–93 °C (stable to at least 280 °C). The product sublimed without residue of sublimation at 0.13 Pa and 80 °C as an oil which slowly crystallized out. Anal. $C_{19}H_{22}BCo$ (320.1): C, H.

MS [IP 70 eV; *m/e* (% rel. int.)]: 320 (47, [M]), 319 (36, [M-H]), 254 (6, [M- C_5H_5]), 201 (22, [M-(CH_3) $_3C_5H_2$]), 200 (100, $[C_5H_5CoC_5H_5B]$), 174 (13, $[C_5H_5CoC_5H_5B]$), 124 (15, $[C_5H_5Co]$), 119 (7, $[C_5H_{11}]$).

1H NMR (270 MHz, $C_2Cl_4:C_6D_6$, 3:1): δ 0.24 (1 H, d, H_{exo}), 1.40 (1 H, dd, H_{endo}), 2.14 (3 H, s, *p*-Me), 2.59 (6 H, s, *o*-Me), 2.88 (1 H, d, H_2), 2.94 (1 H, t, H_5), 4.47 (5 H, s, C_5H_5), 4.72 (1 H, dd, H_4), 6.21 (1 H, dd, H_3), 6.74 (2 H, s, $H_{3'}$ and $H_{5'}$). $J_{H_2-H_3}$, 7.1 Hz, $J_{H_2-H_4}$, 4.9 Hz, $J_{H_2-H_5}$, 6.2 Hz, $J_{H_3-H_4}$, 7.0 Hz, $J_{endo-exo}$, 17.0 Hz.

Cyclopentadienyl[1-(2',4',6'-trimethylphenyl)borinato]cobalt (1d). Zone II. The material above zone II in the column was sucked off and zone II was eluted with pentane containing increasing amounts of toluene (1–6 %). The eluate (750 ml) was evaporated to dryness at 0.13 Pa at room temperature. A deep red semi-solid remained (0.50 g) which slowly crystallized from pentane to give 0.40 g of 1d in red-black crystals, m.p. 65–66 °C. Upon sublimation at 100 °C and 0.13 Pa, 1d was obtained as an oil which slowly crystallized. Anal. $C_{19}H_{21}BCo$ (319.1): C, H.

MS [IP 70 eV; *m/e* (% rel. int.)]: 319 (100, [M]), 253 (9, [M- C_5H_5]), 251 (32, [M- C_5H_5]), 223 (11, [M- C_5H_4]), 189 (98, $[C_5H_5CoC_5H_5B]$), 187 (13, $[C_5H_5CoC_5H_5B]$), 136 (17, $[CoC_5H_5BH]$), 124 (50, $[C_5H_5Co]$), 65 (39, $[C_5H_5]$), 63 (20, $[C_4H_4B]$).

Cyclopentadienyl[1-(2',4',6'-trimethylphenyl)borinato]cobalticenium hexafluorophosphate ($3d-PF_6^-$) was prepared from 0.20 g (0.6 mmol) of 1d as reddish-brown glistening plates. Yield 0.10 g (34 %). Anal. $C_{19}H_{21}BCoPF_6$ (464.1): C, H.

1H NMR (60 MHz, CD_3CN): δ 2.36 (6 H, s, *o*- CH_3), 5.86 (5 H, s, C_5H_5), 5.64 (2 H, dd,

H₂ and H₆), 6.7 (3 H, m, H₃-H₆), 6.90 (2 H, s, m-H), $J_{H_1-H_2}$ 2 Hz, $J_{H_1-H_6}$ 9.0 Hz.

(Methylcyclopentadienyl)[2-methyl-5-*exo*(1'-cyano-1'-methylene)cyclopentadiene]cobalt (5e). 2-Cyanoazopropane (0.59 g, 3.6 mmol) and 1.15 g (5.3 mmol) of 1,1'-dimethylcobaltocene were reacted as described earlier for cobaltocene.⁴ Unreacted 1,1'-dimethylcobaltocene was removed by filtering through a layer of copper(1) chloride. The product obtained was sublimed at 70 °C and 0.13 Pa. 2,3-Dicyano-2,3-dimethylbutane formed as a by-product was crystallized from pentane at -80 °C. After stripping off the solvent 5e was obtained as a red oil free from its isomers and free from 2,3-dicyano-2,3-dimethylbutane according to ¹H NMR analysis. The compound 5e decomposed when chromatographed on alumina (neutral, oxygen-free, deactivated with 7% water) or on silica gel with pentane as the elute.

¹H NMR (60 MHz, C₆D₆): δ 0.62 (6 H, s, gem-CH₃), 1.60 and 2.01 (6 H, two s, CH₃ on the rings), 2.41 (2 H, m, H₁ and H₄), 2.55 (1 H, tr., H₅), 4.3 (4 H, m, Cp-protons), 4.90 (1 H, tr., H₂).

(Methylcyclopentadienyl)[2-methyl-5-*exo*(1'-methyl-1'-phenylethyl)cyclopentadiene]cobalt (5f). 2-Bromo-2-phenylpropane (1.15 g, 5.8 mmol) was reacted with 3.72 g (17 mmol) of 1,1'-dimethylcobaltocene in 180 ml of benzene analogous to Ref. 6. The red oil obtained was sublimed and the sublimate dissolved in pentane. 2,3-Dimethyl-2,3-diphenylbutane crystallized out from the solution at -80 °C. Compound 5f (ca. 1.0 g, 50%) was obtained from the mother liquor free from its isomers according to ¹H NMR analysis.

¹H NMR (60 MHz, C₂Cl₄): δ 0.85 (6 H, s, gem-CH₃), 1.74 and 1.95 (6 H, two s, CH₃ on the rings), 2.3 (2 H, m, H₁ and H₄), 2.77 (1 H, tr., H₅), 4.3 (4 H, m, Cp-protons), 4.75 (1 H, tr., H₃), 7.04 (5 H, s, C₆H₅).

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