Syntheses and Reactivity of Exocyclic Unsaturated Heterodiborolanes and Their Diborylhexadiene Precursors − Formation of 2-Aza-4,5-dicarba-*nido*-hexaboranes(6)

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Dedicated to Prof. Dr. Herbert Schumann on the occasion of his 65th birthday

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The aryl-substituted 3,4-diboryl-2,4-hexadienes **4c–e** are generated when 3,4-bis(dimethoxyboryl)-2,5-dimethyl-2,4-hexadiene (**4a**) and 3,4-bis(dichloroboryl)-2,5-dimethyl-2,4-hexadiene (**4b**) react with two equivalents of xylyllithium or duryllithium. Cyclization reactions of **4b** with heptamethyldisilazane and of **4c** with $MeN(SiMe_3)_2$, $S(SiMe_3)_2$, and $O(SiMe_3)_2$ lead to the corresponding 2,5-diaryl-3,4-diisopropylidene-1-hetero-2,5-diborolanes **5a,b**, **6**, and **7** in excellent yields. 1-Aza-2,5-di-*tert*-butyl-3,4-diisopropylidene-1-methyl-2,5-diborolane (**5c**) is obtained from the reaction of **5a** with two equivalents of *tert*-butyllithium. When the azadichlorodiborolane **5a** is reacted with $Li[BH_4]$ or $Li[DurBH_3]$ the Cl atoms are replaced by hydrogen or duryl and the liberated BH_3 hydroborates the isopropylidene groups to form the 2-aza-4,5-dicarba-4,5-diisopropyl-2-methyl-*nido*-hexaboranes **10a,b**. The new compounds are characterized by MS and ^1H, ^{11}B and ^{13}C NMR spectroscopy. X-ray structure analyses of **4c** and **4e** show that the two halves of the hexadienes are rotated by 80 to 90°. The solid state structures of the three duryl-substituted heterodiborolanes **5b**, **6**, and **7** reveal twist conformations of the C_2B_2X rings.

Introduction

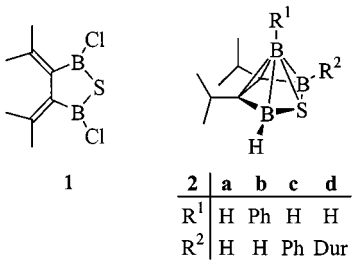
A number of larger azacarboranes with 10−12 vertices are known,[1] but, to the best of our knowledge, examples of smaller clusters with C,B,N framework atoms have not been published. Recently, we reported the hydroboration of appropriate heterocycles to produce carborane[2a] and heterocarborane[2b] compounds. In particular a combined substitution/hydroboration reaction of the thiadiborolane **1** with $Li[RBH_3]$ produces the 4,5-dicarba-2-thia-*nido*-hexaborane(5) derivatives **2a−d** and the thiadicarbanonaborane(8) **3**.[2b]

Analogously, it should be possible to synthesize other heterocarboranes as well. We describe here corresponding reactions of the 1-aza-1-methyl-2,5-diborolane **5a** to give derivatives of the new class of 2-aza-4,5-dicarba-*nido*-hexaboranes(6) (**10**). In addition, the syntheses of some boron-alkyl-substituted 1-aza-, 1-thia-, and 1-oxa-2,5-diborolanes are reported. They are potential precursors for heterodicarba-*nido*-hexaboranes.

Results and Discussion

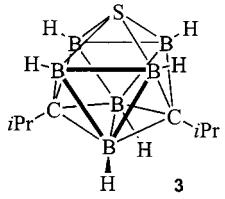
3,4-Diboryl-2,4-hexadienes

Attempts to replace the chlorine atoms in **1** by alkyl groups using organometallic reagents were not successful, as cleavage of B−S bonds occurred. However, as will be demonstrated, such chlorine substitution is possible in the case of the azadiborolane **5a**. Because of this limitation, a generally applicable approach to substituted heterodiborolanes was developed. The key compounds are 3,4-bis(monoorganoboryl)-substituted 2,4-hexadienes of type **4**, which can be transformed into heterodiborolanes.



1

2	**a**	**b**	**c**	**d**
R^1	H	Ph	H	H
R^2	H	H	Ph	Dur



3

In the bis(dimethoxy)- and bis(dichloroboryl)hexadienes **4a,b**, each of the boryl groups may be monosubstituted when bulky xylyllithium or duryllithium are used, to give the compounds **4c−e**. Whereas **4d** is isolated in 70% yield by distillation, the yield of the crystalline duryl compound **4e** was considerably less (13%). The chlorine derivative **4c** was obtained by recrystallization from hexane in 40% yield. When the sterically less demanding *tert*-butyllithium was reacted with **4a,b**, mixtures of alkylated species with different substitution patterns were obtained (Scheme 1).

The derivatives **4d,e** are not suitable for cyclization reactions because the methoxy groups are unreactive toward trimethylsilyl reagents. Also, attempts to exchange OMe for Cl in **4d** using an excess of BCl_3 or PCl_5 did not lead to

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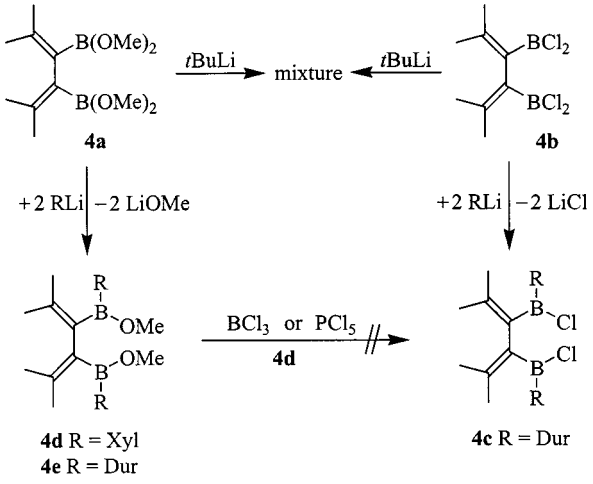
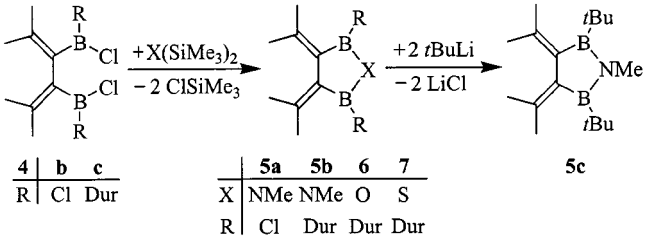


Scheme 1

the desired chlorine compound. Either **4d** did not react or decomposition occurred.

Heterodiborolanes

Cyclization reactions of 1,2-bis(dichloroboryl)- or 1,2-bis[chloro(organo)boryl]arenes, -alkenes, and -alkanes with reagents carrying trimethylsilyl as leaving groups have been successfully employed in the syntheses of various five and six-membered heterocycles.[3] Accordingly, compound **4b** reacts with one equivalent of $MeN(SiMe_3)_2$ to give the azadiborolane **5a** in 90% yield as a pale-yellow, air-sensitive liquid. In spite of the bulky duryl groups, compound **4c** yields the corresponding azadiborolane **5b** almost quantitatively when allowed to react with equimolar amounts of $MeN(SiMe_3)_2$. The formation of the duryl-substituted thia- and oxadiborolanes **6** and **7**, on the other hand, requires an excess of $O(SiMe_3)_2$ or $S(SiMe_3)_2$, the absence of solvent, and higher temperatures (120 °C). Under these conditions, **6** and **7** are obtained in very good yields (Scheme 2).



4	b	c
R	Cl	Dur

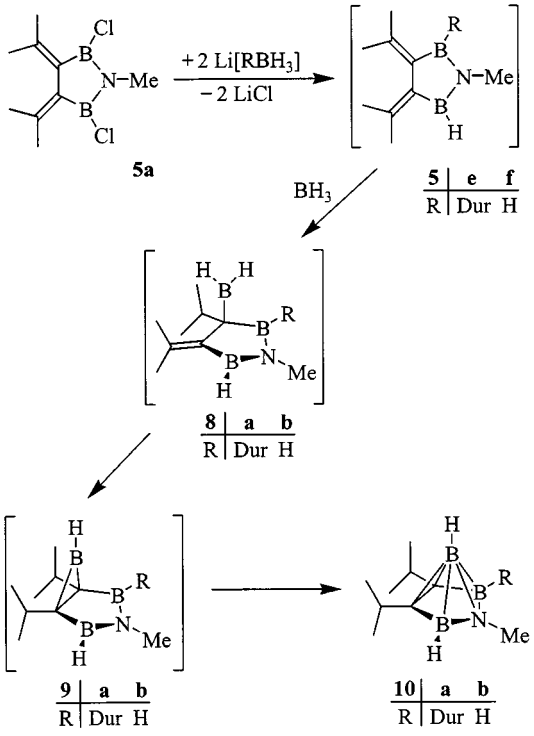
	5a	5b	6	7
X	NMe	NMe	O	S
R	Cl	Dur	Dur	Dur

Scheme 2

As shown above, monosubstitution of the boryl groups in the hexadienes **4a,b** can only be carried out when bulky substituents are used thus blocking a second substitution. A possible way to introduce smaller groups is the replacement of Cl in chloro-heterodiborolanes by alkyl groups; however, this was not successful for **1**. Only the azadiborolane **5a** is readily derivatized by this method. When treated with two equivalents of *tert*-butyllithium, compound **5a** generates the alkylated azadiborolane **5c** as a colorless, thermally labile liquid in 63% yield.

Azadicarba-*nido*-hexaboranes(6)

The only product of the reaction of **5a** with $Li[DurBH_3]$ is the 2-aza-4,5-dicarba-3-duryl-4,5-diisopropyl-2-methyl-*nido*-hexaborane (**10a**) carrying a duryl group in an equatorial position. This result is in agreement with the analogous reaction of the sulfur compound **1** with $Li[DurBH_3]$, whereas the reaction of **1** with $Li[PhBH_3]$ gives two isomers.[2b] This different behavior has been explained[2b] by a different reactivity of the lithium borates. In the first case, a duryl group would initially be transferred to the five-membered ring, which is then hydroborated by BH_3 to form the thiacarborane **2d**. In the second case, $Li[PhBH_3]$ would substitute the chlorine atoms by either hydrogen *or* a phenyl group and a mixture of two compounds (**2b,c**) is obtained. Such reasoning is not necessary if one assumes that the aryl group is always transferred first to give intermediates of type **5e,f** (if the starting material is **5a**) or the corresponding thia derivative (if the starting material is **1**), followed by hydroboration of the double bonds. This leads to a bicyclic organoborane of type **9** (and its thia analog) in which the boryl groups can easily change places by a rearrangement process prior to formation of the cluster structure (Scheme 3). Thus the finding of a mixture of two products (**2b,c**) having the phenyl group in either the apex *or* equatorial position and of only one product with an equatorial duryl substituent (**2d**, **10a**) can be explained by steric reasons. A duryl group in the apex position is strongly disfavored because the *ortho*-methyl groups would come very close to the isopropyl groups and the equatorial boron atoms.[4] For a phenyl group there is no such steric restriction, and both positions are possible.



5	e	f
R	Dur	H

8	a	b
R	Dur	H

9	a	b
R	Dur	H

10	a	b
R	Dur	H

Scheme 3

When **5a** is allowed to react with $Li[BH_4]$, a complex mixture of BH-substituted products is formed (Scheme 3). Three of them can be separated by GC/MS analysis. The compound with the shortest retention time is easily identified as the 2-aza-4,5-dicarba-4,5-diisopropyl-2-methyl-*nido*-hexaborane(6) (**10b**) by MS. The molecular peak is found at $m/z = 175$ and its *nido* structure is inferred from the ^{11}B NMR spectroscopic data. The two other compounds with longer retention times show MS peaks at $m/z = 189$ and 349, respectively. The first peak may be assigned to a product which is formed by hydroboration of **5f** with two equivalents of BH_3; the isotopic distribution pattern supports the presence of an additional BH_3 relative to **10b**. The isotopic pattern of the compound with $m/z = 349$ is in agreement with a molecular formula of $(i\text{PrC})_4(BH)_6(NMe)_2$ suggesting "dimerization" of the azacarborane **10b** or its precursors **8b** or **9b**. Since several structural isomers are possible, a geometry is not proposed at this point.

Spectroscopic and Structural Characterization

Both, the ^1H and ^{13}C NMR spectra of the diborylhexadienes **4c–e** exhibit two signals for the isopropylidene methyl groups. For the aryl ring C atoms in **4d** not adjacent to boron, three resonances are found consistent with freely rotating xylyl groups. The *ortho*-methyl groups of the aryl substituents in **4d,e** produce a strongly broadened signal which shows that ring rotation is somewhat restricted. The NMR spectra of the chlorine derivative **4c** show four singlets for the duryl-methyl protons, and all six aromatic carbon atoms can be distinguished, implying a fully restricted rotation about the B–C bond at ambient temperature. Surprisingly, only one slightly broadened signal for the methyl carbon atoms of the duryl groups is found.

The ^{11}B NMR shifts of the aza- and oxadiborolanes **5b** and **6** are almost identical ($\delta = 55$ and 54, respectively) and the *tert*-butyl derivative **5c** gives a signal at $\delta = 58$, whereas the value for the thiadiborolane **7** is $\delta = 72$. Although the ^1H and ^{13}C NMR spectroscopic data suggest that the duryl groups can rotate freely in **5b** and **6**, the data for **7** are consistent with a restricted rotation, which might be explained by the larger B–S distances compared to B–N and B–O, and the accompanying geometrical changes (see below).

The composition of **10a** follows from the ^1H and ^{11}B NMR and the mass spectra. Although **10a** could not be separated fully from by-products, most of the ^1H NMR signals were assigned. Four doublets are observed for the isopropyl groups and four singlets for the duryl substituents, as expected for the *nido* structure shown in Scheme 3. This is supported by the ^{11}B NMR spectroscopic data showing one doublet at $\delta = -41.5$ ($^1J_{BH} = 202$ Hz) for the apex BH, a second doublet at $\delta = 13.5$ ($^1J_{BH} = 130$ Hz, equatorial BH), and a singlet at $\delta = 23.1$ (equatorial B-duryl). Among the signals of the product mixture obtained from the reaction of **5a** with $Li[BH_4]$, the ^{11}B NMR spectroscopic data of **10b** can be identified when compared to those of **10a**. The equatorial boron atoms give a doublet at $\delta = 13.6$ ($^1J_{BH} = 155$ Hz) and for the apical boron a signal at $\delta = -45.2$ ($^1J_{BH} = 202$ Hz) is found. These data are very similar to those measured for the closely related thiacarborane **1d**, and calculated values[2b] and are in line with the proposed *nido*-6-⟨V⟩ clusters with a pentagonal aperture derived from a pentagonal bipyramid by removal of one apical vertex. This geometry was found for the solid state structure of **1d**. Both azacarboranes show NMR signals for one five-connected boron atom in the high-field region having large B–H coupling constants which are typical of apical bonding situations.[5] At lower field resonances for two three-connected boron atoms are found exhibiting coupling constants in the normal range for equatorial bonding.[5] The alternative *nido*-6-⟨IV⟩ structure established for $N_2B_4H_6$ derivatives which represents a fragment of a pentagonal bipyramid with a missing vertex at the base[6] can thus be excluded. Such a geometry has two kinds of four-connected boron atoms and would give rise to NMR signals in the region between the values found for **10a,b**.

Single crystal X-ray diffraction studies showed that the unit cell of the crystals of **4e** contained two independent molecules with crystallographic C_2 symmetry. The solid state structures of **4c** (Figure 1) and **4e** exhibit, as expected, similar features. The $Me_2C{=}C{-}B(OMe)/Cl$ units are

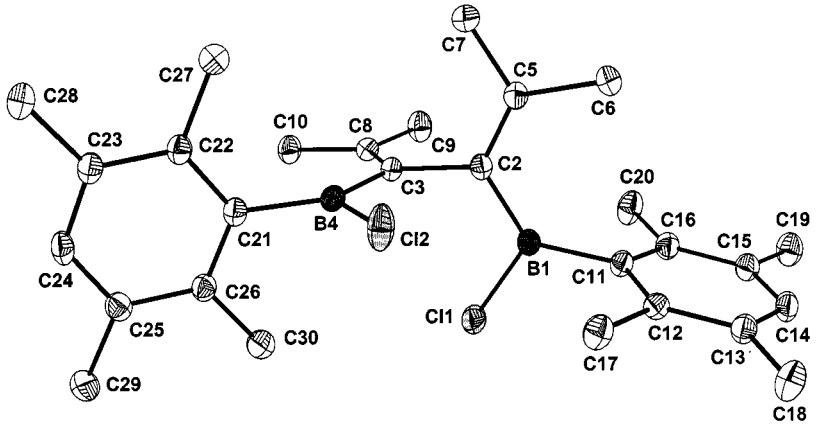


Figure 1. Molecular structure of **4c**; selected bond lengths [Å] (corresponding data for **4e** in square brackets): C3–C8 1.355(3) [1.328(8)], C2–C5 1.360(3) [1.355(8)], C2–C3 1.529(3) [1.520(10), 1.510(11)], C3–B4 1.540(4) [1.574(9)], C2–B1 1.541(4) [1.560(10)], B4–Cl2 1.799(3) [B–O 1.374(8)] B1–Cl1 1.802(3) [B–O 1.377(8)], B4–C21 1.582(4) [1.589(9)], B1–C11 1.581(4) [1.590(8)]

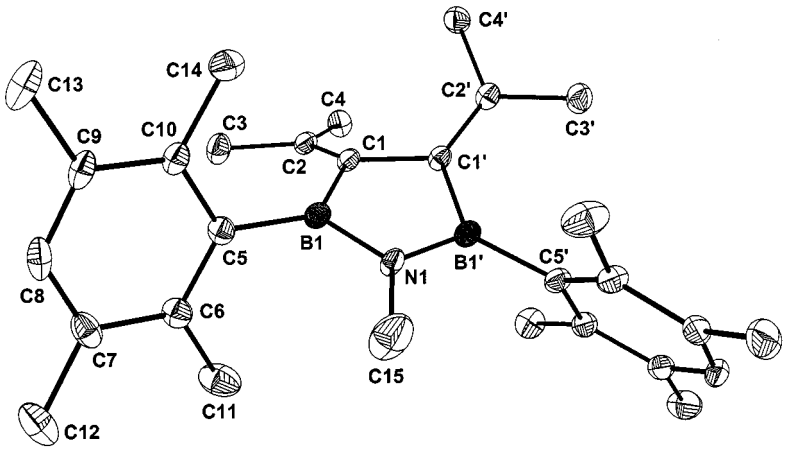


Figure 2. Molecular structure of **5b**; selected bond lengths [Å] and angles [°]: C1−C1′ 1.501(6), C1−C2 1.353(4), C1−B1 1.567(5), B1−C5 1.575(5), B1−N1 1.425(4), N1−C15 1.462(7); C2−C1−C1′−C2′ 51.0

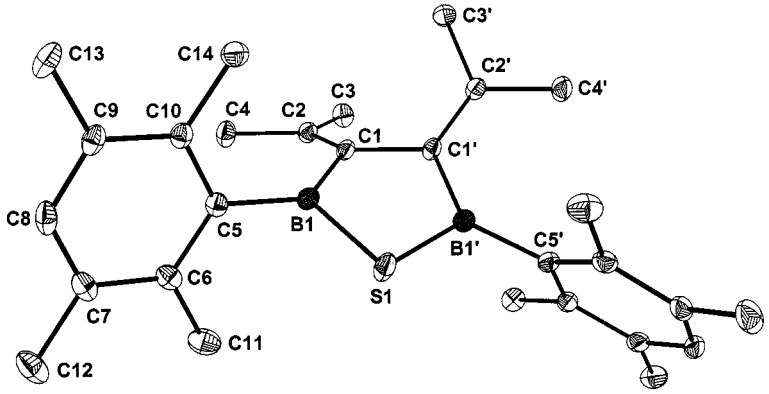


Figure 3. Molecular structure of **7**; selected bond lengths [Å] and angles [°] (corresponding data for **6** in square brackets): C1−C1′ 1.508(3) [1.500(4)], C1−C2 1.359(2) [1.358(3)], C1−B1 1.552(2) [1.571(3)], B1−C5 1.572(2) [1.570(5)], B1−S1 1.824(2) [B1−O1 1.400(2)]; C2−C1−C1′−C2′ 53.8 [50.2]

planar and the two halves of the molecules are rotated by 90° (**4c**) and by 78 and 82° in the two independent molecules of **4e**. This difference is most probably due to crystal packing effects. The duryl groups are positioned almost perpendicular to the $Me_2C{=}C{-}B(OMe)/Cl$ plane (85/89° in **4c** and 88/87° in **4e**).

The molecular structures of **5b** (Figure 2), **6** and **7** (Figure 3) exhibit C_2 symmetry, the axis bisects the C1−C1′ bond and runs through the heteroatom. The five-membered rings are twisted about the C1−C1′ bond by 17.9° (**5b**), 16.0° (**6**) and 22.3° (**7**), respectively (B1−C1−C1′−B1′ torsion angles). Because of the steric bulk, the two neighboring isopropylidene groups are twisted about the double bonds by 18.5° (**5b**), 19.0° (**6**), and 18.1° (**7**) as determined from the [C1′−C1−B1]/[C4−C3−C2] interplanar angles. The duryl groups adopt angles of 67° (**5b**), 66° (**6**), and 69° (**7**) with the corresponding C1−B1−X planes.

Conclusion

In this paper we report a route to transform the azaorganoborane heterocycle **5a** into the 2-aza-4,5-dicarba-*nido*-hexaboranes **10a,b**. The synthetic strategy involves a substitution/hydroboration reaction of **5a** with $Li[RBH_3]$ (R = H, Dur) to give the hydrido-1-aza-2,5-diborolanes **5e,f** which are hydroborated by the freed BH_3. Presumably, the final products **10a,b** are formed via the intermediates **8a,b** and **9a,b**. This reaction sequence allows the formation of other heterodicarbahexaboranes.

Experimental Section

All reactions and manipulations were performed in dry glassware under argon or nitrogen using standard Schlenk techniques. Solvents were distilled from appropriate drying agents under inert gas before use. − $Et_2O{\cdot}BF_3$ was used as the external standard for ^{11}B NMR. As internal references for ^1H and ^{13}C NMR spectra the signals of the deuterated solvents were used and calculated for TMS. NMR: Bruker AC 200 and Bruker DRX 200. − MS: Varian MAT CH7 and GCMS HP 5971. − The following starting materials were prepared by literature methods: lithium durylborate,[7] xylyllithium,[8] duryllithium.[8] Hexamethyldisilathiane, hexamethyldisiloxane, and heptamethyldisilazane were commercially obtained.

3,4-Bis[(chloro)durylboryl]-2,5-dimethyl-2,4-hexadiene (4c): A sample of duryllithium ($DurLi{\cdot}OEt_2$; 5.14 g, 24.8 mmol), obtained from DurBr and LiBu, was suspended in 150 mL of hexane, cooled to 0 °C, and **4b** (3.35 g, 12.4 mmol), dissolved in 20 mL of hexane, was added. The mixture was refluxed for 2.5 h and the precipitate

filtered off and washed twice with 20 mL of hexane. The filtrates were concentrated and cooled to −30 °C. Colorless **4c** (2.31 g, 5 mmol, 40%) precipitated from the solution. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.77, 1.82 (2 s, 2 × 6 H, $(CH_3)_2C$), 2.09, 2.10 (2 s, 2 × 6 H, *m*-aryl-CH_3), 2.24, 2.42 (2 s, 2 × 6 H, *o*-aryl-CH_3), 6.88 (s, 2 H, aryl). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 61. − ^{13}C NMR (C_6D_6, 50 MHz): δ = 19.4 (aryl-CH_3), 26.7, 23.7 [2 × C(*C*H_3)$_2$], 131.5, 131.8, 132.5, 133.8, 134.2 (5 × C_{aryl}), 145, 147 [both br, B*C*C$(CH_3)_2$ and BC_{aryl}], 164.1 [*C*$(CH_3)_2$]. − EI-MS: *m*/*z* (%) = 467 [M^+], (19), 432 [M^+ − Cl] (100), 413 (71), 332 [M^+ − Dur] (23).

3,4-Bis[(2,6-dimethylphenyl)methoxyboryl]-2,5-dimethyl-2,4-hexadiene (4d) and 3,4-bis[(duryl)methoxyboryl]-2,5-dimethyl-2,4-hexadiene (4e): The same procedure as described for **4c** was used. Instead of recrystallization the solvent was stripped off and the remaining viscous product was distilled under high vacuum. Yields: 790 mg (2 mmol, 70%) of **4d** and 100 mg (0.2 mmol, 13%) of **4e**. Compound **4e** crystallizes at room temp. after a few hours, whereas **4d** becomes a glass-like solid

4d: ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.65, 1.69 [2 s, 2 × 6 H, C$(CH_3)_2$], 2.15 (s, broad, 12 H, aryl-CH_3), 3.38 (O−CH_3), 6.91 (d, $^3J_{HH}$ = 7.5 Hz, 4 H, aryl), 7.08 (t, $^3J_{HH}$ = 7.5 Hz, 2 H, aryl). − ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 47. − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 21.3 (aryl-CH_3), 22.4, 24.0 [C(*C*H_3)$_2$], 53.5 (O−CH_3), 126.1, 127.1, 137.9 (3 × C_{aryl}), 141, 143 [both br, B*C*C$(CH_3)_2$ and BC_{aryl}], 147.3 [*C*$(CH_3)_2$]. − EI-MS: *m*/*z* (%) = 402 (22) [M^+], 298 (8) [M^+ − xylyl], 224 (66) [M^+ − (BXylOMe) − OMe], 209 (58) [M^+ − (BXylOMe) − OMe − Me], 147 (100) [XylBOMe$^+$].

4e: ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.84, 1.86 [2 s, 2 × 6 H, $(CH_3)_2$C], 2.17 (s, 12 H, *m*-aryl-CH_3), 2.22 (s, br, 12 H, *o*-aryl-CH_3), 3.32 (s, 6 H, O−CH_3), 6.90 (s, 2 H, duryl). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 49. − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 18.3, 19.6 (aryl-CH_3), 22.7, 24.4 [2 × C(*C*H_3)$_2$], 53.4 (O−CH_3), 131.1, 133.3, 133.7 (3 × C_{aryl}), 147.6 [*C*$(CH_3)_2$]. − EI-MS: *m*/*z* (%) = 458 (12) [M^+], 325 (9) [M^+ − duryl], 309 (4), 252 (37) [M^+ − DurB$(OMe)_2$], 237 (31), 175 (100) [DurBOMe$^+$].

1-Aza-2,5-dichloro-3,4-diisopropylidene-1-methyl-2,5-diborolane (5a): Heptamethyldisilazane (1.52 g, 8.69 mmol) was added at room temp. to a solution of **4b** (2.36 g, 8.69 mmol) in 50 mL of hexane. The mixture was refluxed for 4 h, the solvent evaporated and the residue distilled at 58 °C/8 × 10^{-3} mbar to give 1.80 g (7.8 mmol, 90%) of colorless, air-sensitive **5a**. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.71, 2.15 [2 s, 2 × 6 H, $(CH_3)_2$C, *exo* and *endo*], 2.89 (s, 3 H, N−CH_3). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 44. − ^{13}C NMR (C_6D_6, 50 MHz): δ = 23.1, 26.4 [2 × C(*C*H_3)$_2$, *exo* and *endo*], 29.7 (N−CH_3), 137 [br, B*C*−C$(CH_3)_2$], 146.0 [*C*$(CH_3)_2$]. − EI-MS: *m*/*z* (%) = 229 (51) [M^+], 214 (100) [M^+ − CH_3], 200 (7) [M^+ − C_2H_5], 122 (25) [M^+ − C_8H_{11}].

1-Aza-2,5-diduryl-3,4-diisopropylidene-1-methyl-2,5-diborolane (5b): Heptamethyldisilazane (325 mg, 1.85 mmol) was added to a solution of **4c** (650 mg, 1.4 mmol) in 25 mL of hexane. The mixture was stirred for 15 h, filtered and the solvent removed in vacuo. According to the ^{1}H NMR spectrum the reaction was almost quantitative. Recrystallization from hexane at −80 °C gave 425 mg (1 mmol, 70%) of colorless **5b**. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.81, 1.84 [2 s, 2 × 6 H, $(CH_3)_2$C], 2.16, 2.26 [2 s, 2×12 H, aryl-CH_3], 2.56 (N−CH_3), 6.94 (s, 2 H, duryl). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 55. − ^{13}C NMR (C_6D_6, 50 MHz): δ = 19.0, 19.6 (aryl-CH_3), 25.9, 23.2 [C(*C*H_3)$_2$], 31.6 (N−CH_3), 131.3, 133.5 (2 × C_{aryl}), 142.5 (C_{aryl}H), 143, 144 [both br, B*C*C$(CH_3)_2$ and BC_{Aryl}]. − EI-MS: *m*/*z* (%) = 425 (100) [M^+], 382 (17) [M^+ − C$(CH_3)_2$], 356 (12), 291 (17) [M^+ − Dur].

1-Aza-2,5-di-*tert*-butyl-3,4-diisopropylidene-1-methyl-2,5-diborolane (5c): *tert*-Butyllithium (24 mmol, 1.7 M in pentane) was added to a solution of **5a** (2.74 g, 12 mmol) in hexane at −50 °C. The mixture was stirred for 15 h at room temp., the liquid separated from the precipitate and the solvent removed in vacuo. The remaining oil was distilled at 10^{-2} mbar and a bath temperature of 50−90 °C yielding 2.06 g (7.5 mmol, 63%) of **5c**. Part of the product decomposed under these conditions to a dark brown solid. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ =1.19 (s, 18 H, *t*Bu), 1.66, 1.82 [2 s, 2×6 H, $(CH_3)_2$C], 2.88 (s, 3 H, N−CH_3). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 58. − ^{13}C NMR (C_6D_6, 50 MHz): δ = 21.4 [*C*$(CH_3)_2$], 22.9, 26.9 [2 × C(*C*H_3)$_2$], 28.6 [C(*C*H_3)$_3$], 32.9 (N−CH_3), 126.0 [*C*$(CH_3)_2$], 150 [br, B*C*C$(CH_3)_2$]. − EI-MS: *m*/*z* (%) = 273 (28) [M^+], 216 (24) [M^+ − *t*Bu], 174 (10) [M^+ − C$(CH_3)_2$], 160 (16), 41 (100) [$C_3H_5^+$].

2,5-Diduryl-3,4-diisopropylidene-1-oxa-2,5-diborolane (6): A sample of **4c** (400 mg) was refluxed for six hours in 10 mL of hexamethyldisiloxane. After removal of all volatile components, pure **6** remained as a colorless solid. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.69, 1.86 [2 s, 2×6 H, $(CH_3)_2$C], 2.12, 2.33 (2 s, 2×12 H, aryl-CH_3), 6.94 (s, 2 H, duryl). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 54. − ^{13}C NMR (C_6D_6, 50 MHz): δ = 19.5, 19.3 (2 × aryl-CH_3), 23.5, 25.6 [2 × C(*C*H_3)$_2$], 132.1, 133.5, 134.5 (C_{aryl}H), 147.5 [*C*$(CH_3)_2$]. − m.p. 190 °C (dec.). − EI-MS: *m*/*z* (%) = 412 (100) [M^+], 278 (25) [M^+ − Dur], 252 (38) [M^+ − DurBO].

2,5-Diduryl-3,4-diisopropylidene-1-thia-2,5-diborolane (7): A sample of **4c** (800 mg, 1.71 mmol) was heated for 4 h to 120 °C in 5 mL of hexamethyldisilathiane. The yellow solution was cooled to room temp. which caused the product to precipitate. The colorless solid **7** (610 mg, 1.4 mmol, 83%) was separated and washed with cold hexane. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.77, 1.82 [2 s, 2 × 6 H, $(CH_3)_2$C], 2.07 (s, 6 H, aryl-CH_3), 2.21 (s, 18 H, aryl-CH_3), 6.92 (s, 2 H, duryl). − ^{11}B NMR ($CDCl_3$, 64 MHz): δ = 72. − ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 18.9, 19.3 (2 × *m*-aryl-CH_3), 19.5, 19.8 (2 × *o*-aryl-CH_3), 22.8, 25.4 [2 × C(*C*H_3)$_2$], 131.2, 132.3, 132.5, 133.1, 133.5 (5 × C_{aryl}), 145 [br, B*C*−C$(CH_3)_2$ or BC_{aryl}], 145.5 [*C*$(CH_3)_2$], 148 [br, B*C*−*C*$(CH_3)_2$ or BC_{aryl}]. − EI-MS: *m*/*z* (%) = 428 (100) [M^+], 294 (20) [M^+ − Dur], 253 (69) [M^+ − C$(CH_3)_2$ − Dur].

2-Aza-4,5-dicarba-3-duryl-4,5-diisopropyl-2-methyl-*nido*-hexaborane(6) (10a): Lithium durylborate (990 mg, 6.2 mmol) was suspended in 60 mL of hexane. Compound **5a** (720 mg, 3.1 mmol) was added at room temp. and the mixture was stirred for 48 h. The solution was separated from the precipitate, the solvent evaporated and the residue distilled at 90−100 °C/8 × 10^{-3} mbar to yield 142 mg of a colorless oil consisting mostly of **10a**. − ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.95, 0.99, 1.17, 1.20 [4 d, 4×3 H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 8 Hz], 2.16, 2.19 (2 s, 2 × 3 H, *m*-methyl), 2.21, 2.23 (2 s, 2 × 3 H, *o*-methyl), 2.62 (s, 3 H, *N*-methyl), 6.88 (s, 1 H, *p*-aryl-CH). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 23.1 (s, B-duryl), 13.5 (d, B_{eq}H, $^1J_{BH}$ = 130 Hz), −41.5 (d, B_{apical}H, $^1J_{BH}$ = 202 Hz). − EI-MS: *m*/*z* (%) = 295 (20) [M^+ − B], 280 (3) [M^+ − B − CH_3], 252 (10) [M^+ − B − C_3H_7], 43 (100) [$C_3H_7^+$], 41 [$C_3H_5^+$].

2-Aza-4,5-dicarba-4,5-diisopropyl-2-methyl-*nido*-hexaborane(6) (10b): Li[BH_4] (155 mg, 5.75 mmol) was suspended in 50 mL of hexane and **5a** (660 mg, 2.88 mmol) was added at room temp. After 5 h of stirring at 40 °C, the solvent was removed at 1 mbar and the remaining colorless oil condensed into a dry-ice cooled trap. − ^{11}B NMR (C_6D_6, 64 MHz): δ = −45.2 (d, B_{apical}, $^1J_{BH}$ = 202 Hz), 13.6 (d, B_{eq}, $^1J_{BH}$ = 155 Hz). − EI-MS: *m*/*z* (%) = 175 (22) [M^+], 160 (10) [M^+ − Me], 146 (11) [M^+ − NMe], 132 (45) [M^+ − *i*Pr], 41 (100) [$C_3H_5^+$].

Table 1. Crystal data and structure refinement for **4c**, **4e**, **5b** **6** and **7**

	4c	**4e**	**5b**	**6**	**7**
Empirical formula	$C_{28}H_{38}B_2Cl_2$	$C_{30}H_{44}B_2O_2$	$C_{29}H_{41}B_2N$	$C_{28}H_{38}B_2O$	$C_{28}H_{40}B_2O_{0.09}S_{0.91}$
Formula weight	467.10	458.27	425.25	412.20	428.87
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2na$	$C2/c$	$C2/c$	$C2/c$
a [Å]	10.867(5)	8.852(4)	23.547(12)	23.555(15)	24.3272(16)
b [Å]	11.993(6)	13.814(7)	9.351(7)	9.139(5)	8.7071(6)
c [Å]	21.416(11)	23.761(11)	14.866(9)	15.018(9)	15.4201(10)
α [°]	90	90	90	90	90
β [°]	95.90(3)	90	126.83(3)	127.87(3)	128.412(1)
γ [°]	90	90	90	90	90
V [Å^3]	2776(2)	2906(2)	2620(3)	2552(3)	2559.3(3)
Z	4	4	4	4	4
Calcd. density [g/cm^3]	1.118	1.048	1.078	1.073	1.113
Absorp. coeff. [mm^{-1}]	0.247	0.062	0.060	0.061	0.133
F(000)	1000	1000	928	896	933
Crystal size [mm]	0.65 × 0.50 × 0.35	0.60 × 0.30 × 0.25	0.55 × 0.45 × 0.06	0.65 × 0.40 × 0.35	0.18 × 0.24 × 0.34
Θ_{max} [°]	26.00	23.00	25.00	25.00	28.30
Index ranges	−13/13, 0/14, 0/26	0/8, 0/15, 0/26	−17/25, −11/0, −17/17	−17/28, −10/0, −17/17	−31/25, 0/11, 0/20
No. of reflections					
Unique	5460	2037	1989	2240	3092
Observed [$I > 2\sigma(I)$]	5460	2802	1989	2240	8705
Transmission	0.999−0.875	0.998−0.914		0.999−0.964	0.928−0.763
Parameters	304	322	157	218	222
Final R indices					
$R1$ [$I > 2\sigma(I)$]	0.0527	0.0503	0.0595	0.0441	0.0441
$wR2$	0.1304	0.1055	0.1486	0.1102	0.1102
Res. electron dens.[e/Å^3]	+0.225 / −0.286	+0.171 / −0.185	+0.188 / −0.335	+0.175 / −0.128	+0.332 / −0.532

Crystal Structure Determinations: Crystal data and details of the structure determinations are presented in Table 1. Data collection for **4c**, **4e**, **5b**, and **6**: Siemens Stoe AED2 diffractometer (Mo-K_α radiation, ω-scans) at −70 °C; for **7**: Bruker AXS Smart 1000 area detector (Mo-K_α, ω-scans) at −100 °C. The structures were solved by direct methods (SHELXS 86)[9] and refined by least-squares based on F^2 with all measured reflections (SHELXL 97)[9] using anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located and refined isotropically (**6**, **7**) or inserted in calculated positions (**4c**, **4e**, **5b**). The structure refinement of **7** revealed that sulfur was partially replaced by oxygen (ca. 9%).

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-146539 (**4c**), -146540 (**4e**), -146541 (**5b**), -146542 (**6**), and -146543 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[4] As simple modeling of such a carborane shows the only possible orientation for an apical duryl group is parallel to the basal B−B and C−C vectors. Even in this position the *ortho*-methyl groups are very close to the isopropyl substituents and the equatorial boron atoms, but these steric interactions do not seem to be severe enough that one would completely exclude the possibility of a duryl group in the apical position. There are only two feasible ways from which such a carborane could originate: by an exchange of two boryl groups in **9a** or by a hydroboration with 1,2-diduryldiborane(6). Both reactions would involve intermediates with even shorter duryl−isopropyl contacts, too short for nonbonding interactions. Thus a carborane with a duryl group in an apical position should be stable but in the above discussed cases duryl−isopropyl interactions make the bicyclic intermediates energetically inaccessible so that a carborane cannot form this way.

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