Carboranes

Synthesis, Reactivity, and Structural Characterization of a 14-Vertex Carborane**

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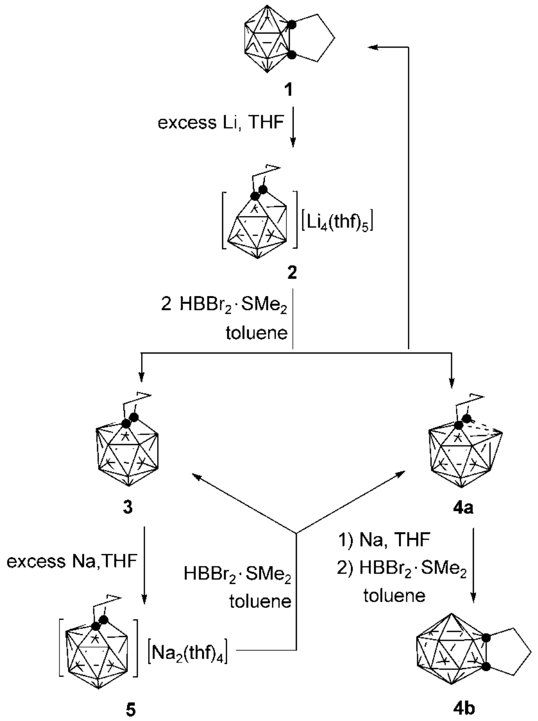
closo-Boranes and carboranes, which have received much attention, are among the simplest cluster systems; their chemistry is dominated by icosahedral molecules with 12 vertices.[1] Carboranes with 13 vertices were unknown until 2003[2] although a series of metallacarboranes of s-, p-, d-, and f-block elements with 13 vertices have been prepared and structurally characterized[3] since the first one was reported in 1971.[4] A few metallacarboranes with 14 vertices are also known.[5] Thus, the question arises as to why the development of supracarborane chemistry is well behind that of the metallacarboranes. One may attribute this fact to the thermodynamic difficulties that arise in building up large carboranes beyond the icosahedron, as suggested by the theoretical calculations on $[B_nH_n]^{2-}$ systems.[6] We believe, on the basis of our own work, that the energies of BH (BR) group additions are not the major issue, rather, the reducing power of the parent *nido*-carborane dianions (*nido*-$[R_2C_2B_{10}H_{10}]^{2-}$) is the key factor for the successful preparation of $C_2B_nH_{n+2}$ when $n > 10$.

It has been well documented that "carbon-atoms-apart" (CAp) *nido*-$[R_2C_2B_{10}H_{10}]^{2-}$ ions are very strong reducing agents that can reduce M^{4+} (M = Group 4 metal atom) and Ln^{3+} (Ln = Sm, Eu, Yb) to the corresponding divalent species,[7,8] but are inert toward Group 1 metals.[9] Conversely, "carbon-atoms-adjacent" (CAd) *nido*-$[R_2C_2B_{10}H_{10}]^{2-}$ ions do react with lithium metal to generate CAd *arachno*-$[R_2C_2B_{10}H_{10}]^{4-}$ ions,[10] which suggests that CAp *nido*-$[R_2C_2B_{10}H_{10}]^{2-}$ ions are more powerful reducing agents than their CAd counterparts. In fact, there are two competitive reactions between *nido*-$[R_2C_2B_{10}H_{10}]^{2-}$ ions and $R'BX_2$ (R' = H, aryl; X = halide): redox and capping reactions. Lowering the reducing power of *nido*-$[R_2C_2B_{10}H_{10}]^{2-}$ ions and the oxidizing ability of $R'BX_2$ is critical for the preparation of supracarboranes. In this regard, we suggest that the isolation of the first carborane with 13 vertices[2a] should be attributed to the relatively weaker reducing power of CAd *nido*-$[1,2\text{-}\{o\text{-}C_6H_4(CH_2)_2\}\text{-}1,2\text{-}C_2B_{10}H_{10}]^{2-}$.[10] We wondered if such a cage-opening and boron-insertion would be applicable to the CAd *arachno*-carborane tetraanions bearing both six- and five-membered bonding faces that were prepared recently in our laboratory.[10] Such a methodology may lead to the formation of carboranes with 14 vertices in one reaction. Herein we report the synthesis, reactivity, and structural characterization of carboranes with 13 and 14 vertices.

Treatment of $1,2\text{-}(CH_2)_3\text{-}1,2\text{-}C_2B_{10}H_{10}$ (**1**)[11] with excess lithium metal in THF at room temperature gave $\{[(CH_2)_3C_2B_{10}H_{10}][Li_4(thf)_5]\}_2$ (**2**) in 85% yield (Scheme 1).



Scheme 1. Synthesis of *closo*-, *nido*-, and *arachno*-carboranes.

This reaction was closely monitored by the ^{11}B NMR spectroscopy as **1** and **2** had distinct splitting patterns. A single-crystal X-ray analysis showed that **2** is a centrosymmetric dimer in which each CAd *arachno*-carborane tetraanion contains both hexagonal and pentagonal bonding faces (Figure 1).[12] The structural motif is the same as in $\{[1,2\text{-}\{o\text{-}C_6H_4(CH_2)_2\}\text{-}1,2\text{-}C_2B_{10}H_{10}][Li_4(thf)_6]\}_2$[10] except for the bridging unit, which offers the possibility of adding two new vertices.

The reaction of **2** with 2.5 equivalents of $HBBr_2{\cdot}SMe_2$ in toluene at −78 to 25 °C gave, after chromatographic separation, a 13-vertex carborane $(CH_2)_3C_2B_{11}H_{11}$ (**3**; 32%), a 14-vertex carborane $(CH_2)_3C_2B_{12}H_{12}$ (**4a**; 7%) and a 12-vertex species (**1**; 2%; Scheme 1). Both **3** and **4a** were characterized by ^1H, ^{13}C, and ^{11}B NMR spectroscopies as well as high-resolution mass spectrometry. The ^{11}B NMR spectrum of **3** displayed a 1:5:5 splitting pattern whereas that of **4a** showed a 1:2:2:1:2:1:2:1 splitting pattern in the range 7.8 to −24.7 ppm. The unique resonance at −24.7 ppm could be attributed to the newly added BH vertex, which is less connected. The isolation of **1** and **3** indicated that $HBBr_2{\cdot}SMe_2$ can oxidize **2** to *nido*-$[(CH_2)_3C_2B_{10}H_{10}]^{2-}$ and finally to *closo*-$(CH_2)_3C_2B_{10}H_{10}$ (**1**). The resulting *nido*-$[(CH_2)_3C_2B_{10}H_{10}]^{2-}$ reacts with

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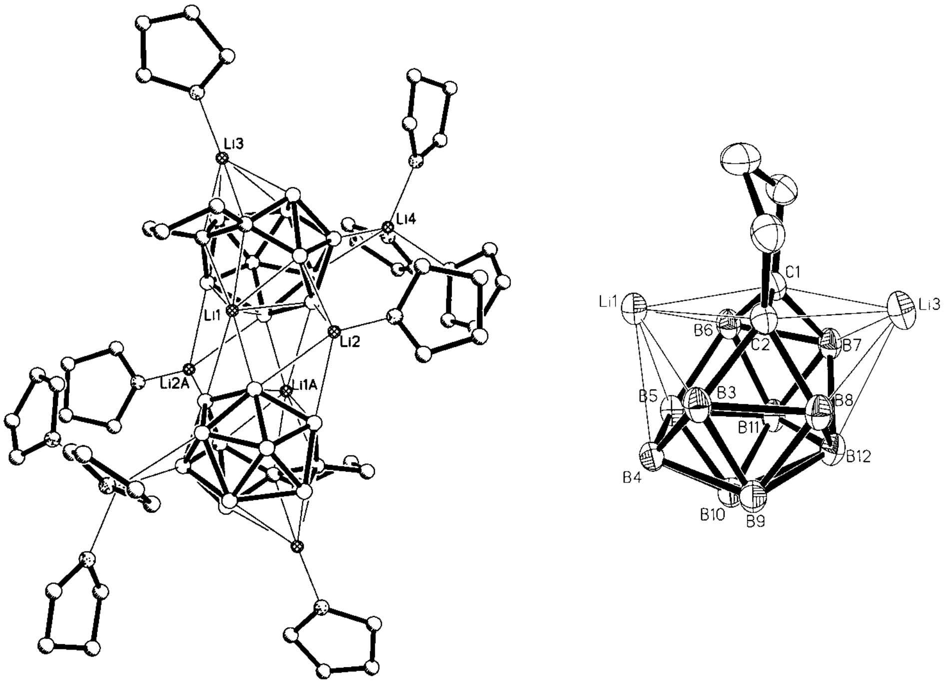

Figure 1. Left: molecular structure of **2**. Right: bonding interactions between Li^+ ions and the open faces of **2**. Selected bond lengths [Å]: C1–C2 1.560(4), B12–B7 1.898(5), B12–B8 1.888(5), B7–C1 1.625(4), B8–C2 1.619(4), C1–B6 1.640(4), B6–B5 1.761(5), B5–B4 1.768(5), B4–B3 1.753(5), B3–C2 1.635(4), av Li3–cage atom 2.257(6), av Li1–cage atom 2.298(6).

$HBBr_2{\cdot}SMe_2$ to form a new 13-vertex carborane *closo*-$(CH_2)_3C_2B_{11}H_{11}$ (**3**).

These results also clearly showed that CAd *arachno*-carborane tetraanions can react with $HBBr_2{\cdot}SMe_2$ to afford carboranes with 14 vertices. We are uncertain, however, if the two BH vertexes are added simultaneously or sequentially. It is assumed that the addition of the first BH vertex to **2** results in the formation of *nido*-$[(CH_2)_3C_2B_{11}H_{11}]^{2-}$ ion, which can either host the second BH vertex to form **4a** or be oxidized by $HBBr_2{\cdot}SMe_2$ to generate *closo*-carborane **3**. Such an assumption prompted us to examine the property of new 13- and 14-vertex carboranes.

Both **3** and **4a** are stable in air, in moisture, and in refluxing toluene as indicated by the ^{11}B NMR spectroscopy, which suggests that they are thermodynamic products. Compounds **3** and **4a** react readily with excess sodium metal at room temperature to give the corresponding *nido*-carborane dianions, $\{nido\text{-}[(CH_2)_3C_2B_{11}H_{11}][Na_2(thf)_4]\}_n$ (**5**) and presumably *nido*-$[(CH_2)_3C_2B_{12}H_{12}][Na_2(thf)_x]$, respectively. Treatment of **5** with 1.5 equivalents of $HBBr_2{\cdot}SMe_2$ produced **4a** and **3** in 30% and 12% yield, respectively. The resulting *nido*-$[(CH_2)_3C_2B_{12}H_{12}][Na_2(thf)_x]$ reacted with $HBBr_2{\cdot}SMe_2$ to afford a new 14-vertex carborane [*closo*-1,2-$(CH_2)_3$-1,2-$C_2B_{12}H_{12}$] (**4b**) in 37% yield, which indicates that the redox reaction was favored (Scheme 1). These results show that **4a** and **4b** are not thermally interchangeable but **4a** can be converted into **4b** through a redox reaction. Compounds **4a** and **4b** have identical molecular masses but the splitting pattern of the ^{11}B NMR spectrum of **4b** is much simpler than that of **4a**, which suggests that they are isomers and **4b** has a much higher symmetry than **4a**.

X-ray analyses revealed that **5** is a coordination polymer in which $[Na(thf)_2]^+$ ions link *nido*-carborane cages to form zigzag polymeric chains (Figure 2).[12] After careful examination of the cage structures in **2** and **5**, we conclude that if the formation of **4a** proceeds by a stepwise mechanism, the first BH vertex adds to the open six-membered bonding face and the second BH vertex then adds to the five-membered bonding face to form **4a**, which has a long B–C bond as depicted in Figure 3. The molecular structure of **3** is similar to that of the anion in **5**, but the B2–B2A bond length of **3** is within the expected range for a normal B–B bond and is the same as that previously reported for a carborane with 13 vertices.[2] Compound **3** accepts two electrons from Na metal to break the B2–B2A bond to form **5**

Single-crystal X-ray analyses showed that **4b** is a bicapped hexagonal antiprism (Figure 4),[12] with a geometry similar to that predicted for $[B_{14}H_{14}]^{2-}$ by computation.[6c] All twenty-four faces are triangulated, with B4 and B4A being seven-coordinated. The average separation of B4 from its connecting vertexes is 1.902(3) Å, the apical B4 is 0.84 Å above the hexagonal plane formed by C1, B3, B6, B7, B5A, and B2A, which is less than the corresponding distance of 0.94 Å observed in icosahedral *o*-carborane.[13] The distance between the two hexagonal planes (1.51 Å) is comparable with that found in icosahedral *o*-carborane (1.50 Å).[13]

In conclusion, we have demonstrated that two BH vertexes can be added to CAd *arachno*-carborane tetraanions in one reaction to give the first 14-vertex *closo*-carborane, the largest carborane presently known. The reactivity of the 13- and 14-vertex *closo*-carboranes has also been examined for the first time. This work suggests that the energies of BH

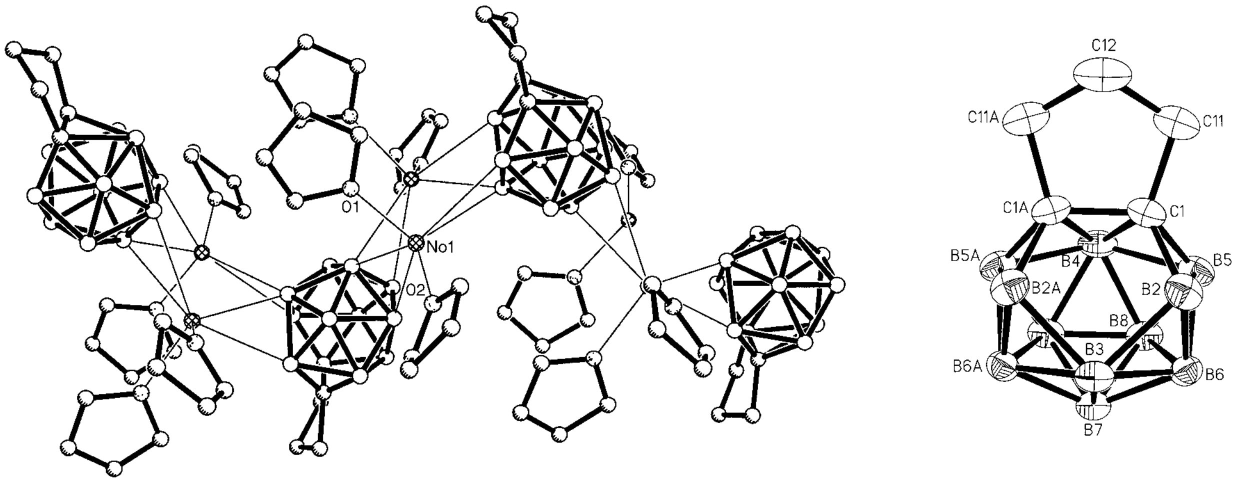

Figure 2. Left: a portion of the infinite polymeric chains in **5**. Right: structure of the anion in **5**. Selected bond lengths [Å]: C1–C1A 1.529(8), C1–B2 1.557(6), B3–B2 1.903(6), B3–B2A 1.903(6), B2A–C1A 1.557(6), B2···B2A 2.677(6).

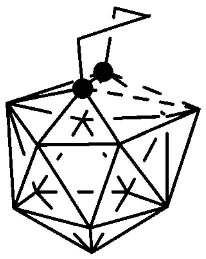

Figure 3. Proposed molecular structure of **4a**.

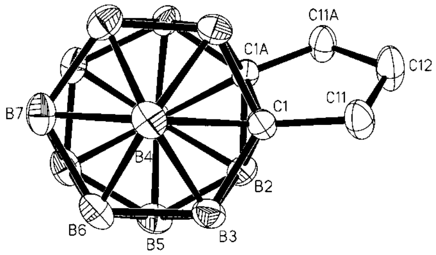

Figure 4. Molecular structure of **4b**. Selected bond lengths [Å]: C1–C1A 1.599(3), B4–C1 1.963(2), B4–B3 1.911(3), B4–B6 1.852(3), B4–B7 1.910(3).

group additions are overstated, and the key issue for the synthesis of supracarboranes is how to block the redox reactions between carborane anions and RBX_2 reagents. It is anticipated that carboranes $C_2B_nH_{n+2}$ with $n > 12$ may be prepared as long as these redox reactions can be suppressed.

Experimental Section

2: Finely cut Li metal (1.80 g, 200 mmol) was added to a solution of **1** (5.52 g, 30.0 mmol) in THF (100 mL)[11], and the mixture was stirred at room temperature for one day to give a red solution. Removal of excess Li and THF yielded a pale-yellow solid. Recrystallization from THF afforded **2** as colorless crystals (14.6 g, 85%). ^{1}H NMR (300 MHz, [D$_5$]pyridine): $\delta = 3.64$ (m, 20H), 1.62 (m, 20H, THF), 2.99 (m, 2H), 2.84 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2C}H_2$), 1.94 ppm (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$); ^{13}C NMR (75 MHz, [D$_5$]pyridine): $\delta = 67.19$, 25.15 (THF), 45.05 ($C\mathrm{H_2CH_2}C\mathrm{H_2}$), 28.98 ppm ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), the cage carbons were not observed; ^{11}B NMR (128 MHz, [D$_5$]pyridine): $\delta =$ 7.71 (2), 3.15 (2), −1.63 (3), −12.93 (1), −16.54 (1), −18.00 ppm (1); IR (KBr): $\tilde{\nu} = 2510$ (vs), 2427 (vs), 2355 cm^{-1} (s) (BH) ; elemental analysis calcd (%) for $C_{21}H_{48}B_{10}Li_4O_4$ (**2**–THF): C 50.40, H 9.67; found: C 50.01, H 9.86.

3 and **4a**: $HBBr_2{\cdot}SMe_2$ (1.0 M in dichloromethane, 75.0 mL, 75.0 mmol) at −78 °C was slowly added to a suspension of **2** (17.2 g, 30.0 mmol) in toluene (100 mL), and the mixture was stirred at this temperature for 1 h and at room temperature for a further 6 h. Removal of the precipitate by filtration and solvents by evaporation gave a brown sticky solid. Chromatographic separation (SiO_2, 300–400 mesh, *n*-hexane) afforded **1** (0.12 g, 2%), **3** (1.88 g, 32%), and **4a** (0.44 g, 7%) as white solids. **3**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.26$ (t, $J = 7.5$ Hz, 4H, $\mathrm{C}H_2\mathrm{CH_2C}H_2$), 2.18 ppm (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 49.11$ ($C\mathrm{H_2CH_2}C\mathrm{H_2}$), 25.55 ppm ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), resonances from the cage carbon atoms were not observed; ^{11}B NMR (128 MHz, $CDCl_3$): $\delta = 3.52$ (1), 0.96 (5), −1.19 ppm (5); IR (KBr): $\tilde{\nu} = 2570$ cm^{-1} (vs) (BH); HRMS: calcd for $[C_5H_{17}B_{11}]^+$, m/z: 195.2457; found: 195.2455. For **4a**: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.15$ (m, 4H, $\mathrm{C}H_2\mathrm{CH_2C}H_2$), 2.31 ppm (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 40.73$ ($C\mathrm{H_2CH_2}C\mathrm{H_2}$), 25.88 ppm ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), resonances from the cage carbon atoms were not observed; ^{11}B NMR (128 MHz, $CDCl_3$): $\delta =$ 7.80 (1), 5.64 (2), 2.87 (2), −4.23 (1), −6.39 (2), −9.29 (1), −12.34 (2), −24.73 ppm (1); IR (KBr): $\tilde{\nu} = 2566$ cm^{-1} (vs) (BH) ; HRMS: calcd for $[C_5H_{18}B_{12}]^+$, m/z: 208.2592; found: 208.2583.

Treatment of **5** (3.20 g, 4.0 mmol) with $HBBr_2{\cdot}SMe_2$ (6.0 mL of 1.0 M in dichloromethane, 6.0 mmol) in toluene (20 mL) by using the above procedure gave **3** (0.09 g, 12%) and **4a** (0.26 g, 30%).

4b: Finely cut Na metal (0.20 g, 8.70 mmol) was added to a solution of **4a** (0.30 g, 1.44 mmol) in THF (10 mL) and the mixture was stirred at room temperature for one day to give a yellow solution. Removal of excess Na metal by filtration and THF by evaporation afforded a pale yellow solid, presumably *nido*-$[(CH_2)_3C_2B_{12}H_{12}][Na_2(thf)_x]$. Toluene (10 mL) was then added to this solid to give a yellow suspension. $HBBr_2{\cdot}SMe_2$ (3.0 mL of 1.0 M in dichloromethane, 3.0 mmol) was slowly added to the suspension at −78 °C, and the mixture was stirred at this temperature for 1 h, and then at room temperature for 6 h. Chromatographic separation gave **4b** as a white solid (0.11 g, 37%). Single crystals suitable for X-ray analysis were obtained by recrystallization from *n*-hexane. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.89$ (br, 4H, $\mathrm{C}H_2\mathrm{CH_2C}H_2$), 2.25 ppm (br, 2H, CH$_2$*C*H$_2CH_2$); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 42.96$ (*C*H$_2$CH$_2$*C*H$_2$), 28.86 ppm (CH$_2$*C*H$_2$CH$_2$), the cage carbons were not observed; ^{11}B NMR (128 MHz, CDCl$_3$): $\delta = 4.48$ (2), 0.14 (2), −2.85 (4), −4.17 (2), −16.78 ppm (2); IR (KBr): $\tilde{\nu} = 2555$ cm^{-1} (vs) (BH); HRMS: calcd for [C$_5$H$_{18}$B$_{12}$]$^+$, *m*/*z*: 207.2629; found: 207.2636.

5: Finely cut Na metal (0.40 g, 17.4 mmol) was added to a solution of **3** (1.00 g, 5.10 mmol) in THF (10 mL) and the mixture was stirred at room temperature for one day to give a clear yellow solution. After removal of excess Na metal by filtration, the resulting yellow solution was concentrated to about 5 mL, to which 4 mL of toluene was added. **5** was obtained as colorless crystals from this solution after one week at room temperature (2.17 g, 80%). ^{1}H NMR (300 MHz, [D$_5$]pyridine): $\delta = 3.63$ (m, 16 H), 1.59 (m, 16 H, THF), 2.46 (t, $J = 6.3$ Hz, 4 H, C*H*$_2$CH$_2$C*H*$_2$), 2.25 ppm (m, 2 H) (CH$_2$C*H*$_2$CH$_2$); ^{13}C NMR (100 MHz, [D$_5$]pyridine): $\delta = 67.15$, 25.11 (THF), 42.93 (*C*H$_2$CH$_2$*C*H$_2$), 29.24 ppm (CH$_2$*C*H$_2$CH$_2$), the cage carbons were not observed; ^{11}B NMR (128 MHz, [D$_5$]pyridine): $\delta = 9.01$ (1), −14.67 (5), −24.64 ppm (5); IR (KBr): $\tilde{\nu} = 2501$ cm^{-1} (vs) (BH); elemental analysis calcd (%) for C$_{17}$H$_{41}$B$_{11}$Na$_2$O$_3$ (**5**−THF): C 44.54, H 9.02; found: C 44.20, H 9.03.

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[12] Crystal data for **2**: C$_{25}$H$_{56}$B$_{10}$Li$_4$O$_5$, $M_r = 572.6$, triclinic, space group $P\bar{1}$, $a = 10.788(1)$, $b = 13.079(1)$, $c = 14.710(2)$ Å, $\alpha = 114.82(1)$, $\beta = 102.68(1)$, $\gamma = 97.49(1)°$, $V = 1779(1)$ Å^3, $T = 293$ K, $Z = 2$, $\rho_{\text{calcd}} = 1.069$ g cm^{-3}, $2\theta_{\max} = 50°$, $\mu(\text{Mo}_{K\alpha}) = 0.71073$ Å, absorption corrections applied by using SADABS,[14] relative transmission factors in the range 0.963–0.981. A total of 7950 reflections were collected and led to 4633 unique reflections, 4633 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.0805$, wR_2 $(F^2) = 0.2350$. Crystal data for **4b**: C$_5$H$_{18}$B$_{12}$, $M_r = 207.9$, orthorhombic, space group *Pnna*, $a = 15.519(1)$, $b = 10.858(1)$, $c = 7.544(1)$ Å, $V = 1271(1)$ Å^3, $T = 293$ K, $Z = 4$, $\rho_{\text{calcd}} = 1.086$ g cm^{-3}, $2\theta_{\max} = 50°$, $\mu(\text{Mo}_{K\alpha}) = 0.71073$ Å, absorption corrections applied by using SADABS,[14] relative transmission factors in the range 0.390–1.000. A total of 6431 reflections were collected and led to 1122 unique reflections, 1122 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.0602$, wR_2 $(F^2) = 0.1553$. Crystal data for **5**: C$_{21}$H$_{49}$B$_{11}$Na$_2$O$_4$, $M_r = 530.5$, orthorhombic, space group *Cmc*2$_1$, $a = 16.717(1)$, $b = 16.997(1)$, $c = 11.377(1)$ Å, $V = 3233(1)$ Å^3, $T = 293$ K, $Z = 4$, $\rho_{\text{calcd}} = 1.090$ g cm^{-3}, $2\theta_{\max} = 50°$, $\mu(\text{Mo}_{K\alpha}) = 0.71073$ Å, absorption corrections applied by using SADABS,[14] relative transmission factors in the range 0.966–0.983. A total of 8657 reflections were collected and led to 2912 unique reflections, 2912 of which with $I > 2\sigma(I)$ were considered as observed, $R_1 = 0.0694$, wR_2 $(F^2) = 0.1802$. These structures were solved by direct methods and refined by full-matrix least squares on F^2 by using the SHELXTL/PC crystallographic program.[15] All non-hydrogen atoms were refined anisotropically and all hydrogen atoms were geometrically fixed by using the riding model. CCDC-256419–2564121 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.

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