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Synthesis and Structure of Novel Organocycloborates

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Abstract: A series of α,ω-boryl(bromo)alkanes of the general formula $R_2B-(CH_2)_n-Br$ ($n=3$, 4, 5, 6) was obtained in high yield following a standard hydroboration protocol. Upon treatment with Mg turnings and formation of the respective Grignard species, all alkanes with $n=4$ to 6 underwent an unprecedented boron-centered cyclisation reaction with formation of boratacyclopentanes, -hexanes, and -heptanes, respectively. All new compounds were isolated in high yields as colourless, crystalline materials and characterised in solution by multinuclear NMR spectroscopy. Four representative examples were chosen for X-ray diffraction studies, thus providing the first structurally characterised ring systems of that size at a tetraalkyl borate centre.

Keywords: borates · boron · cycloborates · hydroboration · magnesium

Introduction

Tetraorganoborates of the general formula $[R_4B]^-$ are a well established class of compounds, which is important for the preparation of organic and organometallic species and as analytical reagents.[1] In particular, tetraaryl- and mixed alkyl(aryl) borates have attracted much attention due to their widespread use as non-coordinating anions in organometallic synthesis and as facile sources for nucleophilic organyl groups.[2] In stark contrast to aryl borates, the chemistry and application of tetraalkyl borates is less developed. Such compounds can be obtained in various ways,[3] for example, from reactions of alkaline metal organyls with BR_3 (R = alkyl),[4] or from the hydroboration of alkenes with Na[HBR_3].[5] It should be mentioned that the synthesis of bulky tetraalkylborates with four sterically demanding alkyl substitutents is often hampered by the formation of trialkyl borates by dehydroboration.[6] Surprisingly, the corresponding cyclic tetralkyl borates are virtually unknown, and none of the aforementioned methods can be applied to their synthesis. As early as 1969 Koster's group reported the high yield synthesis of the spirocyclic tetraalkyl borate **1** from Na[BEt_4] and a cyclic triorganyl borane precursor under thermally harsh conditions at 140 °C; however, they did not obtain much spectroscopic or structural evidence.[7] Likewise, Murahashi and Kondo proposed the formation of the spirocyclic compound **2** in 1979 from the reaction of trialkyl boranes with $BrMg(CH_2)_5MgBr$, again without spectroscopic support.[8] Both syntheses are very specific and their application is restricted to the two examples described, the constitution of which remains far from being definitively ascertained. In addition, only very few cyclic tetraalkyl borates are known, which like compound **3**, were all obtained from 9-borabicyclononane (9-BBN) derivatives.[6]

To address this deficiency and to provide a facile and preferably general access to cyclic tetraalkyl borates, we started to investigate the potential of boron-centered cyclisation reactions very recently. This approach has been occasionally applied to the synthesis of three-coordinate boranes, such as **4** and **5**, which have been obtained by hydroboration of dienes[9] and alkylation of R_2NBCl_2,[10] respectively, but should possess a much broader applicability. Indeed, our preliminary studies did reveal the propensity of certain α,ω-boryl(bromo)alkanes to form novel cyclic borates upon treatment with Mg turnings. Recently, we communicated the first dialkylboratacyclopentanes **6** and -hexanes **7**, respectively, to exemplify this new synthetic approach.[11] Herein we report full synthetic, spectroscopic, and structural details of a representative range of novel five-, six-, and seven-membered cyclic and spirocyclic borates thus obtained.

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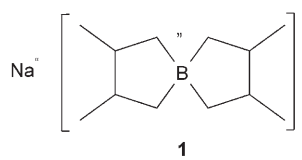

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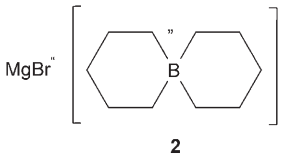

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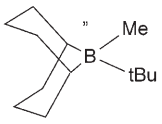

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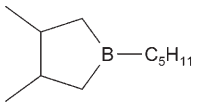

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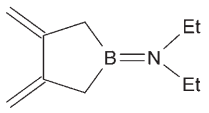

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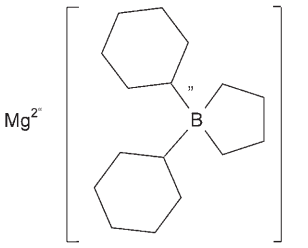

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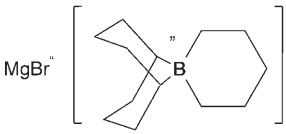

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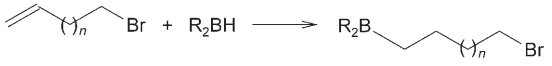
Results and Discussion

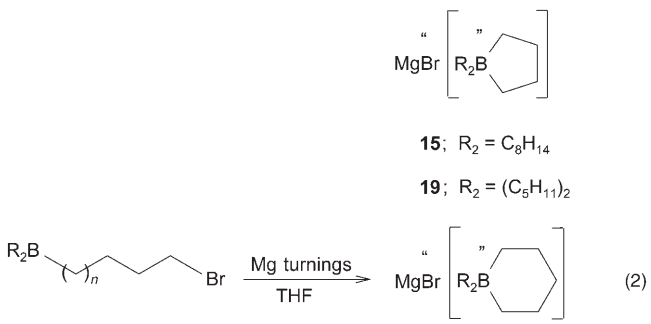
9-BBN, dicyclohexylborane, and disiamylborane were chosen as readily available starting materials for the synthesis of a range of α,ω-boryl(bromo)alkanes. The latter were obtained according to Equation (1) by hydroboration of 4-bromobutene(1), 5-bromopentene(1), and 6-bromohexene(1), respectively. A standard protocol was applied[12] and the new compounds **8–14** were isolated as viscous, colourless oils in very high yields. As was demonstrated by ^{11}B NMR spectroscopy, the conversion into the products was quantitative and the crude materials that were obtained after evaporation of the reaction mixture proved to be of sufficient purity for subsequent syntheses. Hence, further purification procedures of these intractable oils were not pursued.



(1)

No	R_2	*n*
8	C_8H_{14}	1
9	C_8H_{14}	2
10	C_8H_{14}	3
11	(cyclo-C_6H_{11})$_2$	1
12	(cyclo-C_6H_{11})$_2$	2
13	(cyclo-C_6H_{11})$_2$	3
14	(C_5H_{11})$_2$	1

The α,ω-boryl(bromo)alkanes **8–10** and **12–14** were treated with Mg turnings in THF at ambient temperature according to Equation (2). ^{11}B NMR spectra of the reaction mixtures revealed that all conversions except one were complete after 16 h. Only in the case of the sterically most encumbered disiamyl derivative **14** were more forcing conditions, that is, prolonged reflux in THF solution for three days, required to complete the reaction. After workup the boratacyclopentanes **15, 19**, the boratacyclohexanes **7, 17**, and the boratacycloheptanes **16, 18** were isolated as their corresponding MgBr salts. All of these cyclic borates were formed as colourless crystals in very good yields up to 90%, proved to be stable in THF solutions under inert atmosphere, and are only moderately sensitive toward air and moisture.



(2)

8-10; 12-14

15; $R_2 = C_8H_{14}$

19; $R_2 = (C_5H_{11})_2$

7; $R_2 = C_8H_{14}$

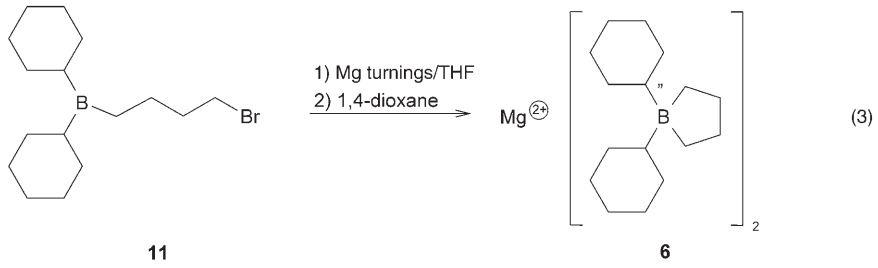
17; R_2 = (cyclo-C_6H_{11})

16; $R_2 = C_8H_{14}$

18; R_2 = (cyclo-C_6H_{11})

As a slight variation of the previously described synthesis, the 5-bromobutylborane **11** was treated with Mg turnings in THF for 16 h, but subsequently, an ethereal solution of 1,4-dioxane was added, thus furnishing the precipitation of $MgBr_2 \cdot C_4H_8O_2$ and the formation of the Mg salt of the boratacyclopentane **6** according to Equation (3). Mg[(cyclo-C_6H_{11})$_2$BC$_4$H$_8$]$_2$ (**6**) was isolated in 86% yield as a colourless, crystalline solid with properties similar to those of the related MgBr salts **7**, **15–19.**

The most characteristic spectroscopic feature of the cyclic borates is their ^{11}B NMR resonances, which range from $\delta =$ −12.5 to −20.5 ppm. These signals are shielded by almost



11 6 (3)

100 ppm with respect to those of their borane precursors, thus proving the increase of the coordination number of the boron centre from 3 to 4. As to be expected, ^{1}H and ^{13}C NMR data are less diagnostic, as all signals appear in the aliphatic region. Electrospray-MS data, however, also confirmed the presence of the proposed borate anions.

The X-ray crystal structures of the boratacyclopentyl (**15**), boratacyclohexyl (**7**)[11] and boratacycloheptyl (**16**) species, which all derive from 9-BBN, and also the related bis(cyclohexyl)boratacyclopentyl compound (**6**),[11] have been determined (Figures 1–4, respectively), and represent, we believe, the only known structurally characterised examples of these ring systems at a tetraalkyl boron centre.[13] The closest analogue for the boratacyclopentyl ring containing compounds **6** and **15** is a trialkyl borohydride species $(H)(PhCH_2)BC_4H_8$ linked to a zirconium centre through a B-H-Zr bridge [CCDC refcode COQTAD].[14] For the boratacyclohexyl moiety (**7**) there are two trialkyl analogues reported: the first is a ring-enlarged version of the closest analogue for the boratacyclopentyl compounds **6** and **15** [i.e., a $(H)(PhCH_2)BC_5H_{10}$ species, COQSUW],[14] whilst the second has a $CH_2CH_2CH_2N(Me)_2$ moiety occupying the other two sites on the boron centre [WOPBEI].[15] Though the quality of the final results from the diffraction experiments on crystals of **16** is rather low,[16] the fact that no structural studies on species including the seven-membered boratacycloheptyl ring have previously been reported in the literature mean that this determination represents the best structural evidence to date for this ring system.

For the structures of **7**, **15** and **16** the restricted bite of the BBN macrocycle is clearly evident, the C-B-C angles being 102.7(2), 103.3(2) and 100.4(16)°, respectively. In the structure of **6** (Figure 4), which has two discrete cyclohexyl ligands in place of the BBN moiety in the other three structures, the release of strain at the boron centre is revealed by the C-B-C angle between these two ligands (109.9(3)°) approaching ideal tetrahedral. Interestingly, this has no effect on the C-B-C angle of the boratacyclopentane rings in **15** and **6**, the respective angles being 100.3(2) and 100.9(3)°. However, the conformation of the boratacyclopentane ring is markedly different in each case. In **15** the C_4B ring adopts an envelope conformation (see Figure S2 in the Supporting Information) with the C(3) centre lying about 0.64 Å out of the B-C(1)-C(2)-C(4) plane (which itself is coplanar to better than 0.01 Å), whereas in **6** the boratacyclopentane ring has a twisted geometry (see Figure S6 in the Supporting Information) with C(2) about 0.36 Å "below" and C(3) about 0.31 Å "above" the B-C(1)-C(4) plane. The related trialkyl species COQTAD has a twisted geometry for this ring, with the central two carbon atoms of the C_4 chain deviating by about −0.41 and +0.23 Å out of the BC_2 plane, with an intra-ring C-B-C angle of 103.5(3)°.[14] In **7** the boratacyclohexane ring adopts a chair conformation (see Figure S3 in the Supporting Information), a geometry seen for every example of this ring so far reported in the litera-

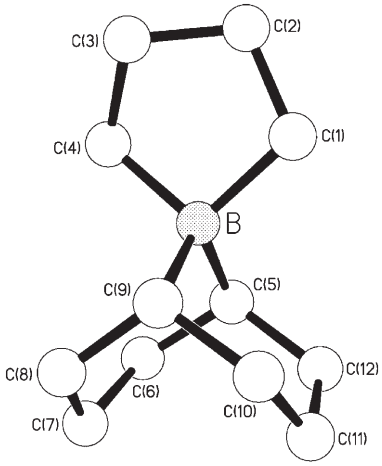


Figure 1. The molecular structure of the tetraalkylcycloborate anion present in the structure of **15** with selected bond lengths [Å] and angles [°]: B−C(1) 1.671(4), B−C(4) 1.656(4), B−C(5) 1.634(4), B−C(9) 1.638(4); C(1)-B-C(4) 100.3(2), C(1)-B-C(5) 114.7(2), C(1)-B-C(9) 112.8(2), C(4)-B-C(5) 113.6(2), C(4)-B-C(9) 112.6(2), C(5)-B-C(9) 103.3(2).

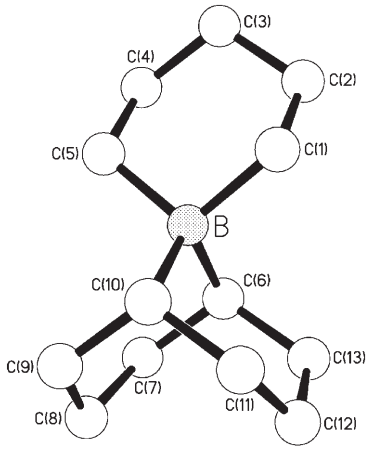


Figure 2. The molecular structure of the tetraalkyl cycloborate anion present in the structure of **7** with selected bond lengths [Å] and angles [°]: B−C(1) 1.649(5), B−C(5) 1.647(5), B−C(6) 1.643(5), B−C(10) 1.644(5); C(1)-B-C(5) 104.8(3), C(1)-B-C(6) 113.2(3), C(1)-B-C(10) 110.9(3), C(5)-B-C(6) 112.6(3), C(5)-B-C(10) 112.9(3), C(6)-B-C(10) 102.7(3).

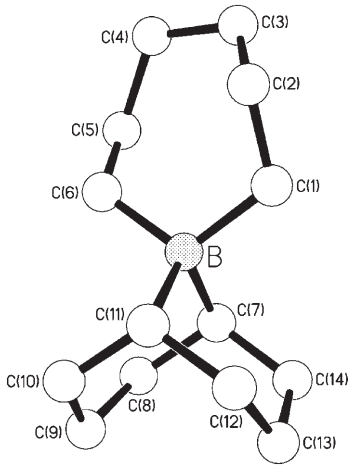


Figure 3. The molecular structure of the tetraalkyl cycloborate anion present in the structure of **16** with selected bond lengths [Å] and angles [°]: B–C(1) 1.67(3), B–C(6) 1.63(3), B–C(7) 1.65(3), B–C(11) 1.69(3); C(1)-B-C(6) 111.3(17), C(1)-B-C(7) 111.5(16), C(1)-B-C(11) 109.5(15), C(6)-B-C(7) 112.5(19), C(6)-B-C(11) 111.1(17), C(7)-B-C(11) 100.4(16).

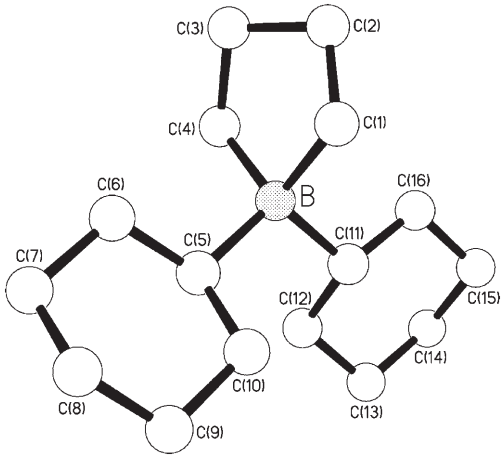


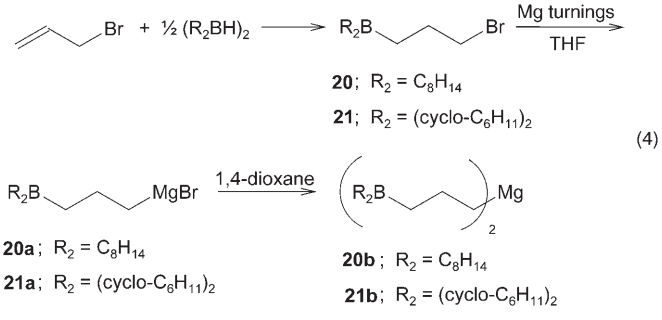
Figure 4. The molecular structure of the tetraalkyl cycloborate anion present in the structure of **6** with selected bond lengths [Å] and angles [°]: B–C(1) 1.663(5), B–C(4) 1.668(5), B–C(5) 1.655(5), B–C(11) 1.659(5); C(1)-B-C(4) 100.9(3), C(1)-B-C(5) 112.0(3), C(1)-B-C(11) 110.4(3), C(4)-B-C(5) 111.4(3), C(4)-B-C(11) 112.0(3), C(5)-B-C(11) 109.9(3).

ture.[17] The C-B-C angle of 104.8(3)° is slightly enlarged compared to the values seen in the boratacyclopentane species **15** and **6**, but is still smaller than the angles of 111.5(5)[14] and 108.9(2)° (109.0(2)°)[15] seen in the trialkyl analogues (the value in square parentheses refers to the second independent molecule present in WOPBEI). The major occupancy orientation for the boratacycloheptane ring in **16** (see Figure S5 in the Supporting Information) has a ring-inverted chair conformation[16] with a C-B-C angle of 111.3(17)°. The intra-ring angles thus show the expected pattern, with boratacyclopentane < boratacyclohexane < boratacycloheptane.

The B–C distances within the five-membered boratacyclopentyl rings in **15** and **6** range between 1.656(4) and 1.671(4) Å, compared to 1.625(5) and 1.633(5) Å in the trialkyl borohydride species COQTAD.[14] The lengthening is probably a consequence of the greater steric requirements of the fourth alkyl substituent in **15** and **6** as compared to hydride in the trialkyl borohydride compound. For the boratacyclohexyl species **7**, all four B–C separations range between 1.643(5) and 1.649(5) Å, and are noticeably longer than those in COQSUW (1.618(5) and 1.624(8) Å)[14] and WOPBEI (in the range 1.613(4)–1.637(4) Å).[15] Here though, the steric argument is not so simple since, whereas COQSUW again shows a hydride in the fourth coordination site on the boron centre, WOPBEI has the nitrogen atom of a $CH_2CH_2CH_2N(Me)_2$ chain. However, the bond to this nitrogen is significantly longer at 1.682(4) Å (1.684(4) Å) than those to either of the carbons in WOPBEI or in **7**. The estimated standard deviations in the structure of the boratacycloheptyl species **16** are too high to allow any meaningful comparisons to be made,[16] even if there were any closely related analogues for this seven-membered C_6B ring.

Obviously, the formation of the cyclic borates proceeds *via* an unprecedented boron-centered cyclisation reaction of the intermediate Grignard species $R_2B–(CH_2)_n–MgBr$ with intramolecular attack of the nucleophilic ω-carbon atom at the highly Lewis acidic boron centre. The cyclisation appears to occur instantaneously, once the reaction with Mg is initiated. Only the bulky $(C_5H_{11})_2B–(CH_2)_4–Br$ (**14**) requires further heating to give the borate formation (vide supra). In that case, the spectroscopic data, particularly the deshielded ^{11}B NMR resonance at $\delta = 85.0$ ppm, which were obtained once the exothermic Grignard reaction has subsided, indicate the exclusive presence of the species $(C_5H_{11})_2B–(CH_2)_4–MgBr$ (**14a**).

In addition, similar experiments targeted corresponding boratacyclobutanes, thus probing for the lower limit of the cyclisation reaction in terms of ring size and strain. To this end potentially useful 3-bromopropylboranes were synthesized by hydroboration of allyl bromide according to Equation (4). The bromides **20** and **21** were converted into the corresponding Grignard species **20a** and **21a** and subsequently, into the magnesium dialkyls **20b** and **21b** by previously described protocols (vide supra). Attempts to achieve a cyclisation reaction of any of these species under similar conditions as in the case of **19**, however, met with no success.



Conclusion

The boron-centered cyclisation of Grignard species $R_2B-(CH_2)_n-MgBr$ ($n=4$, 5, 6) was established as a very convenient and facile method for the high yield synthesis of novel tetraalkyl cycloborates. A wide variety of unprecedented boratacyclopentanes, -hexanes and -heptanes was thus prepared, proving the general applicability of the new method for the synthesis of medium-sized cycloborates. The compounds can be obtained as colourless, crystalline materials of the type $[MgBr][R_4B]$ or $Mg[R_4B]_2$, and the structures of four representative examples in the solid state were elucidated by single-crystal X-ray diffraction methods.

Experimental Section

General remarks: All manipulations of air-sensitive materials were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified and dried according to standard methods and stored over molecular sieve under an inert atmosphere of nitrogen. All starting materials are commercially available and were used as received without further purification. Mg turnings were activated by using small amounts of 1,2-dibromoethane. NMR spectroscopy: JEOL-EX 270 at 269.72 (^{1}H, standard TMS internal), 86.54 (^{11}B, standard $BF_3{\cdot}OEt_2$ in C_6D_6 external), 67.93 MHz (^{13}C{^{1}H}, APT, standard TMS internal), all NMR spectra were recorded at 25 °C in C_4D_8O as solvent unless otherwise stated. Mass spectra were recorded on Micromass "Q-TOF" (70 eV) and elemental analyses (C, H) were obtained from a Carlo Erba EA1108 Elemental Analyser.

8: A solution of 9-BBN (dimer) (2.61 g, 10.70 mmol) in THF (50 mL) was added dropwise to a solution of 4-Br-1-butene (2.89 g, 21.41 mmol) in THF (20 mL) at 0 °C. When the addition was complete, the solution was allowed to reach ambient temperature and stirred overnight. The resulting colourless solution was dried in vacuo to yield **8** as a colourless oil in 92% yield. ^{1}H NMR: $\delta=1.16$–1.92 (m, br, 20H), 3.43 ppm (t, $^3J_{H,H}=6.67$ Hz, 2H; $R_2BCH_2(CH_2)_2CH_2Br$); ^{13}C NMR: $\delta=23.68$, 23.88, 25.73, 30.14, 33.32, 33.80, 36.58 ppm; ^{11}B NMR: $\delta=70.8$ ppm. The crude material was used without further purification for the synthesis of **15**.

9: According to the procedure described for **8**, 9-BBN (dimer) (2.68 g, 11.00 mmol) in THF (50 mL) was treated with 5-Br-1-pentene (2.6 mL, 21.95 mmol) in THF (20 mL) to give **9** as a colourless oil in 93% yield, which was used without further purification for the synthesis of **7**.[11] ^{1}H NMR: $\delta=1.20$–1.94 (m, br, 22H), 3.42 ppm (t, $^3J_{H,H}=6.80$ Hz, 2H; $R_2BCH_2(CH_2)_3CH_2Br$); ^{13}C NMR: $\delta=24.28$, 24.72, 27.46, 31.02, 32.45, 33.82, 34.28 ppm; ^{11}B NMR: $\delta=75.8$ ppm.

10: According to the procedure described for **8,** 9-BBN (dimer) (2.87 g, 11.77 mmol) in THF (50 mL) was treated with 6-Br-1-hexene (3.80 g, 23.30 mmol) in THF (20 mL) to give **10** as a colourless oil in 92% yield, which was used without further purification for the synthesis of **16**. ^{1}H NMR: $\delta=1.18$–1.90 (m, br, 24H), 3.42 ppm (t, $^3J_{H,H}=6.78$ Hz, 2H; $R_2BCH_2(CH_2)_4CH_2Br$); ^{13}C NMR: $\delta=24.43$, 27.57, 29.14, 31.16, 34.26, 33.31, 33.91, 33.98, 34.40 ppm; ^{11}B NMR: $\delta=73.6$ ppm.

11: A solution of cyclohexene (6.0 mL, 59.2 mmol) in THF (20 mL) was added dropwise to a stirred 1.0 M solution of $BH_3{\cdot}$THF (30 mL, 30.0 mmol) in THF at −15 °C. The system was stirred for 1 h, during which time white crystalline dicyclohexylborane precipitated out. Subsequently, a solution of 4-Br-1-butene (3.0 mL, 29.6 mmol) in THF (20 mL) was added dropwise to the suspension of dicyclohexylborane with stirring at 0 °C. The resulting cloudy solution was allowed to reach ambient temperature and stirred overnight. The cloudy solution was centrifuged to separate the off-white solid and the colourless solution was dried in vacuo to give **11** as a colourless oil in 92% yield. ^{1}H NMR: $\delta=1.11$–1.74 (m, 26H), 1.84 (m, 2H, $R_2BCH_2CH_2CH_2CH_2Br$), 3.44 ppm (t, $^3J_{H,H}=6.81$ Hz, 2H, $Cy_2BCH_2CH_2CH_2CH_2Br$); ^{13}C NMR: $\delta=23.64$, 24.73, 28.14, 28.63, 34.21, 36.94, 37.44 ppm; ^{11}B NMR: $\delta=82.4$ ppm. The crude material was used without further purification for the synthesis of **6**.[11]

12: According to the procedure described for **11** cyclohexene (6.0 mL, 59.2 mmol) in THF (20 mL) was treated with a 1.0 M solution of $BH_3{\cdot}$THF (30 mL, 30.0 mmol) in THF and subsequently treated with 5-Br-1-pentene (4.59 g, 30.8 mmol) in THF (20 mL) to give **12** as a colourless oil in 90% yield, which was used without further purification for the synthesis of **17**. ^{1}H NMR: $\delta=1.20$–1.90 (m, 30H), 3.40 ppm (t, $^3J_{HH}=6.92$ Hz, 2H; $R_2BCH_2)_4CH_2Br$); ^{13}C NMR: $\delta=24.30$, 25.72, 28.17, 28.65, 32.96, 33.96, 34.27, 36.95 ppm; ^{11}B NMR: $\delta=82.5$ ppm.

13: According to the procedure described for **11** cyclohexene (4.0 mL, 39.5 mmol) in THF (20 mL) was treated with a 1.0 M solution of $BH_3{\cdot}$THF (20 mL, 20.0 mmol) in THF and subsequently treated with 6-Br-1-hexene (3.26 g, 20.0 mmol) in THF (20 mL) to give **13** as a colourless oil in 93% yield, which was used without further purification for the synthesis of **18**. ^{1}H NMR: $\delta=1.15$–1.86 (m, 32H), 3.41 ppm (t, $^3J_{H,H}=6.80$ Hz, 2H, $R_2B(CH_2)_5CH_2Br$); ^{13}C NMR: $\delta=24.91$, 28.22, 28.67, 29.17, 33.71, 34.05, 34.40, 37.06 ppm; ^{11}B NMR: $\delta=82.5$ ppm.

14: A solution of 2-methyl-2-butene (8.0 mL, 75.5 mmol) in THF (20 mL) was added dropwise to a stirred 1.0 M solution of $BH_3{\cdot}$THF (38.0 mL, 38.0 mmol) at −15 °C. Subsequently, a solution of 4-Br-1-butene (3.8 mL, 37.4 mmol) in THF (20 mL) was added dropwise to the stirred suspension of disiamylborane at 0 °C. The resulting cloudy solution was allowed to reach room temperature and stirred overnight. The solution was dried in vacuo to afford **14** as a colourless oil in 85% yield, which was used without further purification for the synthesis of **19**. ^{1}H NMR: $\delta=0.40$–1.50 (m, 28H), 3.24 ppm (br, 2H; $R_2BCH_2CH_2CH_2CH_2Br$); ^{13}C NMR: $\delta=1.53$, 13.30 (m), 21.70, 23.31 (br), 30.52 (br), 31.16, 31.41, 32.95, 38.50 ppm; ^{11}B NMR: $\delta=84.9$ ppm.

15: All of the previously obtained crude borane **8** was dissolved in THF (20 mL) and added dropwise to a suspension of Mg turnings in THF (50 mL) at ambient temperature. When the addition was complete, the system was allowed to stir at ambient temperature for three days. The resulting grey solution was filtered to give a clear solution, which was concentrated to a small volume in vacuo and cooled to 0 °C to give **15** as colourless crystals in 74% yield. ^{1}H NMR: $\delta=0.04$ (m, br, 6H), 1.20–2.00 ppm (m, 16H); ^{13}C NMR: $\delta=26.81$ (q, $^1J_{C,B}=33.67$ Hz), 28.41, 32.02 (q, $^1J_{C,B}=38.73$ Hz), 33.87, 35.42 ppm; ^{11}B NMR: $\delta=-13.9$; MS (ESI): m/z (%): 177 (100) $[C_{12}H_{22}B]$.

7:[11] According to procedure described for **15** the crude borane **9** was treated in THF (70 mL) with Mg turnings to yield colourless crystals of **7** in 89% yield. ^{1}H NMR: $\delta=-0.33$ (br), 0.80–1.44 ppm (m, br); ^{13}C NMR: $\delta=27.04$, 28.23, 28.88 (br), 30.38, 34.07, 34.51 ppm; ^{11}B NMR: $\delta=-20.5$ ppm; MS (ESI): m/z (%): 191 (100) $[C_{13}H_{24}B]$.

16: According to procedure described for **15** the crude borane **10** was reacted in THF (70 mL) with Mg turnings to yield colourless crystals of **7** in 65% yield. ^{1}H NMR: $\delta=0.14$ (br), 0.29 (br), 1.20–2.00 ppm (br, m); ^{13}C NMR: $\delta=27.33$, 28.43, 29.05 (br), 30.55, 34.07, 35.01 ppm; ^{11}B NMR: $\delta=-19.7$ ppm; MS (ESI): m/z (%): 205 (100) $[C_{14}H_{26}B]$.

17: According to procedure described for **15** the crude borane **12** was treated in THF (35 mL) with Mg turnings to yield colourless crystals of **17** in 76% yield. ^{1}H NMR: $\delta=-0.17$ (br), 0.08 (br), 0.72–1.57 ppm (br, m); ^{13}C NMR: $\delta=23.48$ (q, $^1J_{C,B}=39.49$ Hz; $R_2B(CH_2)_2(CH_2)_3$), 27.31, 28.73, 30.07, 32.09, 33.04, 36.82 ppm (q, $^1J_{C,B}=41.97$ Hz; $[(CH_2)_5CH]_2B-(CH_2)_5$); ^{11}B NMR: $\delta=-18.6$ ppm; MS (ESI): m/z (%): 247 (100) $[C_{17}H_{32}B]$.

18: According to procedure described for **15** the crude borane **13** was treated in THF (35 mL) with Mg turnings to form **18** as a white solid in 70% yield. ^{1}H NMR: $\delta=0.06$ (br), 0.85–1.82 ppm (m, br); ^{13}C NMR: $\delta=27.95$, 28.05, 28.48 30.22, 30.62, 32.16, 32.87, 36.67, 39.92 ppm (q, $^1J_{C,B}=41.33$ Hz; $[(CH_2)_3(CH_2)_2CH]_2B(CH_2)_6$); ^{11}B NMR: $\delta=-16.6$ ppm; MS (ESI): m/z (%): 261 (100) $[C_{18}H_{34}B]$.

14a and 19: All of the previously obtained crude borane **14** was dissolved in THF (20 mL) and the resulting solution was added dropwise to a suspension of Mg turnings in THF (20 mL) at ambient temperature. When the reaction was complete, the system was allowed to reach ambient tem-

perature and a white precipitate started to form. The mixture was stirred overnight, diluted with THF (50 mL), and filtered hot to give a clear solution. A small amount of this solution was dried in vacuo and analysed by NMR spectroscopy.

NMR data for 14a: ^{1}H NMR: $\delta = 0.40$–1.60 (m); ^{13}C NMR: $\delta = 13.41$, 22.50, 23.90 (br), 31.12 (br), 31.25, 32.11, 32.72, 33.50; ^{11}B NMR: $\delta = 85.0$.

The solution of **14a** in THF was refluxed at 66 °C for three days. The resulting clear solution was concentrated to a small volume in vacuo and cooled to 0 °C to give colourless crystals of **19** in 76 % yield. ^{1}H NMR: $\delta = 0.10$ (br), 0.70–1.00 (br, m), 1.20–1.50 (br, m), 1.76 ppm (br); ^{13}C NMR: $\delta = 12.19$, 12.65, 14.40, 21.67, 31.17, 39.52 ppm (br); ^{11}B NMR: $\delta = -20.5$ ppm; MS (ESI): m/z (%): 209 (100) [$C_{14}H_{30}B$].

6: A solution of the crude borane **11** in Et_2O (20 mL) was added dropwise to a suspension of Mg turnings in Et_2O (15 mL) at ambient temperature. When the reaction was complete, the system was allowed to reach ambient temperature and a white precipitate started to form. The mixture was stirred overnight, diluted with THF (50 mL), and filtered hot to give a clear solution. 1,4-Dioxane (2.3 mL, 27.0 mmol) in Et_2O (10 mL) was added dropwise and the resulting solution was stirred overnight. The white precipitate of $MgBr_2$·dioxane was separated from the solution by centrifugation, and the clear solution was concentrated to a small volume in vacuo and cooled to 0 °C to give colourless crystals of **6** in 86 % yield. ^{1}H NMR: $\delta = -0.17$ (br), 0.08 (br), 0.72–1.57 ppm (m, br); ^{13}C NMR: $\delta =$ 30.10, 31.68, 32.66, 32.74 ppm; ^{11}B NMR: $\delta = -12.5$ ppm; MS (ESI): m/z (%): 233 (100) [$C_{16}H_{30}B$].

20: A solution of 9-BBN (dimer) (6.7 g, 27.3 mmol) in THF (50 mL) was added dropwise to a colourless solution of allyl bromide (4.8 mL, 55.5 mmol) in CH_2Cl_2 (10 mL) at −30 °C. When the addition was complete, the solution was allowed to reach ambient temperature and stirred overnight. The resulting colourless solution was dried in vacuo to give **20** as a pale yellow oil in 94 % yield, which was used without further purification for the synthesis of **20a**. ^{1}H NMR: $\delta = 1.15$ (t, $^3J_{H,H} = 8.17$ Hz, 2H; $R_2BCH_2CH_2CH_2Br$), 1.34 (m, 4H; [$(CH_2)_2(CH_2)_4(CH)_2$]B($CH_2)_3$Br)), 1.71–1.80 (m, br, 10H; [$(CH_2)_2(CH_2)_4(CH)_2$]B($CH_2)_3$Br)), 1.96 (m, 2H; $R_2BCH_2CH_2CH_2Br$), 3.40 ppm (t, $^3J_{H,H} = 7.05$ Hz, 2H; $R_2BCH_2CH_2CH_2Br$); ^{13}C NMR: $\delta = 24.56$, 29.59 (br), 30.10, 33.67, 38.04 ppm; ^{11}B NMR: $\delta = 86.6$ ppm.

20a: The previously obtained **20** was redissolved in Et_2O (50 mL) was added dropwise to Mg turnings in Et_2O at ambient temperature. The system was allowed to reach ambient temperature and stirred overnight. The resulting grey solution was filtered and dried in vacuo to give **20a** as a white powder. ^{1}H NMR: $\delta = 1.22$–1.85 ppm (m, br); ^{13}C NMR: $\delta =$ 20.43, 24.29, 31.30 (br), 33.86 ppm; ^{11}B NMR: $\delta = 78.2$ ppm.

20b: The previously obtained Grignard reagent **20a** was redissolved in Et_2O and a solution of 1,4-dioxane (0.57 g, 6.47 mmol) was added dropwise. Immediately, a white precipitate of $MgBr_2$·dioxane formed. After the addition was complete the system was allowed to stir for 2 h. The white precipitate was filtered and washed twice with Et_2O (2×10 mL). The mother liquor was dried in vacuo and **20b** was isolated as a white solid in 85 % yield. ^{1}H NMR: $\delta = 1.21$–1.91 ppm (m, br); ^{13}C NMR: $\delta =$ 20.42, 24.31, 31.10 (br), 33.86 ppm; ^{11}B NMR: $\delta = 77.8$ ppm; elemental analysis calcd (%) for $C_{22}H_{40}B_2Mg$ (350.5): C 75.39, H 11.50; found: C 75.61, H 11.36.

21: According to the procedure described for **20** a solution of cyclohexene (6 mL, 59.2 mmol) in THF (20 mL) was treated with a 1.0 M solution of BH_3·THF (30 mL, 30.0 mmol), and subsequently treated with a solution of allyl bromide (2.6 mL, 30.0 mmol) in THF (20 mL) to give **21** as a colourless oil in 87 % yield, which was used without further purification for the synthesis of **20a**. ^{1}H NMR: $\delta = 1.16$–1.73 (m, br, 24H), 1.96 (m, 2H; $R_2BCH_2CH_2CH_2Br$), 3.42 ppm (t, $^3J_{H,H} = 6.79$ Hz, 2H; $R_2BCH_2CH_2CH_2Br$); ^{13}C NMR: $\delta = 27.90$, 28.06, 28.42, 29.16, 36.60 (br), 37.58 ppm; ^{11}B NMR: $\delta = 81.4$ ppm.

21a: The previously obtained **21** was dissolved in Et_2O (20 mL) and added dropwise to a suspension of Mg turnings in Et_2O at ambient temperature. The system was allowed to reach ambient temperature and stirred overnight. The resulting grey solution was filtered and dried in vacuo to yield **21a**; ^{1}H NMR: $\delta = 1.19$–1.72 ppm (m, br); ^{13}C NMR: $\delta = 15.71$, 28.00, 28.45, 29.95 (br), 36.80 ppm (br); ^{11}B NMR: $\delta = 82.2$ ppm.

21b: The previously obtained Grignard reagent **21a** was redissolved in Et_2O and a solution of 1,4-dioxane (2.3 mL, 27.0 mmol) in Et_2O (10 mL) was added dropwise. The mixture was stirred overnight and the white precipitate of $MgBr_2$·dioxane was separated from the solution by centrifugation. The resulting clear solution was dried in vacuo to give **21b** as an off- white oil in 85 % yield. ^{1}H NMR: $\delta = 1.18$–1.72 (m, br, 26H), 1.96 (m, 2H; $R_2BCH_2CH_2CH_2Br$), 3.42 ppm (t, $^3J_{H,H} = 6.79$ Hz, 2H; $R_2BCH_2CH_2CH_2Br$); ^{13}C NMR: $\delta = 19.39$, 27.95, 28.42, 29.92, 36.74 ppm (br); ^{11}B NMR: $\delta = 82.5$ ppm; elemental analysis calcd (%) for $C_{30}H_{56}B_2Mg$ (462.7): C 77.87, H 12.20; found: C 77.82, H 11.98.

Crystal data for 15: [$C_{20}H_{40}O_5BrMg$]($C_{12}H_{22}B$)·C_4H_8O, $M_r = 713.95$, triclinic, (no. 2), $a = 10.6422(5)$, $b = 13.8529(5)$, $c = 13.9367(6)$ Å, $\alpha = 71.397(4)$, $\beta = 89.688(4)$, $\gamma = 87.648(4)$°, $V = 1945.57(14)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.219$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.113$ mm^{-1}, $T = 173$ K, colourless prisms, Oxford Diffraction Xcalibur 3 diffractometer; 11919 independent measured reflections, F^2 refinement, $R_1 = 0.075$, $wR_2 = 0.126$, 11384 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 64°$], 441 parameters. CCDC-273774 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 16: [$C_{20}H_{40}O_5BrMg$]($C_{14}H_{26}B$)·C_4H_8O, $M_r = 742.00$, monoclinic, $P2_1/n$ (no. 14), $a = 10.7897(9)$, $b = 25.8464(19)$, $c = 14.5063(10)$ Å, $\beta = 93.220(6)$°, $V = 4039.1(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.220$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.074$ mm^{-1}, $T = 173$ K, colourless blocks, Oxford Diffraction Xcalibur 3 diffractometer; 5234 independent measured reflections, F^2 refinement, $R_1 = 0.184$, $wR_2 = 0.448$, 5166 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 45°$], 429 parameters. CCDC-273775 contains the supplementary crystallographic data for this compound. 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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[16] Despite considerable effort it was not possible to grow crystals of better quality of **16**. Numerous attempts were made to get usable X-ray diffraction data from the available crystals, but somewhat inevitably the final results are not satisfying (see Experimental Section). The data reported in this paper for the structure of **16** represent the best that could be obtained, and though we are restricted in what conclusions can be drawn from the structure they unambiguously prove the presence of the boratacycloheptane ring. We were also still able to observe disorder in the boratacycloheptane ring, with C(2) occupying two different positions (see Figure S5 in the Supporting Information), though in each case the C_6B ring adopts a ring-inverted chair conformation.
[17] Though the search of the May-05 update of the Cambridge Crystallographic Database (version 5.26) revealed no examples of a tetraalkylborate centre with a BC_5H_{10} ring, a number of structures (11) containing the $H_2BC_5H_{10}$ moiety were found.

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