Anionic Borylene Complexes

DOI: 10.1002/anie.200801848

A Linear, Anionic Dimetalloborylene Complex**

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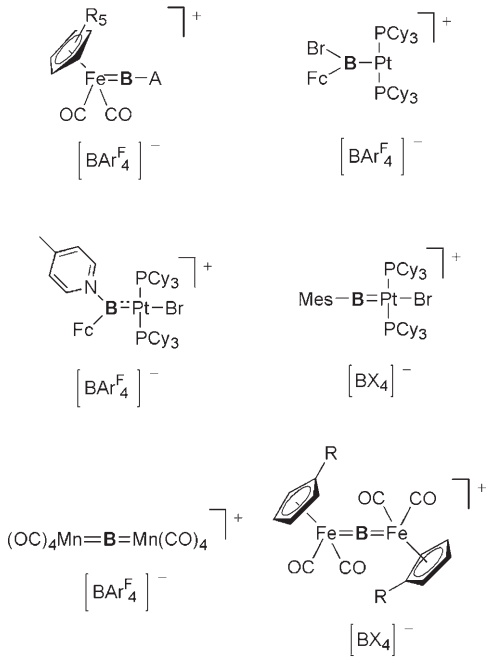
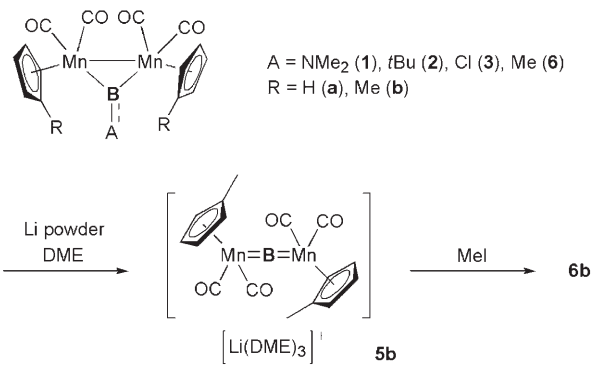
The reduction of boron–halide bonds has attracted the attention of numerous research groups for nearly 50 years, with a view to preparing low-coordinate radical or anionic boron species. The relative ease with which the neighboring isoelectronic carbenes are prepared[1] and the emergence of stable two-coordinate gallide anions[2] had until recently only made the absence of the analogous "boryl anion" more conspicuous. For the most part, forays into B–X bond reduction[3] have yielded products arising from radical-type reactions with solvent molecules (hydrogen-atom abstraction, C–O and C–N bond cleavage),[3j] C–H bond insertion,[3i] or radical homocoupling and/or rearrangement.[3a,c,j,4] The simple two-electron B–X bond reduction of monoboron systems in the absence of these further reactions is presently limited to the borole system of Yamashita and Nozaki and their boryllithium and -magnesium complexes.[5] However, corresponding studies on the reduction of transition-metal-bound B–X moieties do not appear in the literature, which could be explained by the assumption that boryl and borylene transition-metal complexes are less stable than their metal-free haloborane counterparts.[6] In addition to the cationic iron borylene complexes reported by Aldridge and co-workers,[7] a number of surprisingly stable cationic complexes with M–B bonds have been isolated in our laboratories very recently (Scheme 1);[8] however, examples of anionic complexes containing metal-bound monoboron ligands are very rare and are limited to simple boryl complexes.[9]



Scheme 1. Selected cationic complexes containing metal–boron bonds. A = amino, aryl; R = H, Me; X = 3,5-$(CF_3)_2C_6H_3$ (Ar^F), C_6F_5; Fc = ferrocenyl; Mes = 2,4,6-trimethylphenyl.

The first members of the now well-established family of dimanganese borylene complexes [{$L(OC)_2Mn\}_2BA$] (**1**: A = NMe_2; **2**: A = *t*Bu; **a**: L = η^5-C_5H_5; **b**: L = η^5-C_5H_4Me) were synthesized in 1995,[10a] and the aminoborylene examples in particular exhibited unprecedented stability, being indefinitely stable under ambient conditions (Scheme 2).[10] The corresponding chloroborylene complexes **3** (A = Cl), derived from the aminoborylenes by treatment with anhydrous HCl, were notably less stable but resistant to brief handling in air.[10b] Aminoborylenes **1** were found to react cleanly only with strong acids, and complexes **3** react with a range of different nucleophiles, whereas the less synthetically accessible complex **2a** has been shown to react with the weaker nucleophile PCy_3 (Cy = cyclohexyl) to produce the terminal borylene complex [(η^5-C_5H_5)$(OC)_2$Mn=B*t*Bu] (**4**).[10g] It was thought, given their substantial stability, that the chemical reduction of chloroborylene complexes **3** could yield stable and useful anionic species.



Scheme 2. Top: Selected known (**1**–**3**) and new (**6b**) dimanganese borylene complexes. Bottom: Synthesis of anionic complex **5b**.

Stirring a mixture of lithium sand (large excess) and **3a** in DME (1,2-dimethoxyethane) at −10 °C and subsequent warming to room temperature led to a change in position of the ^{11}B NMR signal from $\delta = 134$ to 195 ppm. After filtration of the reaction mixture through celite and removal of the

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[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. R.D.D. thanks the Alexander von Humboldt Foundation for a postdoctoral fellowship.

solvent, the remaining lightly colored oil was layered with hexanes and left to crystallize at −30 °C in a glovebox. Decanting the solvent provided off-white crystals of **5b**, which exhibited the new ^{11}B NMR signal in C_6D_6. In view of the high solubility and highly colored nature of chloroborylene complex **3b**, the sparingly soluble, colorless compound **5b** suggested the presence of a salt. Signals corresponding to three equivalents of DME were present in the ^{1}H NMR spectrum, and the multiplicity of the signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra pointed to a single environment for the nuclei of the η^5-C_5H_4Me rings and the carbonyl carbon nuclei. The IR spectrum of **5b** showed three major signals ($\tilde{\nu}$ = 1911, 1881, 1831 cm^{-1}), the lowest of which has a weak shoulder peak, shifted to significantly lower frequency than those of **3b** ($\tilde{\nu}$ = 1969, 1941, 1912 cm^{-1}).

The large shift to low field of the ^{11}B NMR signal (**3b**: δ = 134 ppm, **5b**: δ = 195 ppm) was encouraging in that a similar downfield shift was noted upon reduction of the diaminoborole anion system of Yamashita and Nozaki (B–Br: δ = 19 ppm, B–Li: δ = 45 ppm).[5a] In addition, such extremely deshielded resonances are known to be indicative of M-B-M moieties, in which a two-coordinate boron atom is linked solely to metal centers. Similarly low-field-shifted ^{11}B NMR signals were found for the cationic complexes [{$(OC)_5Mn$}$_2$(μ-B)][BAr^F_4] (δ = 224.9 ppm), [{$(\eta^5$-$C_5H_5)(OC)_2Fe$}$_2$(μ-B)]-[BAr^F_4] (δ = 191.2 ppm), and [{$(\eta^5$-$C_5H_4Me)(OC)_2Fe$}$_2$(μ-B)]-[BAr^F_4] (δ = 193.7 ppm),[8c] as well as the silylborylene complex [$(OC)_5$Cr=BSi$(SiMe_3)_3$] (δ = 204.3 ppm) and the metalloborylene complex [{$(\eta^5$-$C_5Me_5)(OC)_2$FeB=Cr$(CO)_4$] (δ = 204.6 ppm).[11]

On the basis of the ^{1}H NMR spectrum showing the presence of three molecules of DME, the lithium cation was assumed to be hexacoordinate and separate from its counterion. Thus, from all the experimental data, **5b** was assigned as the salt [Li$(dme)_3$]$^+$[{$(\eta^5$-$C_5H_4Me)(OC)_2Mn$}$_2$B]$^-$ (Scheme 2).

X-ray crystallographic analysis of **5b** confirmed the anionic nature of the Mn_2B fragment, which, in marked contrast to that of the borole-based boryl anion, is separate from its counter cation [Li$(dme)_3$]$^+$ (Figure 1).[5a] Compound **5b** crystallized in triclinic group $P\bar{1}$ as colorless blocks. In the crystallographic asymmetric unit were found one whole C_2-symmetric anion and two separate halves, the latter of which feature boron atoms on inversion centers, thus exhibiting C_{2h} symmetry. As crystal symmetry implies perfect linearity of the Mn-B-Mn axis, discussion of the geometrical parameters is restricted to the C_2-symmetrical anion only.

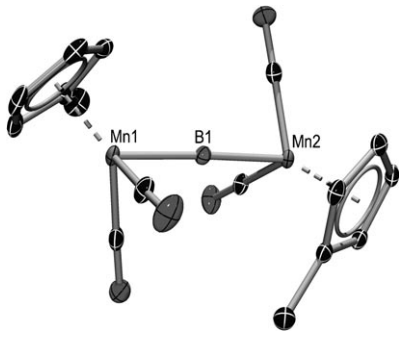

Figure 1. Molecular structure of [{$(\eta^5$-$C_5H_4Me)(OC)_2Mn$}$_2$B]$^-$; selected bond lengths [Å] and angles [°]: B1–Mn1 1.8812(14), B1–Mn2 1.8809(14); Mn1-B1-Mn2 176.11(9).

The Mn-B-Mn linkage is nearly linear (176.1°) and the [$(\eta^5$-$C_5H_4Me)(OC)_2Mn$] moieties are twisted by 147.5°. The short Mn–B distances (1.8812(14) and 1.8809(14) Å) are in agreement with related terminal borylene complex **4** (1.810(1) Å) and are significantly shorter than those of precursor **3b** (1.976(9)–2.039(11) Å).[10h] This result suggests two full borylene-like Mn–B bonds, similar to these found in the cationic species [{$(\eta^5$-$C_5H_4Me)(OC)_2Fe$}$_2$B]$^+$.[8c]

To gauge the nucleophilicity of the boron center in **5b**, an excess of iodomethane was added to a solution of the anion in DME, affording a color change to deep red. After removal of the LiI salts, red crystals of methylborylene **6b** were obtained from hexane which displayed the expected signals for the boron-bound CH_3 group in both ^{1}H (δ = 2.05 ppm) and ^{13}C{^{1}H} (δ = 25.8 ppm, broad) NMR spectra. X-ray crystallographic analysis confirmed the structure of **6b** as a methyl analogue of the *tert*-butylborylene complexes **2a,b**.[10a] The overall geometry of **6b** resembles that of **2a** (Figure 2), although the key B–Mn and B–C distances were all found to

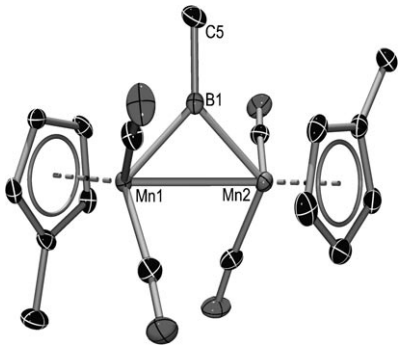

Figure 2. Molecular structure of **6b**; selected bond lengths [Å] and angles [°]: B1–Mn1 2.000(3), B1–Mn2 1.989(3), B1–C5 1.567(4); Mn1-B1-Mn2 88.74(11).

be slightly shorter (**6b**: B1–Mn1 2.000(3), B1–Mn2 1.989(3), B1–C5 1.567(4); **2a**: B1–Mn1 2.029(2), B1–Mn2 2.031(2), B1–C 1.610(2)). Thus, methylborylene complex **6b** is only the fourth example of an alkyl borylene complex after the bridging derivatives **2a,b**[10a] and terminal borylene **4**[10g], and the first with a methyl group.

Given the linear coordination of the boron atom in **5b** and its considerable steric protection, it can be assumed that the anion's efficacy as a boron nucleophile would be significantly lessened relative to the boryl anions of Yamashita and Nozaki.[5] However, the reaction of **5b** with MeI suggests that some nucleophilicity of the boron atom may remain. Consequently, the construction of more exotic borylene species through simple nucleophilic attack by boron is under investigation.

Experimental Section

5b: A Schlenk tube containing lithium (105 mg, 15.1 mmol) and **3b** (480 mg, 1.13 mmol) was cooled to approximately −30 °C, and DME (30 mL) was added with vigorous stirring. The mixture was stirred

overnight and then filtered through a plug of celite. Volatile compounds were removed from the filtrate under reduced pressure to leave a light orange oil, which was transferred to a vial in a glovebox, layered with a threefold volume of hexanes, and cooled to −30 °C overnight. The supernatant was removed from the resulting off-white crystals of **5b** with a Pasteur pipette, and the crystals were dried thoroughly. Yield 540 mg (72 %). ^{1}H NMR (25 °C, C_6D_6): $\delta =$ 4.89 (s, 4H, CH), 4.80 (s, 4H, CH), 3.24 (s, 18H, OCH_3), 3.15 (s, 12H, CH_2), 2.27 ppm (s, 6H, CCH_3). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): $\delta = 232.9$ (CO), 99.1 (CCH_3), 83.1 (CH), 81.2 (CH), 70.8 (CH_2), 59.0 (OCH_3), 14.9 ppm (CCH_3). ^{11}B NMR (25 °C, C_6D_6): $\delta = 195.3$ ppm. ^{7}Li NMR (25 °C, C_6D_6): $\delta = -1.83$ ppm. IR (DME): $\tilde{\nu} = 1911$ (br), 1881 (s), 1831 (br, sh) cm^{-1}.

6b: Iodomethane (13 mg, 5.6 μL, 0.090 mmol) was added to a stirred solution of **5b** (50 mg, 0.075 mmol) in DME (5 mL). The color slowly became more red, and volatile compounds were removed from the mixture after one hour of stirring. The residue was extracted with hexanes and filtered through celite. The filtrate was reduced in volume under vacuum and placed in a vial in a glovebox freezer to evaporate slowly. The supernatant was removed from the resulting red crystals of **6b** with a Pasteur pipette, and the crystals were dried thoroughly. Yield 11 mg (36 %). ^{1}H NMR (25 °C, C_6D_6): $\delta = 4.17$ (d, $J_{HH} = 2.0$ Hz, 4H, CH), 4.11 (d, $J_{HH} = 2.0$ Hz, 4H, CH), 2.05 (s, 3H, BCH_3), 1.91 ppm (s, 6H, CCH_3). ^{13}C{^{1}H} NMR (25 °C, C_6D_6): δ 228.6 (CO), 101.3 (CCH_3), 84.1 (CH), 83.4 (br, CH), 25.8 (br, BCH_3) 12.0 ppm (CCH_3). ^{11}B NMR (25 °C, C_6D_6): $\delta = 158.4$ ppm. C,H analysis (%) calcd for $C_{17}H_{17}BMn_2O_4$: C 50.29, H 4.22; found: C 50.46, H 4.07.

The crystal data of **5b** and **6b** were collected on a Bruker X8 APEX diffractometer with a CCD area detector and multilayer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved by using direct methods, refined with the SHELX software package (G. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122), and expanded by Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and were included in structure factor calculations.

Crystal data for **5b**: $C_{28}H_{44}BLiMn_2O_{10}$, $M_r = 668.26$, colorless block, $0.30 \times 0.25 \times 0.15$ mm^3, triclinic space group $P\bar{1}$, $a = 9.1624(4)$, $b = 18.5299(7)$, $c = 20.5143(9)$ Å, $\alpha = 108.663(2)$, $\beta = 96.256(2)$, $\gamma = 94.629(2)$°, $V = 3255.3(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.364$ g cm^{-3}, $\mu = 0.826$ mm^{-1}, $F(000) = 1400$, $T = 100(2)$ K, $R_1 = 0.0491$, $wR^2 = 0.0791$, 19695 independent reflections [$2\sigma \leq 64.32$°] and 776 parameters.

Crystal data for **6b**: $C_{17}H_{17}BMn_2O_4$, $M_r = 406.00$, red plate, $0.04 \times 0.14 \times 0.19$ mm^3, orthorhombic space group $P2_12_12_1$, $a = 9.1760(4)$, $b = 12.0603(5)$, $c = 14.9120(5)$ Å, $V = 1650.24(11)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.634$ g cm^{-3}, $\mu = 1.547$ mm^{-1}, $F(000) = 824$, $T = 100(2)$ K, $R_1 = 0.0505$, $wR^2 = 0.1191$, 6408 independent reflections [$2\theta \leq 69.2$°] and 221 parameters.

CCDC-685485 and -685486 contain 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

Received: April 21, 2008
Published online: June 20, 2008

Keywords: boron · borylene ligands · manganese · nucleophilicity · reduction

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