Heterodicarba-*nido*-hexaboranes from Hydroborations of Exocyclic Unsaturated Heterodiborolanes

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Dedicated to Prof. Dr. Dieter Sellmann on the occasion of his 60th birthday

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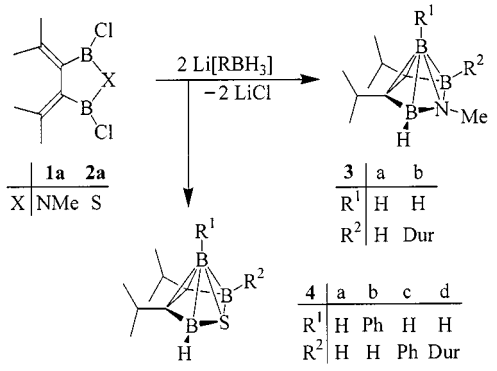
The hydroboration of 1-aza-2,5-diduryl-3,4-diisopropylidene- and 2,5-diduryl-1-thia-3,4-diisopropylidene-2,5-diborolanes (**1b**, **2b**) with equimolar amounts of BH_3·thf leads to the corresponding 2-aza-4,5-dicarba- and 4,5-dicarba-2-thia-*nido*-hexaboranes **3c** and **4e**. When an excess of BH_3·thf reacts with the azadiborolane **1b** the azadiborole derivative **5** is obtained as the main product. This surprising result is explained by the addition of three BH_3·thf moieties and the subsequent loss of B_3H_7·thf. The reaction of the sterically less hindered *tert*-butylazadiborolane **1c** with BH_3·thf yields two 2-aza-4,5-dicarba-*nido*-hexaboranes (**3d,e**), both of which carry a *t*Bu group in the apical position. A possible reaction pathway is suggested. The new heterocarboranes **3c,d,e** and **4e** are identified by multinuclear NMR spectroscopy and mass spectrometry. X-ray crystallographic studies of **3c** and **4e** confirm the *nido*-arrangement of the cluster atoms.

Introduction

Recently we described the formation of the 2-aza-4,5-dicarba-*nido*-hexaboranes(6) **3a,b** by substitution/hydroboration reactions of a chlorine-substituted azadiborolane with lithium borates (Scheme 1).[1] The corresponding 4,5-dicarba-2-thia-hexaboranes(5) (**4a**−**d**) have also been prepared by us exploiting the same methodology.[2] This route only gives access to fully BH-substituted derivatives or compounds with one aryl/alkyl group. Since by-products are also formed and the desired compounds are sensitive liquids which are difficult to separate, only the thiacarborane **4d** could be isolated. In order to overcome this problem the aza- and thiadiduryldiborolanes **1b**, **2b** and the didurylox-adiborolane **6** were synthesized[1] as potential starting materials for the preparation of crystalline and more stable heterodicarbahexaboranes. This paper describes how this goal is achieved by using BH_3·thf as the hydroboration agent and presents the first completely refined crystal structure analysis of an azadicarba-*nido*-hexaborane(6) and a thiadicarba-*nido*-hexaborane(5). Ab initio calculations are used to model the reaction sequence and give an explanation for the formation of different products depending on the ratio azadiborolane/BH_3·thf.

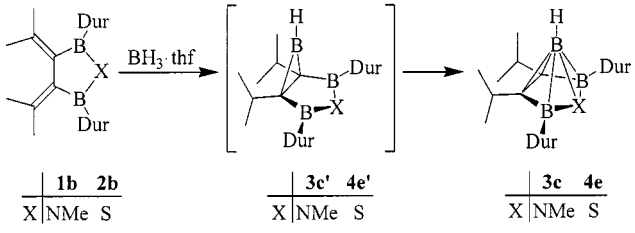


Scheme 1

Results and Discussion

Hydroboration with BH_3·thf

Treatment of the heterodiborolanes **1b** and **2b** with equimolar amounts of BH_3·thf in hexane solution leads to 2-aza-4,5-dicarba-3,6-diduryl-4,5-diisopropyl-2-methyl-*nido*-hexaborane(6) (**3c**) and 4,5-dicarba-3,6-diduryl-4,5-diisopropyl-2-thia-*nido*-hexaborane(5) (**4e**) in good yields (Scheme 2). These colorless, moisture-sensitive compounds are obtained by recrystallization from hexane. The formation of the heterocarboranes is assumed to proceed by bridging hydroboration of the double bonds by one molecule of BH_3. This generates bicyclic heteroorganoboranes (**3e′**, **4e′**) as intermediates which transform into the more stable polyhedral heterocarborane structures.



Scheme 2

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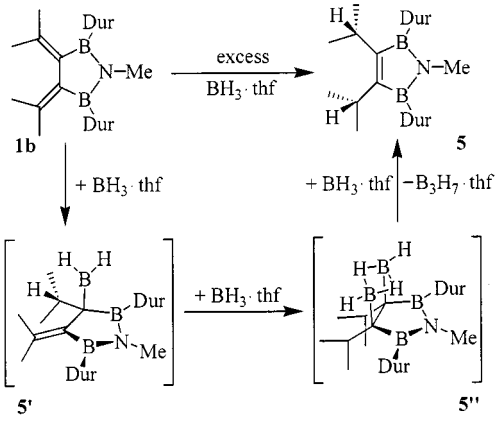
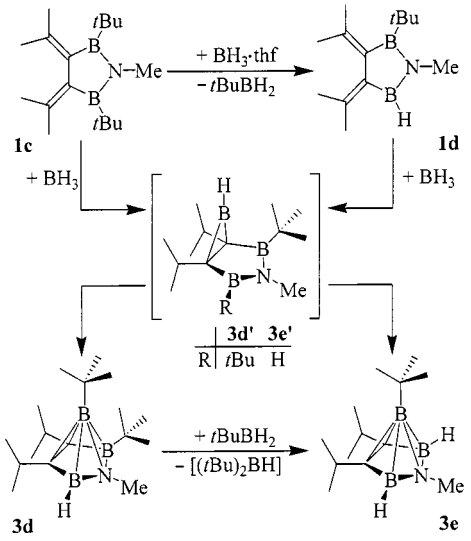
When an excess of BH_3·thf is employed for the hydroboration of **1b** the azadiborole **5**[3] is the main product instead of the azacarborane **3c**, which is now found in only small amounts. The reaction of **2b** with more than one equivalent of BH_3·thf, on the other hand, does not lead to the corresponding thiadiborole. In this case a partial exchange of substituents obviously takes place since, besides the thiacarborane **4e**, 1,2-diduryldiborane(6) is also found after workup. The formation of **5** formally corresponds to a 1,4-addition of H_2 to the hexadiene part of **1b**. In a related hydroboration reaction an exocyclic doubly unsaturated 1,3-diborolane yielded the expected tricarbahexaborane on treatment with $(EtBH_2)_2$ and, surprisingly, a diborole derivative.[4] Apparently, the excess of BH_3 present during the course of the reaction plays an important role. The addition of two BH_3 molecules to **1b**, one to each double bond, in a *syn* fashion would lead to the BH_2B bridged species **5′′** (via **5′**), which could lose B_2H_4 to give **5**. However, this process seems rather unlikely because of the inherent instability of B_2H_4 unless a suitable Lewis base (e.g. PMe_3) is present. More likely is an attack by a third BH_3·thf on the B_2H_4 moiety in **5′′** followed by the elimination of THF-stabilized B_3H_7 and the simultaneous generation of the azadiborole.

The second hydroboration of **1b** can either be intramolecular, leading to the bicyclic **3c′** (as shown in Scheme 2), or intermolecular involving an additional BH_3 molecule which yields **5′′** (according to Scheme 3). MP2 and DFT computations[5] indicate that the second possibility is favored over the intramolecular reaction by ca. 8 kcal/mol. It thus follows that if an excess of BH_3 is present in solution the BH_2B-bridged **5′′** is more likely to be formed than **3c′/3c**. The *anti* addition of two BH_3 molecules to **1b** is also possible but was not examined since only **5′′** can react to **5**. The transition states for the addition of the third BH_3 and the subsequent liberation of B_3H_7 could not be located. They are assumed to be low in energy. The proposed reaction pathway for the formation of **5** is shown in Scheme 3.



Scheme 3

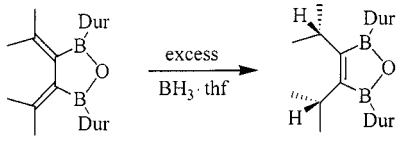
The reaction of the sterically less constrained di-*tert*-butylazadiborolane **1c** with one equivalent of BH_3·thf yields two azadicarbahexaborane(6) derivatives. Surprisingly, **3e** contains only one *t*Bu substituent, which is located in the apical position. Compound **3d** carries the expected two *t*Bu groups, one in the apical and the other in an equatorial position. At room temperature the ratio **3d:3e** is approximately 2.5:1. After the reaction no BH_3 is found, although $(tBuBH_2)_2$ and **1c** are detected. As ^{11}B NMR spectra reveal, refluxing the solution for some time gives about equal amounts of both azacarboranes and decreases the fraction of $(tBuBH_2)_2$. These findings suggest the following reaction sequence: BH_3 hydroborates **1c** to give a bicyclic intermediate **3d′** in which the BH group can easily exchange its position with one of the *t*BuB groups leading to **3d** (Scheme 4). Alternatively, prior to a hydroboration one of the *t*Bu groups or *t*BuB units in **1c** can be replaced by a hydrogen atom or a BH unit, which in both cases produces **1d** and $tBuBH_2$. After the addition of BH_3 to the double bonds the azaorganoborane **3e′** rearranges to **3e**. Since the ratio **3d:3e** changes at elevated temperatures, i.e. more **3e** is formed although no BH_3 is left in the mixture, additional reactions must occur. Two processes seem rational: **3d** and $(tBuBH_2)_2$ can exchange their H and *t*Bu substituents leading directly to **3e**, or additional BH_3 is generated from $tBuBH_2$. At higher temperatures the BH_3 immediately attacks the remaining **1c** to yield **3d** or **3e**, but now **3e** may be the favored product. Both routes imply the formation of $(tBu)_2BH$, which, however, was not observed in the NMR spectra. Nevertheless, this would explain why more of the azacarborane derivative with only one *t*Bu group is generated and less $tBuBH_2$ is found after heating.



Scheme 4

Hydroboration of the oxadiborolane **6** could in principle lead to an oxacarborane, a heterocarborane family which is as yet unknown. The reaction with BH_3·thf is considerably slower at ambient temperature than the above-mentioned BH_3 additions and produces a mostly insoluble colorless solid. No spectroscopic evidence for an oxacarborane or a bicyclic organoborane is found. In the mass spectrum of the soluble part peaks for the oxadiborole **7** are present (Scheme 5). Ab initio computations show that an oxadicarba-*nido*-hexaborane(5) structure should be more stable

than its bicyclic organoborane structure (of type **3d/e′**) if all substituents are H or only one boron atom carries a methyl group.[6] Accordingly, the reaction of **6** with BH_3 should yield an organoborane which might be highly reactive toward oligomerization and is thus not isolated.



6 **7**

Scheme 5

Hydroboration with Thexylborane

During the reaction of **1c** with BH_3·thf the starting material and $(t\text{BuBH}_2)_2$ are present in solution at the same time and no reaction between these components, i.e. the formation of an azacarborane carrying three *t*Bu groups, is observed. In order to evaluate the hydroboration ability of alkyldihydridoboranes $(\text{RBH}_2)_2$ thexylborane (thexyl = 1,1,2-trimethylpropyl) was allowed to react with the duryl-substituted heterodiborolanes **1b** and **2b** as well as with the *tert*-butyl-substituted **1c**. Compounds **1b** and **2b** do not react with $(\text{thexBH}_2)_2$ in refluxing hexane, probably for steric reasons. At room temperature **1c** also shows no reaction but refluxing the hexane solution for several days causes a slow exchange of substituents and a mixture of equatorially hydrogen-substituted azacarboranes is formed. Organodihydridoboranes are dimers in solution and must separate into monomeric species before they can react. Furthermore, it seems that a hydroboration reaction with RBH_2 is always preceded by an exchange of substituents reducing the steric bulk in the heterocycle and thereby allowing the reaction to take place. No fully alkyl-substituted azacarborane is found which means that a direct hydroboration of **1c** by thexBH_2 does not occur.

Spectroscopic and Structural Characterization

In the ^{1}H and ^{13}C NMR spectra of the heterocarboranes **3c** and **4e** all carbon atoms and methyl groups of the duryl rings and isopropyl substituents can be distinguished indicating a restricted rotation. The isopropyl protons of **4e** give two doublets and a septet, and for **3c** a septet and a pseudo triplet are observed. The signal of a cage carbon atom broadened by coupling to the neighboring boron atoms was observed only in the ^{13}C NMR spectrum of **3c**. The ^{11}B NMR spectra of the heterocarboranes show doublets at high field for the apical BH units at $\delta = -38.2$ ($^1J_{BH} \approx 202$ Hz) (**3c**) and $\delta = -35.2$ ($^1J_{BH} \approx 216$ Hz) (**4e**). The coupling constants have typical values for apical bonding situations. For the basal boron atoms singlets are observed at $\delta = 23.2$ (**3c**) and 28.5 (**4e**). Compounds **3d** and **3e** were obtained as a mixture and only their ^{11}B NMR spectroscopic data can be interpreted. Compound **3e** gives a singlet at $\delta = -34.2$ for the apical boron and a doublet at $\delta = 15.9$ ($^1J_{BH} \approx 160$ Hz) for the equatorial BH units whereas **3d** has a singlet at $\delta = -32.3$ (apical B), a singlet at $\delta = 30.1$ for the equatorial *t*Bu-substituted boron atom and a

Table 1. Crystal data and structure refinements for **3c** and **4e**

	3c	**4e**
Empirical formula	$C_{29}H_{44}B_3N$	$C_{28}H_{41}B_3S$
Mol. wt.	439.08	442.10
Crystal system	Triclinic	Monoclinic
Space group	*P*1(bar)	*C*2/*c*
Unit cell		
a [Å]	10.4398(9)	23.9309(5)
b [Å]	11.5443(10)	7.4024(2)
c [Å]	12.5675(11)	15.7655(4)
α [°]	81.287(2)	90
β [°]	88.893(2)	102.265(2)
γ [°]	67.792(2)	90
V [Å^3]	1384.9(2)	2729.05(12)
Z	2	4
Calcd. density [g/cm^3]	1.053	1.076
Absorp. coeff. [mm^{-1}]	0.058	0.132
F(000)	480	960
Crystal size [mm]	0.42 × 0.40 × 0.20	0.36 × 0.24 × 0.19
Θ_{max} [°]	23.0	26.4
Index ranges	−11/11, −12/12, −13/7	−29/29, 0/9, 0/19
No. of reflections		
Unique	3855	2794
Observed [$I > 2\sigma(I)$]	2545	1925
Transmission	0.928−0.835	0.822−0.894
Parameters	383	193
Final *R* indices		
R1 [$I > 2\sigma(I)$]	0.069	0.055
wR2	0.204	0.166
Res. electron dens. [e/Å^3]	+0.27/−0.27	+0.74/−0.19

doublet at δ = 15.9 ($^1J_{BH} \approx 160$ Hz). These data are in line with polyhedral *nido* structures.

The NMR spectroscopic data of **5** reflect its high symmetry. Two doublets and a septet are found for the isopropyl protons, the methyl groups of the freely rotating duryl rings give only two ^{1}H and ^{13}C NMR signals.

The solid state structures determined by X-ray crystallography (Table 1) confirm that the heterocarboranes **3c** (Figure 1) and **4e** (Figure 2) are *nido*-6<V> clusters as already suggested by their spectroscopic data. The shapes of the molecules are mostly determined by the bulky duryl and isopropyl groups; the apical BH units have only a minor influence. This is the reason for a disordered orientation of the molecules in the crystal, where the apical BH groups may lie above or below the idealized ring plane. The refinements of these disordered structures do not yield very accurate values for the distances and angles, which are in the expected ranges. The gross structural parameters of **3c** and **4e** are very similar. In both structures the substituents adopt almost identical positions: the duryl rings are virtually perpendicular to the B−C−C−B basal planes. The angles of these planes with the three-membered rings C1−B3−C2 in **3c** and C1−B2−C1′ in **4e** differ by 2.8° (58.4° vs. 55.6°) and, because of its smaller covalence radius, which results in shorter bond lengths, the distortion of the nitrogen atom from the B−C−C−B plane (24.8°) toward the apical atom is more pronounced than for the sulfur atom in **4e** (12.0°).

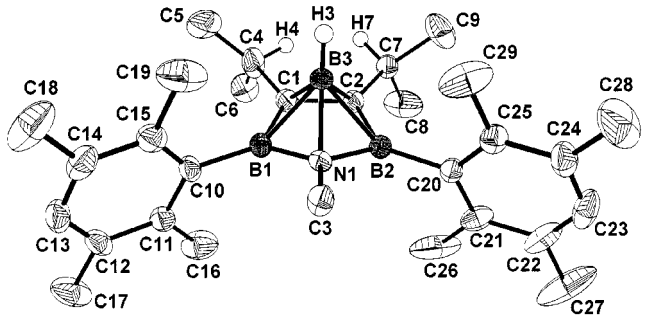


Figure 1. Molecular structure of **3c**; selected bond lengths [Å] and angles [°]: B1−C1 1.501(4), B2−C2 1.502(4), C1−C2 1.499(4), N1−B1/B2 1.491−1.547(8), B3−N1 1.676, 1.693(10), B3−B1/B2 1.901−1.963(8), B3−C1/C2 1.714−1.749(8); [C1−B3−C2]/[B1−C1−C2−B2] 58.4, [B1−C1−C2−B2]/[B1−N1−B2] 24.8

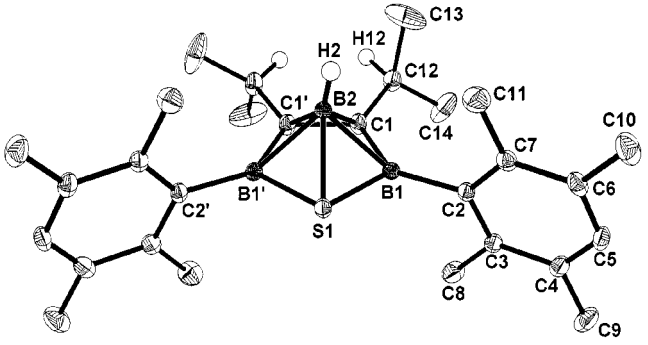


Figure 2. Molecular structure of **4e**; selected bond lengths [Å] and angles [°]: B1−S1 1.881(3), B1′−S1 1.860(4), B2−S1 1.989(4), B1−C1 1.493(4), C1−C1′ 1.508(4), B2−C1 1.606(5), B2−C1′ 1.632(5), B1−B2 1.917(5), B1′−B2 1.892(5), [C1′−B2−C1]/[B1′−C1′−C1−B1] 55.57, [B1−S1−B1′]/[B1−C1−C1′−B1′] 11.96

Conclusion

The above reactions clearly show the influence that the steric shielding of the boron atoms has during hydroborations. Compounds **1b** and **2b** carrying the most bulky groups give only apically BH-substituted heterocarboranes — a B-duryl unit in this location would interfere with the other substituents, especially with the second duryl group. However, under certain conditions, such as a large excess of BH_3·thf, other reactions also occur and $(DurBH_2)_2$ and the azadiborole **5** are obtained. On the other hand, the hydroboration of the double bonds in **1c** leads to **3d**, which surprisingly carries one of the *t*Bu groups in the apical position. In this case the smaller substituents also allow an exchange of *t*Bu for H generating $(tBuBH_2)_2$ and the azacarborane **3e** with only one *t*Bu group bound to the apical boron atom. This indicates that compounds with an apical *t*BuB unit are sterically and/or energetically highly favored over other possible *t*Bu substituted isomers. Compounds having apical BH and equatorial B*t*Bu units were not detected. Furthermore, it can be concluded that neither $tBuBH_2$ nor $thexBH_2$ is an efficient hydroborating agent in the above described cases. Again, steric reasons are the most likely factors inhibiting a reaction.

Experimental Section

General: 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 ^{1}H and ^{13}C NMR spectra the signals of the deuterated solvents were used and calculated relative to 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: **1b, 1c**, **2b**, and **6**,[1] 1,2-dithexyldiborane(6).[7] BH_3·thf (1 M) was commercially obtained (Aldrich).

2-Aza-4,5-dicarba-3,6-diduryl-4,5-diisopropyl-2-methyl-*nido*-hexaborane(6) (3c): To a solution of **1b** (330 mg, 0.78 mmol) and 25 mL of hexane was slowly added BH_3·thf (0.78 mL, 0.78 mmol) at −25 °C. The solution was stirred at this temperature for 15 min. and for 15 h at ambient temperature. The solvent was removed, the remaining solid dissolved in hexane and the solution filtered. From the concentrated solution 255 mg (0.58 mmol, 74%) of **3c** was obtained at −30 °C. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.22 [pseudo t, $^3J_{HH}$ = 7 Hz, 12 H, $CH(CH_3)_2$], 2.16, 2.18, 2.21, 2.34 (4 s, 4×6 H, C_{aryl}-CH_3), 2.44 [sept, $^3J_{HH}$ = 7 Hz, $CH(CH_3)_2$], 2.53 (N−CH_3), 6.97 (s, 2 H, duryl). − ^{11}B NMR (C_6D_6, 64 MHz): δ = −38.2 (d, B_{apical}, $^1J_{BH}$ = 202 ± 3 Hz), 23.2 ($B_{eq.}$). − ^{13}C NMR (C_6D_6, 50 MHz): δ = 19.8, 20.0, 20.5, 21.4 (4×C_{aryl}-CH_3), 24.5, 24.2 [2×$CH(CH_3)_2$], 25.5 [$CH(CH_3)_2$], 31.8 (N−CH_3), 90.1 [br, BC−$CH(CH_3)_2$], 132.1, 133.3, 133.5, 135.4, 138.0 (5×C_{aryl}). − EI-

MS: *m/z* (%) = 439 [M^+] (98), 427 [M^+ − BH] (81), 396 [M^+ − *i*Pr] (100), 384 (72). − CI-MS (isobutane): *m/z* (%) = 440 [M^+ + H] (100), 428 [M^+ − B] (46), 296 [M^+ + H − BDur] (29). − HR-EIMS ($^{12}C_{29}{}^{1}H_{44}{}^{14}N^{11}B_3$): calcd. 439.3757; found 439.3753 (Δmmu = +0.4).

4,5-Dicarba-3,6-diduryl-4,5-diisopropyl-2-thia-*nido*-hexaborane(5) (4e): The same procedure was used as described for **3c**. Yield: 74 mg (60%) − ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.12, 1.20 [2 d, 2×6 H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$], 2.14, 2.16, 2.33, 2.50 (4 s, 4×6 H, C_{aryl}-CH_3), 2.53 [sept, $^3J_{HH}$ = 7 Hz, CH(CH$_3$)$_2$], 6.95 (s, 2 H, duryl) − ^{11}B NMR (C_6D_6, 64 MHz): δ = −35.2 (d, B_{apical}, $^1J_{BH}$ = 216 ± 3 Hz), 28.5 ($B_{eq.}$) − ^{13}C NMR (C_6D_6, 50 MHz): δ = 20.0, 20.5, 20.7, 21.1 (4×C_{aryl}-CH$_3$), 23.23, 23.28 [2×CH(CH$_3$)$_2$], 28.6 [CH(CH$_3$)$_2$], 132.3, 133.57, 133.62, 134.9, 138.0 (5×C_{aryl}). − EI-MS: *m/z* (%) = 442 [M^+] (100), 399 [M^+ − CH(CH$_3$)$_2$] (21), 266 [M^+ − *i*Pr − Dur] (46), 223 [M^+ − *i*Pr$_2$ − Dur] (30). − HR-EIMS ($^{12}C_{28}{}^{1}H_{41}{}^{11}B_3{}^{32}S$): calcd. 442.32080; found 442.32037 (Δmmu = −0.4).

1-Aza-2,5-diduryl-1,2-dihydro-3,4-diisopropyl-1-methyl-2,5-diborole (5): A sample of **1b** (80 mg 0.19 mmol) was dissolved in 5 mL of hexane and treated with BH_3·thf (0.6 mL, 0.6 mmol, excess) at ambient temperature. The mixture was stirred for 15 h, all volatile components were removed in vacuo and the residue was dissolved in hexane. The filtered and concentrated solution gave, at −30 °C, 42 mg (0.1 mmol, 50%) of crystalline, colorless and air-stable **5**. − ^{1}H NMR (C_6D_6, 200 MHz): δ = 1.07, 1.11 [2 d, 2×6 H, $^3J_{HH}$ = 7 Hz, CH(CH_3)$_2$], 2.14, 2.27 (2 s, 2×12 H, C_{aryl}-CH_3), 2.34 (s, 3 H, N−CH_3), 3.01 [sept, $^3J_{HH}$ = 7 Hz, CH(CH$_3$)$_2$], 6.92 (s, 2 H, duryl). − ^{11}B NMR (C_6D_6, 64 MHz): δ = 54. − ^{13}C NMR (C_6D_6, 50 MHz): δ = 19.3, 19.7 (2×C_{aryl}-CH$_3$), 22.5 [CH(CH$_3$)$_2$], 28.9 [CH(CH$_3$)$_2$], 31.9 (N−CH_3), 131.4, 133.2, 133.5 (3×C_{aryl}), 141.6 [br, BC−C(CH$_3$)$_2$], 142.6 (B-C_{aryl}). − EI-MS: *m/z* (%) = 427 [M^+] (100), 384 [M^+ − *i*Pr] (62), 293 [M^+ − durylH] (30).

2-Aza-1,3-di-*tert*-butyl-4,5-dicarba-4,5-diisopropyl-2-methyl-*nido*-hexaborane(6) (3d) and 2-aza-1-*tert*-butyl-4,5-dicarba-4,5-diisopropyl-2-methyl-*nido*-hexaborane(6) (3e): BH_3·thf (2.1 mL, 2.1 mmol) was slowly added to a solution of **1c** (560 mg, 2.1 mmol) in 25 mL of hexane at −60 °C. The mixture was stirred for 15 h and analyzed by ^{11}B NMR spectroscopy and GC/MS showing a ratio **3e:3d** of 1:2.5. After refluxing the solution for 6 h, samples were again taken and analyzed. The ratio **3e:3d** was now 1:1. All volatile components were removed at about 10 mbar leaving behind a colorless oil (a mixture of **3d**, **3e**) and starting material **1c**. − ^{11}B NMR (C_6D_6, 64 MHz): δ = −34.2 (s, **3e**), −32.3 (s, **3d**), 15.9 (d, $^1J_{BH}$ ≈ 160 Hz, **3e,d**), 30 (s, **3d**). − EI-MS (**3e**): *m/z* (%) = 231 [M^+] (27), 216 [M^+ − Me] (4), 188 [M^+ − *i*Pr] (23), 174 [M^+ − *t*Bu] (13), 41 (100). − EI-MS (**3d**): *m/z* (%) = 287 [M^+] (5), 230 [M^+ − *t*Bu] (4), 41 (100).

X-ray Crystallographic Study: Crystallographic data and details of the structure determinations are presented in Table 1. Data collection: Bruker AXS Smart 1000 area detector (Mo-K_α, ω-scans) at −100 °C. The structures were solved by direct methods and refined by least-squares based on F^2 with all measured reflections[8] and using anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located and refined isotropically or inserted in calculated positions. A refinement of **4e** in the space group *Cc* gave no satisfactory results.

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-151546 (**3c**) and -151547 (**4e**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CBV2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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