Bis(boryl)metallocenes. 1. 1,1′-Bis(diisopropylboryl)cobaltocenium Cation: A Novel Anion-Binding Ligand

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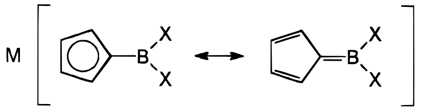
*Summary: Three situations are observed when the new cobaltocene derivative $Co(C_5H_4BPr^{i}_{2})_2$ (**2**) is oxidized. The cobaltocenium salt [**2**]PF_6 (**3**) is obtained with $[FeCp_2]PF_6$ as oxidant. With $Cu(OH)_2$ the inverse chelate [**2**]OH (**4**) with a μ-OH group bridging the two boron centers is formed. Oxidation with C_2Cl_6 gives a zwitterionic chloride (**5**) with a trigonal and a quaternized boron center; in solution **5** is fluxional.*

Anion binding or anion recognition may be effected by hydrogen bonding, through polar bonds with Lewis-acidic centers, or by the electrostatic attraction of cationic centers; often these act in combination.[1] Several systems with two boron centers are known which are able to act as molecular pincers, thereby binding anions in inverse chelates.[2] For instance, Katz et al. have shown that 1,8-bis(boryl)naphthalenes bind H^-, F^-, OH^-, and Cl^-; in each case the anion bridges the two boron atoms.[2c−e] In this communication we give the first account of a novel, cationic molecular pincer, a bis(boryl)cobaltocenium ion which displays a remarkable variability in its interactions with anions.

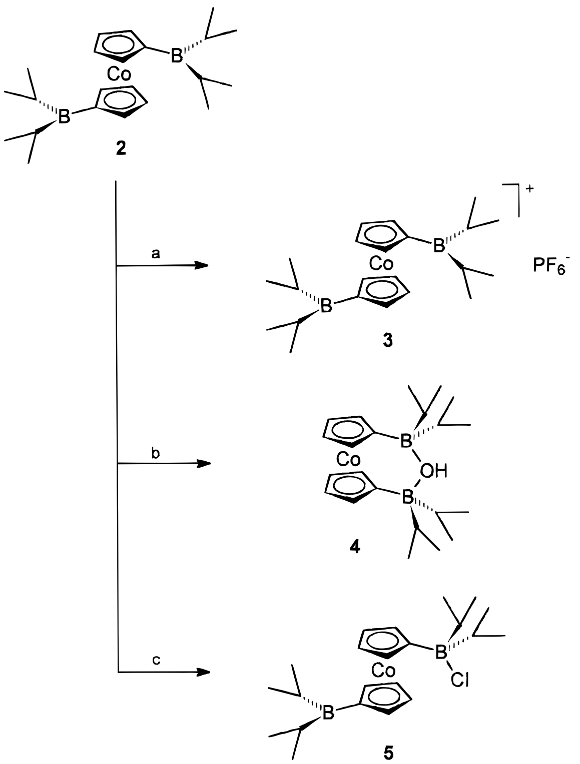
We have recently described the alkali-metal borylcyclopentadienides $M(C_5H_4BX_2)$ (**1**; M = Li, Na).[3] These new reagents allow the direct synthesis of boryl-substituted cyclopentadienyl complexes. In many cases boryl functionalities can be introduced by electrophilic aromatic substitution with boron trihalides, and the dibromoborylation of ferrocene is a pertinent example.[4] In other cases, as, for example, Cp_2TiCl_2 or $NiCp_2$, where the borylation reaction does not work, our new reagents offer a synthetic alternative to be tested.



1, M = Li or Na

a, X = Me; **b**, X = Pr^i; **c**, X = NMe_2; **d**, 2 X = $OCMe_2CMe_2O$

Scheme 1[a]



[a] Legend: (a) $[FeCp_2]$ in CH_2Cl_2; (b) $Cu(OH)_2$ in toluene; (c) C_2Cl_6 in toluene.

In this vein, treatment of $CoBr_2 \cdot DME$ with **1b** afforded the purple, paramagnetic cobaltocene derivative $Co(C_5H_4BPr^{i}_{2})_2$ (**2**).[5] Oxidation to give the cation $\mathbf{2}^+$ is seemingly trivial, but three different situations materialize experimentally (Scheme 1).

Oxidation with $[FeCp_2]PF_6$ in CH_2Cl_2 gives the yellow, diamagnetic hexafluorophosphate **3**.[6] The crystal structure of **3** is that of a salt without specific interactions between the B atom and the anion (Figure 1).[7] In solution the boron resonance for **3** is found at $\delta(^{11}B)$ 79, in the range expected for a dialkylarylborane.[8] Furthermore, in the ^1H NMR spectrum, a single doublet is seen for the methyl groups, which consequently are chemically equivalent. Again, there is no specific

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[1] (a) Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Bruening, R. L. *Chem. Rev.* **1995**, *95*, 2529. (b) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, 1995; Chapter 3. (c) Kaufmann, D. E.; Otten, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1832. (d) Yang, X.; Knobler, C. B.; Zheng, Z.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1994**, *116*, 7142 and literature quoted therein.

[2] (a) Biallas, M. J. *J. Am. Chem. Soc.* **1969**, *91*, 7290. (b) Saturnino, D. J.; Yamauchi, M.; Clayton, W. R.; Nelson, R. W.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 6063. (c) Katz, H. E. *J. Am. Chem. Soc.* **1985**, *107*, 1420. (d) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 5027. (e) Katz, H. E. *Organometallics* **1987**, *6*, 1134. (f) Köster, R.; Seidel, G. *Chem. Ber.* **1992**, *125*, 627. (g) Köster, R.; Seidel, G.; Wagner, K.; Wrackmeyer, B. *Chem. Ber.* **1993**, *126*, 305. (h) Cf. also: Jäkle, F.; Mattner, M.; Priermeier, T.; Wagner, M. *J. Organomet. Chem.* **1995**, *502*. 123.

[3] Herberich, G. E.; Fischer, A. *Organometallics* **1996**, *15*, 58.

[4] (a) Ruf, W.; Renk, T.; Siebert, W. *Z. Naturforsch.* **1976**, *31B*, 1028. (b) Appel, A.; Jäkle, F.; Priermeier, T.; Schmid, R.; Wagner, M. *Organometallics* **1996**, *15*, 1188 and literature quoted therein.

[5] Preparation of **2**: Cyclopentadienyldiisopropylborane (29.7 g, 0.183 mol) was added with stirring to LiCp (11.4 g, 0.158 mol) in THF (300 mL) at ambient temperature; stirring was continued for 70 h.[3] $CoBr_2 \cdot 1.18DME$ (25.8 g, 0.080 mol, DME content determined by elemental analysis) was added at −78 °C. The reaction mixture was warmed to ambient temperature. Careful removal of all volatiles under vacuum, suspension of the residue in hexane (150 mL), filtration with the help of Kieselgur, and washing with hexane (4 × 20 mL) gave a purple product solution. This was then concentrated to 20 mL and kept at −30 °C to give **2** (29.78 g, 98%) as somewhat sticky crystals; mp 68−70 °C. MS (EI): *m/z* (I_{rel}) 381 (61, M^+), 213 (100, $M^+ - 4\ C_3H_6$).

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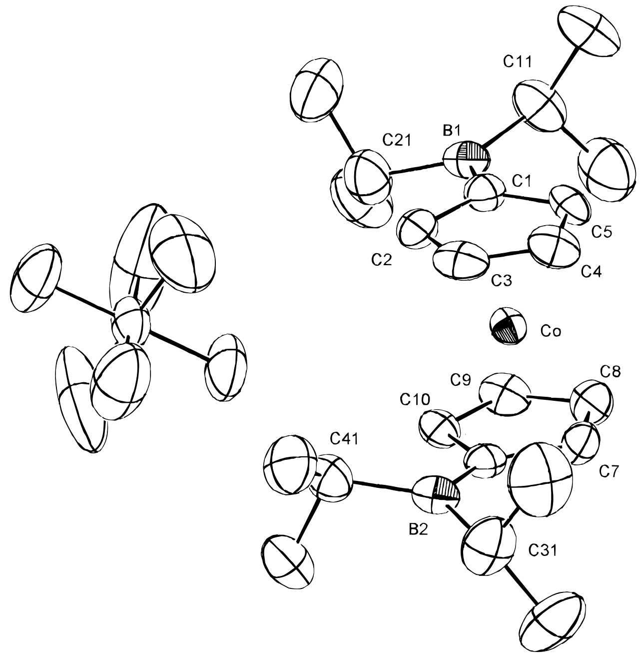

Figure 1. ORTEP plot of **3** (at the 30% probability level). Bond distances (pm): Co−C(ring), 201.6(3)−204.8(3); Co···B1, 315.1(3); Co···B2, 315.3(3); C−C(ring), 140.6(5)−144.4(4); C1−B1, 156.1(5); C11−B1, 156.4(5); C21−B1, 157.7(5); C6−B2, 158.1(4); C31−B2, 156.0(5); C41−B2, 158.2(5). Distances from the ring plane (pm): 15.6(5) for B1, 15.0(5) pm for B2, both towards the metal. Bond angles (deg): C1−B1−C11, 121.7(2); C1−B1−C21, 116.3(2); C11−B1−C21, 121.8(3); C6−B2−C31, 121.6(4); C6−B2−C41, 116.3(2); C31−B2−C41, 122.1(3).

interaction between the B atom and the anion. Nevertheless, cation $\mathbf{2}^+$ is a strong Lewis acid. It forms 1/1 and 1/2 adducts with pyridine and polymerizes THF at ambient temperature.

Upon oxidation of **2** with $Cu(OH)_2$ in toluene the soluble, deep yellow complex **4** is formed.[9] The X-ray crystal structure determination[10] (Figure 2) reveals a molecular structure with a bridging μ-OH group between two B atoms; in other words, $\mathbf{2}^+$ forms an *inverse chelate* with OH^-. The boron resonance at $\delta(^{11}B)$ 0 lies in the range expected for tetracovalent boron, and a pair of diastereotopic methyl groups is seen in the ^1H NMR spectrum. Thus, the same inverse chelate structure prevails in solution.

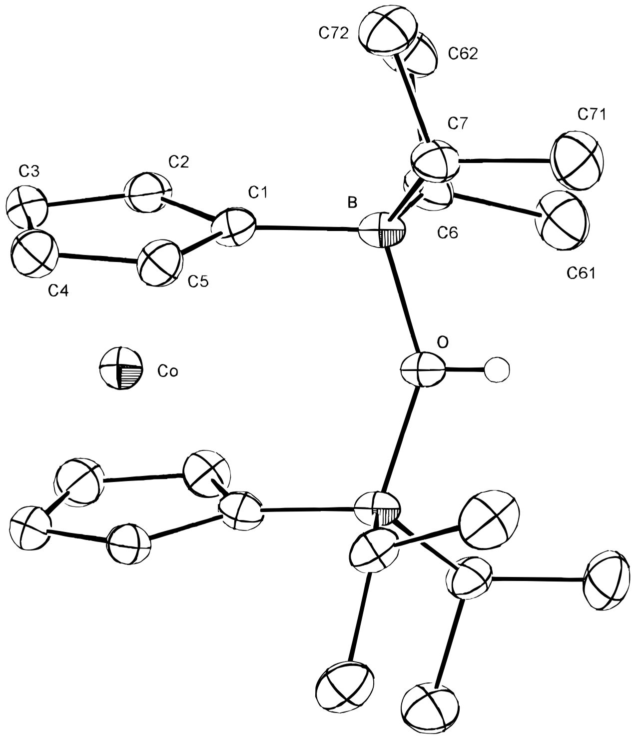

Figure 2. ORTEP plot of **4** (at the 30% probability level). The molecule possesses crystallographic C_2 symmetry with the Co and O atoms lying on the symmetry axis. Bond distances (pm): Co−C1, 203.8(5); Co−C2, 201.2(5); Co−C3, 204.0(5); Co−C4, 204.1(5); Co−C5, 201.1(5); Co···B, 325.5(5); Co···O, 335.8(5); C−C(ring), 140.7(6)−142.8(6); C1−B, 162.8(7); B−C6, 164.4(7); B−C7, 163.2(8); B−O, 160.5(6). Distance from the ring plane for B: 5.5(7) pm toward the metal. Bond angles (deg): B−O−B′, 144.8(5); O−B−C1, 107.2(4); O−B−C6, 103.9(4); O−B−C7, 106.3(4); C1−B−C6, 107.3(4); C1−B−C7, 111.1(4); C6−B−C7, 120.2(4).

Oxidation of **2** with C_2Cl_6 (or less smoothly with CuCl) affords the deep yellow chloride **5**.[11] In the crystal one B atom is trigonal and the other is tetracoordinate with a rather long B−Cl bond (Figure 3).[12] In solution one would expect to see two boron resonances and two different $C_5H_4BPr^i_2$ ligands with three different methyl groups (4/2/2) in the respective NMR spectra. Experimentally a single boron resonance is observed at $\delta(^{11}B)$ 40, corresponding to a mean chemical shift for tricoor-

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[6] Preparation of **3**: $[FeCp_2]PF_6$ (2.95 g, 8.92 mmol) in CH_2Cl_2 was added to a solution of **2** (3.41 g, 8.96 mmol) in CH_2Cl_2 (50 mL). After careful removal of the solvent, the residue was suspended in hexane to dissolve the ferrocene formed, collected on a frit, and washed several times with hexane to give **3** (3.94 g, 84%) as a highly sensitive, greenish yellow powder. Recrystallization from CH_2Cl_2 at −30 °C gave yellow crystals; mp 137−139 °C. MS (SIMS): m/z (I_{rel}) 381 (100, M^+) from cation spectrum, 145 (100, PF_6^-) from anion spectrum. ^1H NMR (500 MHz, CD_3NO_2) for C_5H_4 δ 6.00 (m, 8H), for BPr^i_2 δ 2.03 (sept, J = 7.3 Hz, 4 BCH), 1.16 (d, J = 7.3 Hz, 8 Me). ^{11}B NMR (160 MHz, CD_3NO_2): δ 79. $^{13}C\{^1H\}$ NMR (63 MHz, CD_3NO_2): for C_5H_4 δ 91.4, 89.7, signal of C-1 not observed; for BPr^i_2 δ 24.3 (br, BCH) and 18.7 (Me). ^{19}F NMR (470 MHz, CD_3NO_2): δ −73.90 (d, J = 707 Hz). ^{31}P NMR (202 MHz, CD_3NO_2): δ −145.05 (sept, J = 707 Hz).

[7] Crystal data for **3**: yellow crystals, 0.6 × 0.6 × 0.4 mm, monoclinic, $a = 840.0(2)$ pm, $b = 2189.9(7)$ pm, $c = 1404.2(4)$ pm, $\beta = 96.67(2)°$, $V = 2.565(2)$ nm^3, $Z = 4$, space group $P2_1/c$ (No. 14), $d_{calc} = 1.359$ g cm^{-3}, $\mu = 7.76$ cm^{-1}, $F(000) = 1096.0$. Data collection: ENRAF-Nonius CAD4, Mo Kα radiation, graphite monochromator, ω scan ($3 < \theta < 25°$) at 243 K; 5055 reflections measured, 3595 unique reflections with $I > 1.5\sigma(I)$, no absorption correction applied. Solution and refinement:[15] 434 parameters, $R = 0.054$, $R_w = 0.070$, $w^{-1} = \sigma^2(F_o)$, GOF = 2.09; non-hydrogen atoms were refined anisotropically and all hydrogen atoms were refined isotropically; PF_6^- disordered.[16]

[8] For reference data see: (a) Nöth, H.; Wrackmeyer, B. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, 1978; Vol. 14. (b) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61. (c) Siedle, A. R. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 205.

[9] Preparation of **4**: A solution of **2** (440 mg, 1.16 mmol) in toluene (6 mL) was stirred with $Cu(OH)_2$ (57 mg, 0.58 mmol) for 10 min. Filtration and crystallization from toluene gave **4** (355 mg, 77%) as deep yellow microcrystals mp 131 °C dec. MS (SIMS): m/z (I_{rel}) 398 (100, M^+). ^1H NMR (300 MHz, C_6D_6): for C_5H_4 δ 4.79 (m, 4H), 4.18 (m, 4H); for BPr^i_2 δ 1.09 (sept, J = 7.0 Hz, 4 BCH), 1.40 (d, J = 7.0 Hz, 4 Me), 1.20 (d, J = 7.0 Hz, 4 Me); for OH δ 2.61. ^{11}B NMR (29 MHz, $CDCl_3$): δ 0. $^{13}C\{^1H\}$ NMR (67.9 MHz, C_6D_6): for C_5H_4 δ 111 (s, br, C-1), 87.8, 82.1; for BPr^i_2 δ 22.6 (Me) and 21.8 (Me), signal for BCH very broad, partially hidden.

[10] Crystal data for **4**: yellow crystals, 0.25 × 0.45 × 0.6 mm, orthorhombic, $a = 785.8(2)$ pm, $b = 1451.2(1)$ pm, $c = 1877.4(2)$ pm, $V = 2.1410(9)$ nm^3, $Z = 4$, space group $Pccn$ (No. 56), $d_{calc} = 1.235$ g cm^{-3}, $\mu = 8.06$ cm^{-1}, $F(000) = 856$. Data collection: ENRAF-Nonius CAD4, Mo Kα radiation, graphite monochromator, ω scan ($3 < \theta < 28°$) at 253 K; 2851 reflections measured, 1344 unique reflections with $I > \sigma(I)$, no absorption correction applied. Solution and refinement:[15] 119 parameters, $R = 0.082$, $R_w = 0.079$, $w^{-1} = \sigma^2(F_o)$, GOF = 1.71; non-hydrogen atoms were refined anisotropically and all hydrogen atoms were treated as riding.[16]

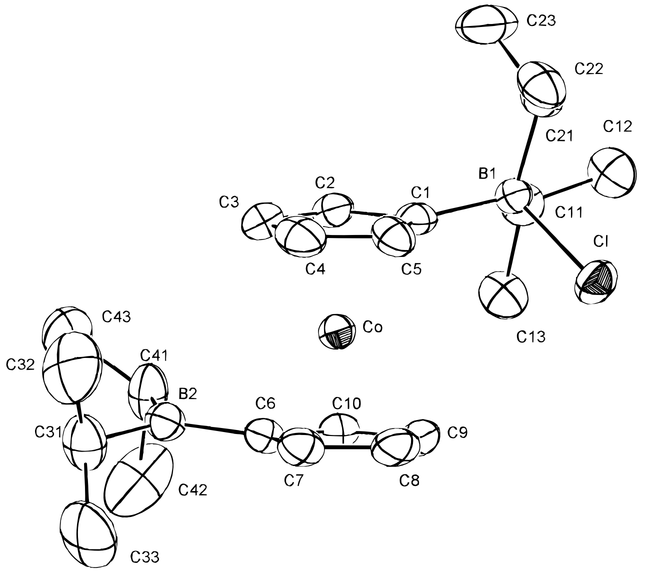

Figure 3. ORTEP plot of **5** (at the 30% probability level). Bond distances (pm): Co–C(ring), 200.5(4)–209.6(2); Co···B1, 346.1(3); Co···B2, 317.2(3); Co···Cl, 397.79(9); C–C(ring), 139.7(5)–144.1(5); C1–B1, 162.1(5); C11–B1, 163.2(5); C21–B1, 164.4(5); C6–B2, 157.5(4); C31–B2, 156.6(5); C41–B2, 156.5(5); Cl–B1, 198.2(3). Distances from the ring plane (pm): for B1 24.7(3) away from the metal, for B2 13.9(4) pm toward the metal. Bond angles (deg): Cl–B1–C1, 105.9(2); Cl–B1–C11, 108.5(2); Cl–B1–C21, 106.9(2); C1–B1–C11, 115.3(3); C1–B1–C21, 107.7(3); C11–B1–C21, 112.2(2); C6–B2–C31, 122.6(3); C6–B2–C41, 117.4(3); C31–B2–C41, 119.8(3).

dinate boron as in **3** and tetracoordinate boron as in **4**. The two $C_5H_4BPr^i_2$ ligands appear equivalent in the ^{1}H and ^{13}C NMR spectra down to −80 °C. Obviously, the chloride **5** is highly fluxional in solution.

When MeOH is added to a solution of the μ-OH complex **4** in toluene, a small fraction is transformed into the μ-OMe complex $Co(C_5H_4BPr^i_2)_2(\mu\text{-}OMe)$ (**6**).[13] Equilibrium ($K = [3.2(5)] \times 10^{-2}$ at 20 °C) is reached within minutes. When CF_3CO_2H (1–4 equiv) is added to **4** in toluene, a common proton resonance is observed for the protons of the acid and the μ-OH group. Thus, we see fast exchange of the protic hydrogens but no decomplexation of the μ-OH group. Taken together, these observations demonstrate high stability of the inverse chelate **4**. At longer reaction times (3–4 days, 20 °C) slow protolytic cleavage of one of the two BPr^i_2 groups takes place.

The molecular pincer $\mathbf{2}^+$ differs from the 1,8-bis(boryl)naphthalenes by its charge and by the flexibility of its molecular skeleton. In any case, it does interact with anions by the field effect[14] of the cobaltocenium moiety. However, the flexibility of $\mathbf{2}^+$ allows for more varied anion binding. Thus, we have the three situations exemplified above: simple salt formation with PF_6^- as in **3** and coordination to one or two boron centers as in **5** or **4**. In the inverse chelate **4** the internal flexibility of $\mathbf{2}^+$ is decreased to allow the formation of the energetically favorable B–O–B′ group. The Cl^- bridge formation is obviously less favorable than the open zwitterionic structure **5**.

It will be of interest to replace the bulky isopropyl substituents with the sterically less demanding methyl groups or with more electronegative substituents such as chlorine. In addition to these aspects the selectivity of $\mathbf{2}^+$ in binding different anions and the dynamics of the anion coordination are currently under investigation.

Acknowledgment. We thank Dr. U. Englert for advice with the structure determinations. This work was generously supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of bond distances and angles, anisotropic thermal parameters, and atom coordinates for **3**–**5** (17 pages). Ordering information is given on any current masthead page.

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[11] Preparation of **5**: A solution of **2** (1.28 g, 3.36 mmol) in toluene (30 mL) was treated with hexachloroethane (0.61 g, 2.58 mmol) for 10 min. Careful removal of all volatiles and crystallization from toluene gave **5** (1.195 g, 85%) as deep yellow microcrystals; mp 104–106 °C. ^{1}H NMR (80 MHz, C_6D_6): for C_5H_4 δ 5.05 (m, 4H), 4.83 (m, 4H); for BPr^i_2 1.43 (sept, $J = 6.0$ Hz, 4 BCH), 1.13 (d, $J = 6.0$ Hz, 4 Me). ^{11}B NMR (29 MHz, C_6D_6): δ 40. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6): for C_5H_4 δ 88.3, 84.9, signal of C-1 not observed; for BPr^i_2 δ 22.3 (br, BCH) and 20.6 (Me).

[12] Crystal data for **5**: yellow crystals, 0.5 × 0.45 × 0.2 mm, monoclinic, $a = 1115.1(2)$ pm, $b = 819.6(3)$ pm, $c = 1247.7(2)$ pm, $\beta = 96.25(1)°$, $V = 1.1335(8)$ nm^3, $Z = 2$, space group $P2_1$ (No. 4), $d_{calc} = 1.220$ g cm^{-3}, $\mu = 8.77$ cm^{-1}, $F(000) = 444$. Data collection: ENRAF-Nonius CAD4, Mo Kα radiation, graphite monochromator, ω scan ($3 < \theta < 27°$) at 253 K; 2770 reflections measured, 2358 unique reflections with $I > \sigma(I)$, empirical absorption correction (PSI[17]). Solution and refinement:[15] 234 parameters, $R = 0.031$, $R_w = 0.037$, $w^{-1} = \sigma^2(F_o)$, GOF = 1.31; non-hydrogen atoms were refined anisotropically and all hydrogen atoms were treated as riding.[16]

[13] Observation of **6**: MeOH (7.9 mg, 246 μmol) was added to a solution of **4** (9.7 mg, 24.4 μmol) in C_6D_6 (0.6 mL) at 20 °C. The equilibrium constant was calculated from initial weights of the reactants and relative intensities in the ^{1}H NMR spectrum; $K = [3.2(5)] \times 10^{-2}$, from five runs. ^{1}H NMR (250 MHz, C_6D_6): for C_5H_4 δ 5.04 (m, 4H), 4.29 (m, 4H); δ 3.32 (s, 3H, OMe); for BPr^i_2 δ 1.43 (m, 8 Me), 1.2–1.1 (m, hidden, 4 BCH). ^{11}B NMR (29 MHz, C_6D_6): δ 2. $^{13}C\{^1H\}$ NMR (63 MHz, C_6D_6): for C_5H_4 δ 87.5, 81.3, signal of C-1 not observed; for OCH_3 δ 51.4; for BPr^i_2 δ 21.2 (Me) and 18.4 (br, BHC).

[14] For some recent examples of anion binding by the field effect, see: Weiss, R.; Pomrehn, B.; Hampel, F.; Bauer, W. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1319. Worm, K.; Schmidtchen, F. P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 65. Steed, J. W.; Juneja, R. K.; Atwood, J. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2456.

[15] Frenz, B. A. ENRAF-Nonius SDP Version 5.0, Delft, The Netherlands, 1989, and local programs.

[16] Further details of the crystal structure analyses are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-391010 for **3**, CSD-391011 for **4**, and CSD-391012 for **5**, the names of the authors, and this journal citation.

[17] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.