Derivatives of Aza-*nido*-tetraborane and Diaza-*arachno*-pentaborane from Tri-*tert*-butylazadiboriridine

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The Lewis acids RBH_2 are added to the basis B−B bond of tri-*tert*-butylazadiboriridine, NB_2tBu_3 (**1a**), to give 5-alkyl-1,2,3-tri-*tert*-butyl-1-aza-*nido*-tetraboranes of type **3** (two *endo*-H atoms at B5) or type **4** (one H atom in a B2−B5 bridging position, one *exo*-H atom at B5), either as a mixture of **3** and **4** (**3**, **4b**−**d**: R = Me, *t*Bu, CMe_2iPr) or with the isomer **4** in high excess (**4e**, **f**: R = Ph, *s*Bu). The reaction of dialkylboranes R_2BH with **1a** yields 5,5-dialkyl-1,2,3-tri-*tert*-butyl-1-aza-*nido*-tetraboranes of type **4** (one H atom in a B2−B5 bridging position; **4g**, **h**: $R_2 = Et_2$, cycloocta-1,5-diyl). In boiling THF, trialkylboranes BR_3 transform **1a** into NB_2tBu_2R which, expectedly, dimerizes spontaneously to give a dialkyl-tetra-*tert*-butyl-2,5-diaza-*nido*-hexaborane of type **2** (**2a**, **b**: R = Me, Et). The products of the addition of aminoboranes $H_2B{=}NRR'$ to **1a** are identified as alkyl derivatives of 2,5-diaza-*arachno*-pentaborane, $N_2B_3H_2tBu_3RR'$ (**5a**−**d**, R/R′ = H/Pr, H/*t*Bu, Me/Me, Et/Et). The aminoborane $H_2B{=}NiPr_2$ with a sterically more demanding amino group hydroborates the B−B bond of **1a** to give the acyclic product $iPr_2N{=}BH{-}B(tBu){-}N(tBu){=}B(tBu)H$ (**6**). In contrast to the B atoms, the N atoms in the electron-deficient cluster skeletons of **2**−**5** need not take part in (3c,2e) bonds of the σ type. The molecular structures of **4c**, **5d**, and **6** are confirmed by X-ray structural analyses.

Azadiboriridine NB_2H_3 may be discussed in terms of a Hückel 2π-electron system, isoelectronic with the cyclopropenyl cation $C_3H_3^+$ and characterized by a large resonance energy, but only a weak BB π bond[1], or in terms of a diborane(2) H−B=B−H which donates π electrons to a nitrene NH via a σ bond and accepts nitrene p electrons via antibonding π orbitals[2]. Actually, the NBB ring of $MesNB_2tBu_2$ exhibits the shortest BB bond ever found experimentally and a C−B−B−C chain which is not far away from linearity[3]. Beyond such structural peculiarities, azadiboriridines have proven unexpected reactivity. The tri-*tert*-butyl derivative NB_2tBu_3 (**1a**) is stable at ambient temperature, but alkyl groups with less steric demand than *tert*-butyl make molecules $NB_2RR'R''$ unstable with respect to a fusion reaction to give diaza-*nido*-hexaboranes **2** [eq. (1)][4,5]. The BB bond of **1a** is easily cleaved by the action of CO or NR (from RN_3) [eq. (2)][6] or by the addition of unsaturated molecules a=x (a=x: alkynes[4], iminoboranes[4], oxoalkanes[7]) [eq. (3)]. Lithium alkanides open a BN bond of **1a** followed by a migration of *t*Bu [eq. (4)][3]. The BB bond of **1a** is protonated by Broensted acids HX [eq. (5)][8], and the Lewis acid BH_3 adds in the same way across the BB bond of **1a** [eq. (6)]; the driving force of the addition reaction (6) exceeds that of the reaction of BH_3 with the Lewis base NH_3[9]. It is the basicity of **1a** that prompted us to investigate the addition of the boranes H_2BR, HBR_2, BR_3 and $H_2B{=}NRR'$ to **1a**.

Aza-*nido*-tetraboranes from 1a

We first generalized the reaction (6) by starting from $L{-}BH_3$ with L = NMe_3, NEt_3, SMe_2 instead of $THF{-}BH_3$. There is a 100% yield of **3a** in the case of L = SMe_2 after 5 min at 25 °C in hexane. The low solubility of $Me_3N{-}BH_3$ makes the addition of BH_3 to **1a** a slow reaction in hexane; upon addition of a small amount of THF, however, the reaction is completed within 5 min. The application of $Et_3N{-}BH_3$ requires stirring for 12 h in hexane/THF (1:1), thus exhibiting some steric strain from the back of the base.

A solution of $(MeBH_2)_2$ in THF (freshly prepared from $Li[MeBH_3]$ and ethereal HCl) reacts rapidly with **1a** to yield **3b**. This product is not stable in THF. After 20 d at 21 °C or after 8 h at 55 °C, a 15:85 mixture of **3b** and **4b** is formed. This ratio is not changed by further heating. It is considered to be an equilibrium mixture.

An equilibrium mixture of **3c** and **4c** in the ratio 25:75 at 21 °C is immediately formed, when a solution of $(tBuBH_2)_2$ in THF (freshly prepared from $Li[tBuBH_3]$ and I_2) is added to **1a**. The ratio observed at 21 °C is not changed by applying an excess of one of the starting materials, by varying the temperature of formation, or by replacing the solvent THF by pentane. The ratio is slightly changed, however, by varying the temperature during the NMR observation. We followed the ^1H-NMR intensities in a 0.11 ^{m} solution of **3c**/**4c** in $[D_8]THF$ at temperatures ranging from −60 to 40 °C, and we found constants *K* for the

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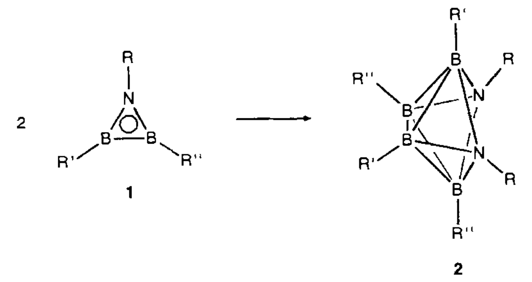

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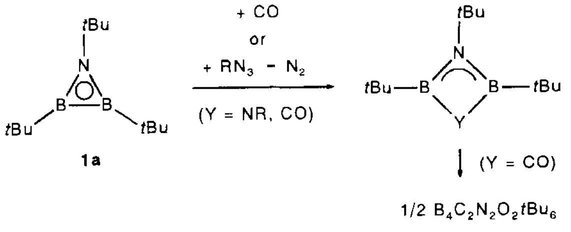

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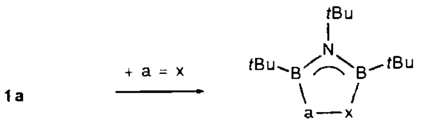

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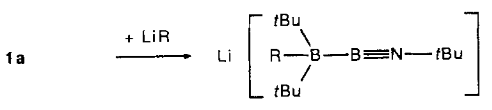

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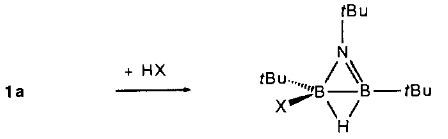

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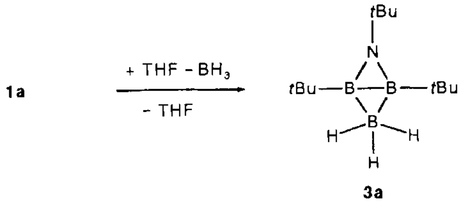
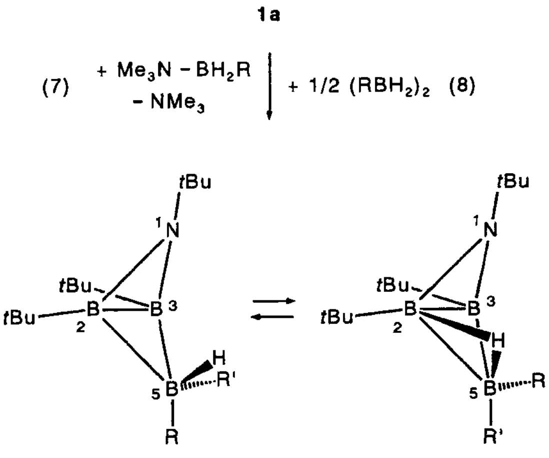


(6)

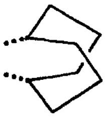
rapid rearrangement equilibrium **3c** ⇄ **4c** in a range from 4.8 to 2.8. A linear plot of six values ln*K* against 1/*T* makes values $\Delta H = -3.0\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = -1.0\ \mathrm{J\ K^{-1}\ mol^{-1}}$ for the rearrangement **3c** → **4c** available. These data illustrate that a BHB hydrogen bridge is energetically favored as compared with an *endo*-bound H atom in a *nido* cluster structure; in addition, they reveal the steric rigidity of such a bridged structure. – Though spontaneous in solution, a rearrangement **4c** → **3c** does not occur in the crystal. We grew a crystal of **4c** from an equilibrium mixture in hexane at −27°C in the course of 7 d, which turned out to be suitable for an X-ray determination of its structure. Apparently, **4c** is less soluble than the more symmetric and less polar **3c**. The ratio **3c**/**4c** is unaltered in the mother liquor, and this ratio is immediately established, when crystalline **4c** is redissolved in hexane.

The thexylborane (iPr$-$CMe$_2-$BH$_2$)$_2$ and **1a** give an equilibrium mixture of **3d**/**4d** in a 7:93 ratio, whereas the products from the reaction of $(PhBH_2)_2$ in THF (freshly prepared from $Li[PhBH_3]$ in THF and ethereal HCl) or from the reaction of Me_3N-BH_2*s*Bu in hexane with **1a** are almost exclusively the H-bridged isomers **4e**, **f**; only traces of **3e**, **f** are detectable by the observation of a few NMR peaks of an intensity less than 5% at the expected shift values, and there are also some peaks of unidentified products in the NMR spectra of **4e**. The product **4f**, on the other hand, exhibits two sets of NMR signals in a 54:46 ratio that represent the diastereomers to be expected, when a chiral molecule of type **4** is formed from prochiral **1a** and racemic *s*BuBH$_2$. – The dialkylboranes $(Et_2BH)_2$ and $(C_8H_{14}BH)_2$ (9-borabicyclo[3.3.1]nonane) add **1a** to give exclusively the products **4g** and **4h**, respectively.

All products of type **3**/**4** or **4** are formed quantitatively without byproducts according to the ^{11}B-NMR spectra of the reaction solutions. The yields of pure products are less than 100%, partly much less, because the products are thermally unstable and are easily soluble in polar and unpolar solvents, thus causing loss upon both distillation and crystallization. – It is noteworthy that the reaction from **3** to **4** or vice versa involves a kind of inversion of configuration at the five-coordinate B5 atom.



3a-f **4b-h**

	R,R'	Eq.	%3/4
3, 4a	H,H	(7)	100/0
b	Me,H	(8)	15/85
c	*t*Bu,H	(8)	25/75
d	CMe$_2$(iPr),H	(8)	7/93
e	Ph,H	(8)	<5/>95
f	*s*Bu,H	(7)	<5/>95
g	Et,Et	(8)	0/100
h		(8)	0/100

The structures of **3b**–**d** and **4b**–**h** in solution are deduced from NMR data (Tables 1, 2), which are in accord with the known crystal structures of **3a**[9] and of **4c**, presented here.

Two ^{11}B-NMR signals in the ratio 2:1 and two ^{1}H- and ^{13}C-NMR signals for *t*Bu in the ratio 2:1 (or in the ratio 2:1:1 in the case of **3c**) prove the C_s symmetry of type **3** products. The C_1 symmetry of type **4** products causes a 1:1:1 ratio of the corresponding B atoms and *t*Bu groups (1:1:1:1 in the case of **4c**). The H atoms, which are terminally bound to boron, give quartets in the ^{1}H-NMR spectrum; the more strongly bound *exo*-H atoms of **4b–f** [^{1}J(BH) = 105–116 Hz] are low-field-shifted with respect to the less strongly bound two equivalent *endo*-H atoms of **3a–d** [^{1}J(BH) = 67–69 Hz]. The bridging H atoms of **4b–h** are found in a typical high-field range. The 2D ^{11}B/^{1}H-NMR spectra of **3b–d** and **4b–f** reveal couplings of the terminally bound H atoms with B5; couplings of the bridging H atoms with B2 and B5 are found for **4b–h**. Cross peaks in the 2D ^{11}B/^{11}B-NMR spectra are present for B2,3/B5 in **3b,c** (the amount of **3d** in the mixture **3d**/**4d** is too small for the detection of such a cross peak) and for B3/B5 in **4b–d, f, g**. The cross peaks for the bridged atoms B2 and B5 are expectedly weak and are found in the case of **4b, e–g** (including both diastereomers of **4f**); no cross peaks B2/B3 can be detected in the case of **4b–h** because of the "bridging" imino group[10,11].

Table 1. ^{1}H-NMR signals of **3b–d** and **4b–h**

	H_μ	H(B5)[a]	H(*t*Bu) (s, 27 H)	H(R)
3b[b]	/	1.44	1.07 1.35 2:1	0.20 s, 3 H
c	/	1.74	1.17 1.30 2:1	1.16 s, 9 H
d		1.76[c]	1.19 1.23 2:1	0.98 1.28 2.01 d, s, sept, 6:6:1, 13 H
4b[b]	0.64	2.55	1.01 1.11 1.34 1:1:1	0.65 s, 3 H
c	0.43	3.66	1.07 1.17 1.23 1:1:1	1.18[d]
d	0.38	3.42	1.10 1.17 1.24 1:1:1	0.86 0.98 1.14 1.28 1.53 s, d, d, s, sept, 3:3:3:3:1, 13 H
e	1.01	3.38	1.09 1.11 1.26 1:1:1	7.00-7.30 5 H
f	0.83	2.55[e] 2.64[e]	1.16 1.27 2:1	0.91 1.05 1.27 1.45 1.69 5 mc[f], 3:1:3:1:1, 9 H
g	0.29		1.06 1.10 1.25 1:1:1	0.76 1.00 1.17 1.23 1.37 5 mc, 2:3:3:1:1, 10 H
h	0.77		1.12 1.18 1.21 1:1:1	1.58 1.74 1.88 2.00 2.18 5 mc, 14 H

[a] q; ^{1}J = 69, 67 Hz (**3b, c**, 2 H_{endo}); ^{1}J = 105, 116, 110, 110, ca. 110 Hz (**4b–f**, 1 H_{exo}). – [b] Solvent [D$_8$]THF. – [c] Signal detected by a 2D ^{11}B/^{1}H experiment – [d] Assignment of 4 *t*Bu groups arbitrary. – [e] Signals of diastereomers. – [f] Diastereomers and diastereotopic CH$_2$ protons cause complicated peak structures.

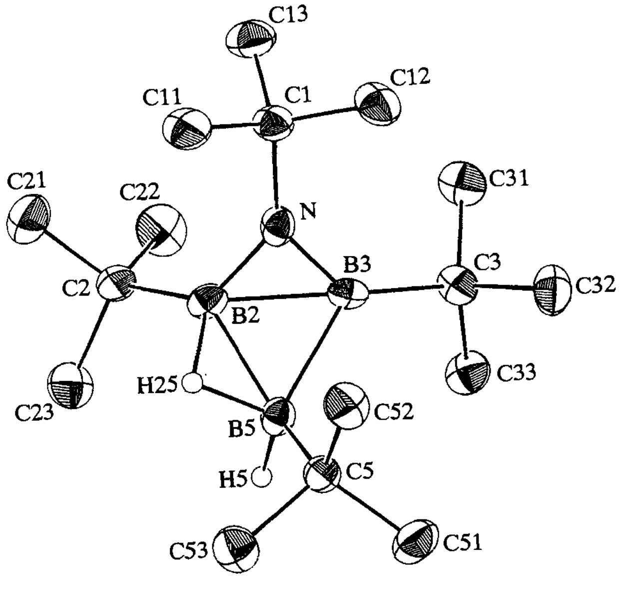
Table 2. ^{11}B- and ^{13}C-NMR signals of **3b–d** and **4b–h**

	^{11}B2	^{11}B3	^{11}B5	^{13}C(*t*Bu) (s, 3 q)[a]			
3b[b]	29.0	29.0	-2.6[c]	53.3	30.8	30.8	32.7
c	28.0	28.0	6.8[c]	53.1	31.3	31.3	32.3
d	27.6	27.6	ca. 8[d]	ca. 55[d]	31.6	31.6	32.3
4b[b]	22.6	32.5	1.9	53.3	30.7	32.1	33.5
c	22.6[e]	38.7	12.8[f]	54.5	31.0	31.4	32.2
d	24.7[e]	40.1	8.0[f]	54.7	31.0	31.5	32.2
e	20.7	31.7	6.0	53.9	30.8	32.2	33.5
f[g]	24.3	31.6	3.3	52.5	31.0	32.16	33.5
	24.7	31.6	4.5	52.5	31.1	32.19	33.6
g	19.8[e]	33.1	16.8	52.9	30.9	31.1	32.3
h	26.6	36.1	16.0[f]	53.9	31.2	32.0	32.4

[a] ^{13}C-NMR signals of R [the signals of *B*-bound C atoms could not be detected or were found to be broad (**4h**)]: δ = 34.1 (q) (**3c**); 18.3, 26.0 (2 q) (**3d**); 34.5 (q) (**4c**, assignment of 4 *t*Bu groups arbitrary); 18.9, 19.3, 28.3, 29.8 (4 q), 43.6 (d) (**4d**); 127.9 128.1, 132.7, (3 d) (**4e**); 14.2/14.4 (q), 17.1/17.5 (q), 27.9/28.0 (t) (**4f**); 12.9, 15.9, (2 q) (**4g**); 24.3, 24.4, 33.6, (3 t, 1:3:2), 26.2 (br.), 35.8 (br.) (**3h**). – [b] Solvent [D$_8$]THF; ^{13}C-NMR at 75.429 MHz. – [c] t, ^{1}J = 69, 67 Hz (**3b, c**). – [d] Signals not distinguishable from those of **4d**. – [e] d, ^{1}J = 60, 55, 49 Hz (**4c, d, g**). – [f] d, ^{1}J = 116, 110, 55 Hz (**4c, d, h**). – [g] Diastereomers in the ratio 53:47.

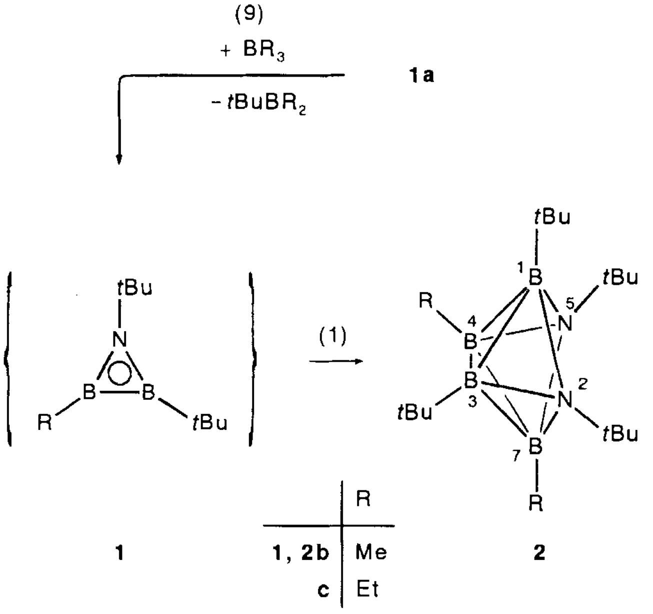
According to an X-ray structural analysis, the molecular structure of **4c** is characterized by a bicyclobutane-type NB_3 skeleton whose triangles enclose an angle of 139.8°, which is typical of the *nido* derivative of a trigonal bipyramid (Figure 1). The triangles are strongly distorted from regularity. The N–B3 bond (139.4 pm) represents a typical double bond[12], the N–B2 bond (147.3 pm) a short single bond. Such bond description is completed by assuming a BBB closed and a BHB open (3c,2e) bond. The symmetrically bridging atom H2 is 46(5) pm apart from the B–B–B plane in *endo* direction. The *t*Bu group at B5 is shifted away from an ideal *endo* position, defined by the *endo*-H atoms of **3a**, in order to avoid overlappings with the *exo*-*t*Bu group at B3.

Figure 1. Molecular structure of **4c** (thermal ellipsoids at 30% probability). Selected interatomic distances [pm] and angles [°]: N–B2 147.3(6), N–B3 139.4(6), B2–B3 181.2(8), B2–B5 176.6(7), B3–B5 185.6(7), B2–H25 123(4), B5–H25 124(4), B5–H5 110(5), N1–C1 147.6(6), B2–C2 161.3(7), B3–C3 159.3(7), B5–C5 164.9(7); B2–N–B3 78.3(3), N–B2–B3 48.9(3), B3–B2–B5 62.5(3), B2–B3–B5 57.5(3), B2–H25–B5 91(3), B2–B5–H5 116(2), B3–B5–H5 131(2), B2–B5–C5 130.8(4), B3–B5–C5 107.5(4), B2–N–C1 139.2(3), B3–N–C1 141.1(4)



Diaza-*nido*-hexaboranes from **1a**

Trialkylboranes BR_3 (R = Me, Et) do not add to **1a** at room temperature. In boiling THF, however, **1a** is transformed into the *nido* clusters **2b,c**. Apparently, the azadiboriridines **1b, c** are formed first according to eq. (9) and dimerize rapidly, as expected, according to eq. (1). We suppose that the central step during reaction (9) is the alkyloboration of **1a**, which proceeds with opening of the B−B bond. One would expect an intermediate of the type tBu−B(R)−N(tBu)−B(tBu)−BR_2 to give either a reaction back to **1a** and BR_3 or forward to **1b,c** and tBuBR_2. The side-products tBuBR_2 were not isolated but are in agreement with ^{11}B-NMR signals observed at δ = 80 (R = Me) and 84 (R = Et). A mechanism of this type means that a BtBu unit of **1a** is replaced by BR. As is well-known from redistribution equilibria of BR_3 and BR'_3, a simple exchange tBu/R might also be considered.

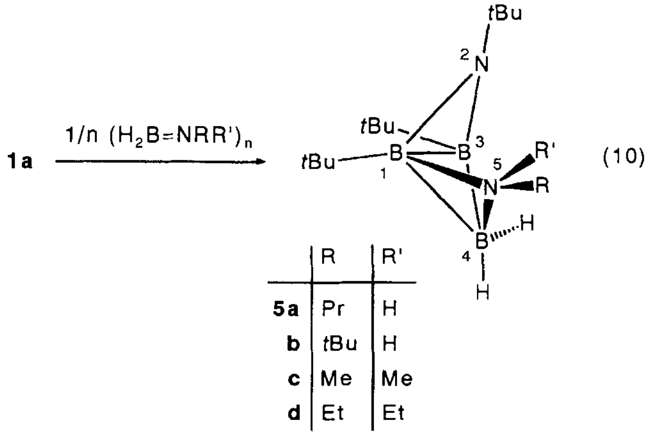


	R
1, 2b	Me
c	Et

As we had observed earlier[5], the racemic C_1 isomers of type **2** are the only fusion products from azadiboriridines with different boron-bound ligands, if the alkyl ligands are large enough. We are making the same observation here for **2b,c** with four different B atoms and four different tBu groups in the NMR spectra. No indications of C_{2v} isomers with either tBu or R in the two apical positions are found.

Diaza-*arachno*-pentaboranes from **1a**

We observed the formation of the diaza-*arachno*-pentaboranes **5a−d** upon addition of aminoboranes $H_2B{=}NRR'$ to **1a** in hexane according to eq. (10). The aminoboranes $H_2B{=}NHt$Bu and $H_2B{=}NR_2$ (R = Me, Et) were generated by refluxing their well-known cyclodimers in hexane; the aminoborane $H_2B{=}NHPr$ was added as a monomeric species in an excess of a freshly prepared mixture, that contained about 49% of the total boron content as borazine $(HBNPr)_3$, 45% as aminoborane $H_2B{=}NHPr$, 3% as trimeric and 2% as dimeric material of formula $(H_2BNHPr)_n$ (n = 3, 2) as well as 1% as amine−borane $PrNH_2{-}BH_3$, according to the ^{11}B-NMR spectra. The product **5a** was generated as a non-volatile oil of about 95% purity. The products **5b** and **5c** were purified by crystallization at −78°C, **5d** at −27°C; the products **5b** and **5d** are colorless liquids at room temperature, **5c** is a solid.



	R	R'
5a	Pr	H
b	tBu	H
c	Me	Me
d	Et	Et

The chiral structure of the diazapentaboranes **5a−d** (point group C_1) is concluded mostly from the NMR spectra (Table 3). Three non-equivalent B atoms and three tBu groups (four in the case of **5b**) are present in **5a−d**, the groups Me and Et of **5c,d** are non-equivalent, and the same is true for the H atoms of the group NCH_2 of **5a, d**. The 2D ^{11}B/^{1}H-NMR spectra reveal that two H atoms are bound to B4, which is also indicated by the corresponding coupling constants ^2J(HH) in the case of **5b,c**. The 2D ^{11}B/^{11}B-NMR spectra exhibit cross peaks B3/B4 of **5a−d**, whereas the bridging N atoms prevent the observation of the cross peaks B1/B4 and B1/B3 for **5a,c,d**; nevertheless, the B1/B4 cross peak is found for **5b**. The NMR data confirm that only one of two hypothetical isomers is present in the case of **5a,b**; we suppose this isomer to exhibit the group Pr or tBu, respectively, in an *exo* position, which is sterically favored compared with the *endo* position. The IR vibrations at $\tilde{\nu}$ = 3374 (**5a**) and 3355 cm^{-1} (**5b**) prove the presence of an NH group, which is absent in **5c, d**.

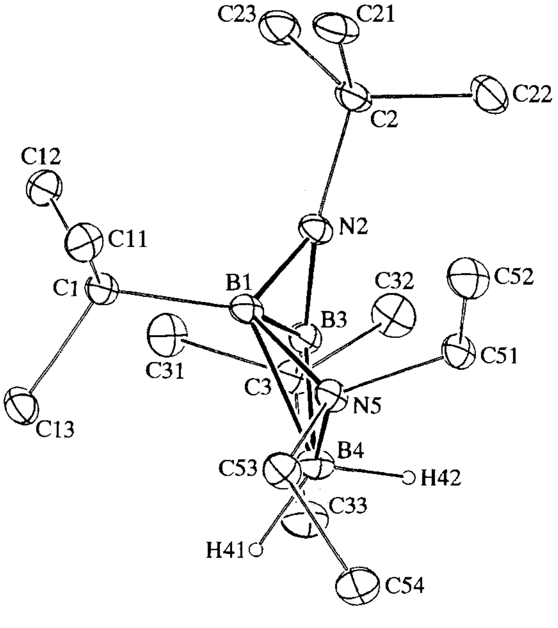
The proposed structure is confirmed by an X-ray structural analysis of crystalline **5d** (Figure 2). The tricyclic skeleton exhibits three B−B bond lengths, 182.0−187.1 pm, in the typical cluster bond range, two B−N bonds of equal length, 159.2 pm, connecting the ammonium-type N5 atom and the atoms B1 and B4, a B−N single bond length, 149.9 pm, for the bond between N2 and the highly coordinated B1, and a B−N double bond length[12], 138.2 pm, for the bond between N2 and the low-coordinated B3. Typically for borane clusters, *exo* bonds are shorter than comparable *endo* bonds; this holds for BH_2 (B−H 113 vs. 115 pm) as well as for NEt_2 (N−C 148.5 vs. 149.2 pm). The three triangles B1−N2−B3 (Δ1), B1−B3−B4 (Δ2), and B1−B4−N5 (Δ3) enclose interplanar angles of 38.9 (Δ1/Δ2) and 37.5°C (Δ2/Δ3).

Table 3. ^{1}H- , ^{11}B-, and ^{13}C-NMR signals of **5a**–**d**

	$^1H_{endo}$	$^1H_{exo}$	^{1}H(*t*Bu) (s, 27 H)	^{1}H(NRR')	^{11}B1	^{11}B3	^{11}B4[h]	^{13}C(*t*Bu) (s, 3q)[i]			
5a	1.30[a]	1.90[a]	0.95 1.29 1.30 1:1:1	0.57 1.17 1.75[b] 2.01 2.25 t, mc, s, 2 mc[c], 3:2:1:1:1	-8.0	37.4	-22.4	50.1	28.9	29.3	31.7
b	1.67[d] d[e]	1.69[d] d[e]	0.97 1.34 2:1	1.30[j] 1.87[b] 2 s, 9:1	-7.7	38.9	-27.4	51.7	28.5	30.4	30.7
c	1.55[d] d[e]	1,90 d[e], q[f]	1.07 1.25 1.27 1:1:1	2.01 2.37 2 s	-6.1	37.1	-15.7	51.3	30.3	32.9	33.1
d	1.33[d]	1.78 q[f]	1.08 1.25 1.31 1:1:1	0.79 0.91 2.36 2.61 2.84 2 *t*[g], 3 mc, 3:3:1:1:2	-5.3	36.7	-17.5	50.4	29.4	31.8	32.0

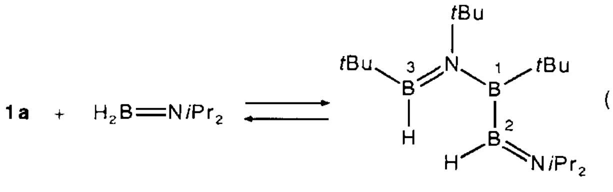
[a] Signals detected by 2D ^{1}H/^{11}B-NMR experiments. – [b] NH. – [c] $^2J = 12.1$, $^3J = 9.4, 5.8, 5.8$ Hz ($\delta = 2.01$); $^2J = 12.8$, $^3J = 9.3, 7.5, 5.7$ Hz ($\delta = 2.25$). – [d] Signals detected by $^1H\{^{11}B\}$ decoupling. – [e] $^2J = 9, 10$ Hz, detected by $^1H\{^{11}B\}$ decoupling (**5b**, **c**, respectively). – [f] $^1J = 130, 120$ Hz (**5c**, **d**, respectively). – [g] $^3J = 7.1, 6.9$ Hz, respectively. – [h] Pseudotriplets, $^1J = 113, 110, 116, 116$ Hz (**5a**–**d**, respectively). – [i] ^{13}C-NMR signals of R: $\delta = 9.8$ (q), 21.7, 49.0 (2 t) (**5a**); 52.9 (s), 32.7 (q) (**5b**); 45.5, 48.3 (2 q) (**5c**); 9.3, 10.1 (2 q), 42.5, 43.6 (2 t) (**5d**). – [j] Assignment of 4 *t*Bu groups arbitrary.

Figure 2. Molecular structure of **5d** (thermal ellipsoids at 30% probability). Selected interatomic distances [pm] and angles [°]: B1–N2 149.9(1), B1–B3 184.7(1), B1–B4 187.1(1), B1–N5 159.2(1), N2–B3 138.2(1), B3–B4 182.0(1), B4–N5 159.3(1), B1–C1 163.0(1), N2–C2 148.4(1), B3–C3 160.6(1), B4–H41 113(1), B4–H42 115(1), N5–C51 149.2(1), N5–C53 148.5(1); B1–N2–B3 79.64(6), B1–B3–N2 52.96(5), B1–B3–B4 61.35(5), B1–B4–B3 60.03(5), B1–B4–N5 54.00(4), B1–N5–B4 71.97(5), N2–B3–B4 104.84(7), B3–B4–N5 105.21(7), H41–B4–H42 115.4(7), C51–N5–C53 111.14(6)



A Boryl[diboran(4)yl]amine from 1a

In contrast to the aminoboranes of the preceding section, the aminoborane $H_2B{=}NiPr_2$ hydroborates the B–B bond of **1a** in hexane yielding the boryl(diboranyl)amine **6**, eq. (11). This reaction represents an equilibrium, which is slow enough to allow the observation of the NMR signals of all three components, even at 65°C. If crystals of **6** are dissolved in hexane, the ratio of **6** to $H_2B{=}NiPr_2$ is 52:48 at 65°C and 93:7 at −40°C. In the crystal, however, grown at −78°C from hexane, the product **6** remains stable at room temperature.



(11)

6

The NMR spectra of **6** at low temperature show three ^{11}B signals, none of which is shifted to the typical high-field cluster area. Three different *t*Bu groups, two different *i*Pr groups, and two different BH groups are in accord with an acyclic [2-aminodiboran(4)yl]borylamine structure (Table 4). The situation changes distinctly at 65°C: The two B*t*Bu and the two *B*-bound H atoms become equivalent. These findings can be explained by a degenerate rearrangement which is rapid on the NMR time scale [eq. (12)]. An intermediate of this rearrangement might be a molecule of type **3**. The same intermediate may be produced during the formation of **6**, eq. (11). According to a generalization of this mechanistic picture, the first step in the reaction of any Lewis acid with **1a** would be an addition across its B–B bond. The subsequent migration of an amino group into a B–B bridging position according to eq. (10) is prevented in the case of the N*i*Pr$_2$ group because of steric congestion with one of the *t*Bu groups, thus making the acyclic molecule **6** the thermodynamically most favorable product. – The aminoborane *t*BuBH=NH*t*Bu does not react with **1a**, apparently for steric reasons.

The molecular structure of **6** is confirmed by an X-ray structural analysis (Figure 3). The five atoms in the chain B3–N1–B1–B2–N2 are almost planarly configurated. The four bonds in this chain are characterized by the dihedral angles C31–B3–N1–B1, B3–N1–B1–B2, N1–B1–B2–N2, and B1–B2–N2–C41, 159.4, 112.1, 82.6, and 177.8°, respectively. These angles permit strong π-bond contributions to the bonds B3–N1 and B2–N2, represented by typical double bond lengths of 139.5 and 139.1 pm, respectively[12], whereas the bond length of 149.0 pm for B1–N1 means a typical single bond between

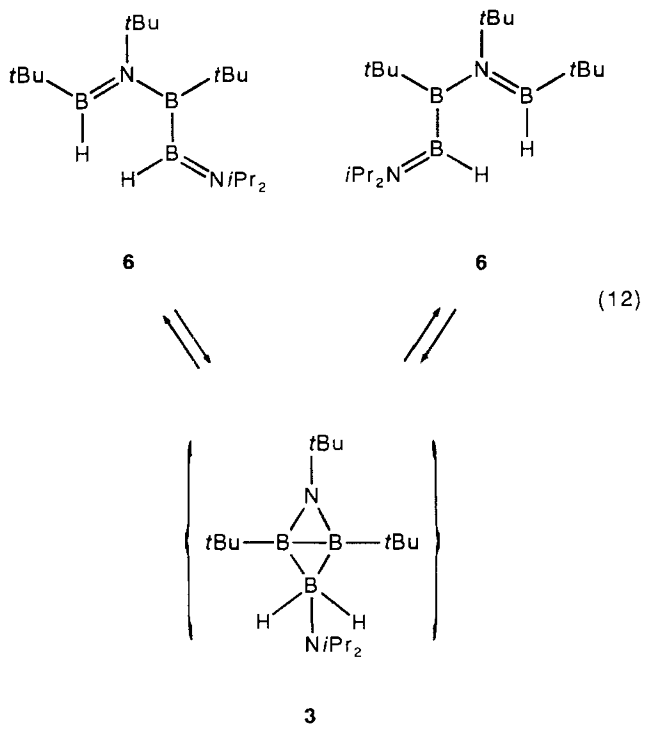


Table 4. ^{1}H- and ^{11}B-NMR signals of **6** at different temperatures[a]

	^{1}H-NMR *N*tBu	*B*tBu	Me(*i*Pr)[b]	CH(*i*Pr)[b]	BH[c]	^{11}B-NMR B1/3	B2
338 K	1.31	1.12	1.02	3.07	4.75	34.4	45.1
			1.17	3.74			
295 K	1.30	1.14	0.99	3.01	4.75	31.3	45.0
			1.17	3.67		39.2	
295 K[d]	1.33	0.96	1.10	3.28	4.75	30.6	44.9
			1.16	3.67		38.7	
263 K[d]	1.32	0.88	1.09	3.28	3.88[e]	30.4[e]	44.6[e]
		1.08	1.15	3.64	5.36[e]	41.0	
233 K[d]	1.32	0.85	1.08	3.28	3.81	[f]	[f]
		1.09	1.14	3.59	5.36		

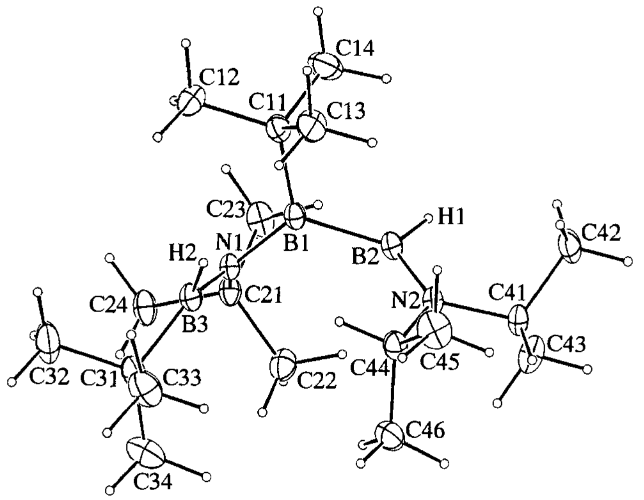
[a] ^{13}C-NMR (295 K, 75.429 MHz): δ = 22.2, 26.9, 30.3, 33.5 (4 q), 44.7, 52.8, 53.8 (3 s). – [b] Broad signals at 338 K, no HH coupling observable; ^3J(HH) = 6.7 (295 K), 6.5 Hz (263, 233 K). – [c] Broad signals with $\omega_{1/2}$ = 130, 950, 900, 160, 70 Hz, respectively, in the five recorded spectra; ^{1}H{^{11}B} decoupling experiments do not remarkably sharpen the peaks. – [d] In [D$_8$]THF. – [e] The 2D ^{11}B/^{1}H-NMR spectrum gives cross peaks 30.4/3.88 and 44.6/5.36. – [f] Strong broadening makes distinct shift values unobservable.

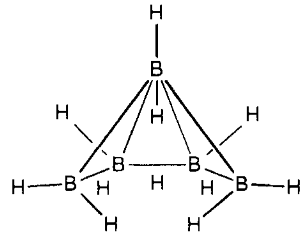
three-coordinated B and N atoms in orthogonal bond planes[13,14]. The bond length of 171.3 pm for B1–B2 is typical of the B–B bond in diborane(4) derivatives, which is known not to be largely influenced by the dihedral angle. The product **6** is the first structurally characterized diborane(4) that contains a BH bond.

Electron Deficiency in the Clusters of Type 4 and 5

The products of type **3** and **4** are identified to be *nido* clusters by conventional electron-count procedures. The structure of the NB$_3$ skeleton is derived from the trigonal bipyramid by omitting an equatorial vertex. The products of type **5** represent *arachno* clusters, whose N$_2$B$_3$ skeleton is derived from the pentagonal bipyramid by omitting an apical and an equatorial vertex. The clusters **5** are isoelectronic with *arachno*-pentaborane(11) (**7**) and they exhibit the same structure; this is in accord with the chosen numbering system, that places the atom B1 at the apex of the pyramidal fragment. – The well-known skeletal isomers **8** are isoelectronic with **5**, but their N$_2$B$_3$ skeleton forms a pentagonal fragment of the pentagonal bipyramid[15].

Figure 3. Molecular structure of **6** (thermal ellipsoids at 30% probability). Selected interatomic distances [pm] and angles [°]: B3–N1 139.51(9), N1–B1 149.03(8), B1–B2 171.3(1), B2–N2 139.10(9), B3–H2 1.089(7), B2–H1 1.124(8), N1–C21 149.23(7), B3–C31 160.60(9), B1–C11 160.04(9), N2–C41 149.09(7), N2-C44 147.31(8); N1–B3-C31 138.14(6), H2–B3–N1 112.5(4), H2–B3–C31 109.4(4), B1–N1–B3 104.96(5), C21–N1–B1 120.05(5), B3–N1–C21 132.85(5), N1–B1–B2 120.41(5), N1–B1–C11 121.68(5), C11–B1–B2 117.65(5), B1–B2–N2 126.00(6), H1–B2–N2 113.9(4), H1–B2–B1 120.0(4), B2–N2–C41 121.99(5), B2–N2–C44 122.45(5), C41–N2–C44 115.55(5)





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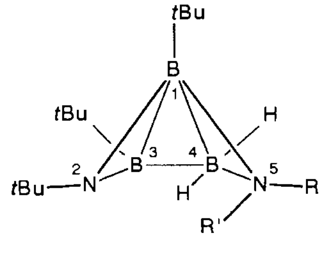
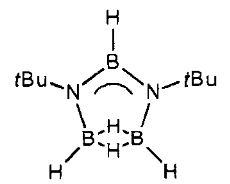


5a-b



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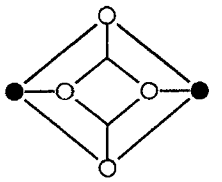
Apparently, the cluster skeletons of **2**–**5** are electron-deficient. Apart from the abstract description of the cluster electrons as a completely delocalized system, some qualitative insight may come from the picture of localized (2c,2e) and (3c,2e) bonds[16], where (3c,2e) bonds could be closed or open, and open (3c,2e) bonds could be B–B–B, B–H–B or π-type B–N–B bonds. Having Lipscomb's *styx* scheme in mind (*s* B–H–B, *t* B–B–B or B–N–B, *y* B–B, and *x* $B-H_{endo}$ bonds), we immediately find the numbers $s + x = 0, 2, 2$, respectively, from the formulae $N_2B_4H_6$, NB_3H_6, and $N_2B_3H_7$ of the parent molecules **2**–**5**. A cluster orbital balance ($3s + 3t + 2y + 2x = 18, 14, 17$) and a cluster electron balance ($2s + 2t + 2y + 2x = 16, 12, 16$) give easily the sequences *styx* = 0260 (**2**), 0222 (**3**), 1131 (**4**), and 0152 (**5**). Note that the B–N double bonds of the 0152 and the 1131 structures are in accord with the X-ray structural findings. A common feature of the resulting structures is that nitrogen does not participate in (3c,2e) bonds, which are not of the π type, thus representing a principal tendency of nitrogen. It is only in larger azaboranes that nitrogen is forced to participate in closed (3c,2e) bonds, which are so typical of electron-deficient structures; examples of such larger azaboranes are *closo*-NB_9H_{10}[17], *closo*-$NB_{11}H_{12}$[18], *nido*-$NC_2B_8H_{11}$[19], or *nido*-$NB_{10}H_{13}$[20].



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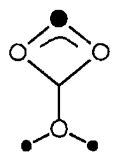

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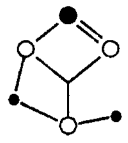

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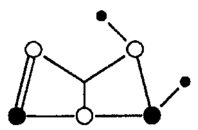

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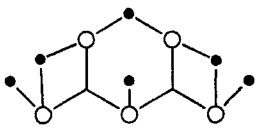

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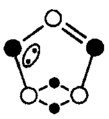

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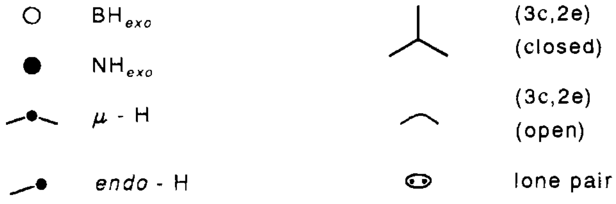

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Experimental

NMR: Varian Unity 500 at 499.843, 160.364, and 125.697 MHz (^1H, ^{11}B, ^{13}C, respectively, with TMS, $BF_3 \cdot OEt_2$, TMS as standards) in C_6D_6. – X-ray structures: Enraf-Nonius CAD4, graphite monochromator, data collection parameters in Table 5; no absorption correction; structure solution with SHEXLS86, refinement with SDP. – CHN analyses: Carlo-Erba elements analyzer 1106. – All synthetic procedures are conducted under dry nitrogen; anhydrous solvents have to be used.

Table 5. Crystal data, X-ray data collection parameters, and refinement results[a]

	4c	**5d**[b]	**6**
Space group (no.)	*I*4$_1$*cd* (110)	*P*2$_1$/*n* (14)	*P*1 (2)
a [Å]	25.67(1)	9.692(7)	9.386(4)
b [Å]	25.67(1)	10.587(7)	15.061(5)
c [Å]	11.986(9)	21.934(6)	9.231(4)
α [°]	90	90	98.89(4)
β [°]	90	95.84(4)	118.39(4)
γ [°]	90	90	86.49(3)
V [nm^3]	7.898(21)	2.239(4)	1.134(2)
Z	16	4	2
Calc. density [g cm^{-3}]	0.932	0.994	0.937
Crystal dimensions [mm^3]	0.7x0.6x0.3	0.5x0.5x0.4	0.8x0.5x0.5
Wave length [Å]	0.7107	1.5418	1.5418
Temperature [K]	253	183	193
Absorption coeff. [cm^{-1}]	0.469	3.709	3.510
Scan range [°]	3<Θ<25	5<Θ<74	5<Θ<73
Independent refls. ($2\Theta_{max}$)	3045	4184	4126
Obs. indep. refls. [$I > \sigma(I)$]	1412	3486	3833
No. of refined parameters	187	395	381
R	0.074	0.055	0.057
R_w [$w^{-1} = \sigma^2(F_o)$]	0.082	0.068	0.072
Goodnes of fit	1.418	3.182	5.089
Max. res. electr. dens. [e Å^{-3}]	0.28	0.32	0.25

[a] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-401038, -401039, -401040, the names of the authors, and the journal citation. – [b] Crystals contain 0.5 mol of clathrated hexane per mol **5d**.

1,2,3-Tri-tert-butyl-5-methyl-1-aza-nido-tetraborane (**3b**, **4b**): Within 10 min, 40.0 ml of a 0.5 M solution of HCl in Et_2O is added to 20.0 ml of a 1.0 M solution of Li[$MeBH_3$][21] in THF at 0°C. The resulting solution of $(MeBH_2)_2$[22] is dropped within 30 min to a solution of 1.50 g (7.23 mmol) of **1a**[4] in 4 ml of THF at 0°C. After stirring at 0°C for 15 min, volatile material is removed at 22°C/10 mbar. Extraction with four portions of 10 ml of pentane, removal of pentane and distillation at 42°C/0.001 mbar give 1.10 g (65%) of **3b**. – $C_{13}H_{32}B_3N$ (234.8): calcd. H 13.73, N 5.96; found H 13.66, N 7.95. – Storage for 20 d or heating for 8 h of **3b** in [D_8]THF yields a 15:85 mixture of **3b**/**4b**, identified by NMR.

1,2,3,5-Tetra-tert-butyl-1-aza-nido-tetraborane (**3c**, **4c**): 0.89 g (3.51 mmol) of iodine is added in several portions to 5.9 ml of a 1.2 M solution of Li[tBuBH$_3$][23] in THF at 0°C. If a brownish solution results, the addition of a few drops of the borate solution will make it colorless. The solution exhibits two ^{11}B-NMR signals at $\delta = 24.4$ (d, $J = 114$ Hz) and 10.4 (broad), which are attributed to a 4:1 mixture of $(tBuBH_2)_2$ and $tBuBH_2 \cdot THF$. The mixture is quickly dropped to a solution of 1.45 g (7.01 mmol) of **1a** in 3 ml of THF at 0°C. After stirring the solution at 0°C for 5 h, volatile material is removed at 22°C/10 mbar. The product is then extracted from the residue with pentane. After removal of volatile material at 22°C/0.001 mbar, 1.40 g (72%) of a 1:3 mixture of **3c**, **4c** is obtained by condensation into a cooled receiver at 65°C/0.001 mbar. The glassy product melts at about 70°C. – $C_{16}H_{38}B_3N$ (276.9): calcd. C 69.40, H 13.83, N 5.06; found C 69.48, H 14.35, N 5.12.

1,2,3-Tri-tert-butyl-5-(1,1,2-trimethylpropyl)-1-aza-nido-tetraborane (**3d, 4d**): 3.6 ml of a freshly prepared 1.0 M solution of (1,1,2-trimethylpropyl)borane[24] in THF is added to 0.70 g (3.38 mmol) of **1a** at −78°C. The solution is stirred at 0°C for 4 h. After removal of the solvent in vacuo, 0.70 g (68%) of **3d, 4d** is obtained by crystallization from pentane at −78°C. The 7:93 mixture melts at about 5°C. It can be heated up to 100°C without decomposition, without distinctly changing the ratio of isomers and without boiling in high vacuo. − $C_{18}H_{42}B_3N$ (305.0): calcd. H 13.88, N 4.59; found H 14.02, N 4.47.

1,2,3-Tri-tert-butyl-5-phenyl-1-aza-nido-tetraborane (**4e**): By slowly mixing 6.0 ml of a 1.1 M solution of $Li[PhBH_3]$[21] and 13.2 ml of a 0.5 M solution of HCl, both in THF, a solution of diphenyldiborane[25] is obtained and at 0°C promptly added to 0.70 g (3.38 mmol) of **1a** in 10 ml of THF. Stirring of the mixture at 0°C for 1 h is followed by removal of the volatile components in vacuo and condensation of the product into a cooled receiver at about 100°C/0.001 mbar with partial decomposition. The ^{11}B-NMR peaks of **4e** (Table 2) represent 90% of the intensity among some other peaks. An amount of 0.48 g of condensed product means a yield of ca. 45% **4e**.

5-sec-Butyl-1,2,3-tert-butyl-1-aza-nido-tetraborane (**4f**): A mixture of 0.60 g (2.90 mmol) of **1a** and 0.40 g (3.10 mmol) of $s\mathrm{BuBH_2 \cdot NMe_3}$[26] in 10 ml of hexane is refluxed for 4 h. After removal of volatile materials at 22°C in vacuo, 0.80 g (99%) of **4f** is condensed at about 90°C/0.001 mbar into a cooled receiver. Further purification is achieved by crystallization from hexane at −78°C; the ratio 54:46 of the diastereomers corresponds to the ^{13}C-NMR intensities of the Me(*t*Bu) signals. The yield of solid product is 0.42 g (52%), mp ca. −15°C. − $C_{16}H_{38}B_3N$ (276.9): calcd. H 13.83, N 5.06; found H 13.59, N 4.66.

1,2,3-Tri-tert-butyl-5,5-diethyl-1-aza-nido-tetraborane (**4g**): Tetraethyldiborane(6) is prepared according to the same procedure as reported for tetramethyldiborane(6)[22] by adding 5 ml of a 0.5 M solution of HCl in Et_2O to 2.0 ml of a 1.25 M solution of $Li[Et_2BH_2]$[27] in THF at 0°C. At the end of the evolution of H_2, a ^{11}B-NMR signal at $\delta = 28.1$ indicates the formation of pure $(Et_2BH)_2$. The solution is cooled to −78°C, and 0.41 g (1.98 mmol) of **1a** is added. After stirring at −78°C for 2 h and at 22°C for 2 h, the solvent is removed in vacuo and the product condensed into a cooled receiver at 70°C/0.001 mbar. A second condensation gives 0.45 g (81%) of **4g** which is pure according to NMR data. − $C_{18}H_{38}B_3N$ (276.9): calcd. H 13.83, N 5.06; found H 13.72, N 4.72.

1,2,3-Tri-tert-butyl-5,5-(cycloocta-1,5-diyl)-1-aza-nido-tetraborane (**4h**): 0.85 g (4.11 mmol) of **1a** in 4 ml of hexane is added to 0.50 g (4.1 mmol) of 9-borabicyclo[3.3.1]nonane in 12 ml of hexane. After stirring of the solution for 20 h, all volatile components are removed in vacuo. The residue is dissolved in 10 ml of hexane. The solution is filtered over siliceous earth. After half of the solvent has been removed in vacuo, 1.24 g (92%) of **4h** crystallizes at −78°C. − $C_{20}H_{42}B_3N$ (328.9): calcd. H 12.87, N 4.26; found H 13.82, N 4.25.

1,2,4,5-Tetra-tert-butyl-3,7-dimethyl-2,5-diaza-nido-hexaborane (**2b**): A mixture of 0.30 g (1.45 mmol) of **1a** in 5 ml of THF and 2.0 ml of a 3.0 M solution of BMe_3[28] in Et_2O is refluxed for 48 h, the condenser being cooled to −78°C. After removal of volatile components in vacuo, the residue is taken up in 5 ml of pentane. After filtration of the mixture the solvent is removed from the filtrate at 70°C/0.001 mbar. The remaining solid is **2a** (0.14 g, 59%), which may be crystallized from pentane at −78°C.

1,2,4,5-Tetra-tert-butyl-3,7-diethyl-2,5-diaza-nido-hexaborane (**2c**): 0.60 g (2.90 mmol) of **1a** and 0.60 g (6.1 mmol) of BEt_3 are refluxed in 12 ml of THF for 60 h. After removal of the volatile materials at 60°C/0.001 mbar, 0.34 g (65%) of **2c** is isolated by crystallization from Et_2O at −78°C.

1,2,3-Tri-tert-butyl-5-propyl-2,5-diaza-arachno-pentaborane (**5a**): 6.71 g (26.4 mmol) of I_2 in 20 ml of THF is added to a mixture of 2.00 g (52.9 mmol) of $NaBH_4$ and 3.12 g (52.8 mmol) of $i\mathrm{PrNH_2}$ in 20 ml of THF, the addition being accompanied by spontaneous decolorization and warming to reflux temp. After removal of the solvent in vacuo, the remaining solid, which is essentially a mixture of $PrNH_2{-}BH_3$ and NaI, is thermolyzed at 90°C without solvent until the evolution of H_2 has been almost finished after 4 h. A mixture of volatile products is condensed from the thermolysis flask into a cooled trap at 50−80°C/0.001 mbar. The products are identified by their ^{11}B-NMR signals $\delta = -18.4$ (q, $J = 95$ Hz, $PrNH_2{-}BH_3$, 1%), −6.6 and −5.7 [$^{11}B\{^1H\}$ signals, *cis*/*trans* isomers of $(PrNH{-}BH_2)_3$, 3%], −3.1 [$^{11}B\{^1H\}$ signal, $(PrNH{-}BH_2)_2$, 2%], 27.9 [d, $J = 128$ Hz, $(PrN{-}BH)_3$, 50%], 33.5 (d, $J = 116$ Hz, $H_2B{=}NHPr$, 45%). This liquid mixture can be stored without change at −27°C. − A portion of 0.7 ml of the mixture is added to 0.20 g (0.97 mmol) of **1a** in 8 ml of hexane at −78°C. After stirring at 22°C for 90 min, all volatile products are removed in vacuo, finally at 70°C for 6 h. The remaining product (0.26 g) can neither be destilled nor crystallized. According to the NMR spectra it is **5a** of about 95% purity (96% **5a** with respect to **1a**).

1,2,3,5-Tetra-tert-butyl-2,5-diaza-arachno-pentaborane (**5b**): 0.61 g (2.94 mmol) of **1a** is added to 0.25 g (1.47 mmol) of $(H_2B{=}NH\mathit{t}Bu)_n$ in 10 ml of hexane at −78°C; the aminoborane, predominantly the cyclodimer ($n = 2$), is available according to a known procedure[29]. After 5 h at reflux temp. and then removal of volatile components in vacuo, 0.48 g (56%) of **5b** is crystallized from hexane at −78°C. − $C_{16}H_{39}B_3N_2$ (291.9): calcd. H 13.47, N 9.60; found H 12.52, N 8.78

1,2,3-Tri-tert-butyl-5,5-dimethyl-2,5-diaza-arachno-pentaborane (**5c**): The known dimeric aminoborane $(H_2BNMe_2)_2$[30] is synthesized from the amine-borane $Me_2NH{-}BH_3$ by a procedure analogous to that described above for $H_2B(NHPr)$. A solution of 0.80 g (3.86 mmol) of **1a** and 0.22 g (1.93 mmol) of $(H_2BNMe_2)_2$ in 12 ml of hexane is refluxed for 3 h. Removal of the volatile components in vacuo and crystallization from pentane at −78°C give 0.92 g (90%) of colorless, solid **5c**. − $C_{14}H_{35}B_3N_2$ (263.9): calcd. H 13.37, N 10.62; found H 13.78, N 10.53.

1,2,3-Tri-tert-butyl-5,5-diethyl-2,5-diaza-arachno-pentaborane (**5d**): The known dimeric aminoborane $(H_2BNEt_2)_2$[30] is synthesized from the amine−borane $Et_2NH{-}BH_3$ by a procedure analogous to that described above for $H_2B{=}NHPr$. From 0.80 g (3.86 mmol) of **1a** and 0.33 g (1.94 mmol) of $(H_2BNEt_2)_2$ 1.06 g (94%) of **5d**, mp ca. 0°C, is obtained according to the procedure used for the preparation of **5c**. − $C_{16}H_{39}B_3N_2$ (221.9): calcd. H 13.47, N 9.60; found H 12.70, N 9.56.

tert-Butyl(tert-butylboryl)[1-tert-butyl-2-(diisopropylamino)-diborane(4)yl]amine (**6**): 0.50 g (4.43 mmol) of $H_2BN\mathit{i}Pr_2$[31], prepared in the same way as $(H_2BNEt_2)_2$, is dissolved in 20 ml of hexane and the solution is added to 0.91 g (4.40 mmol) of **1a** at −78°C. From the colorless oil, that remains after removal of the solvent in vacuo, 1.22 g (87%) of **6**, mp 39°C, are crystallized from hexane at −78°C. − $C_{18}H_{43}B_3N_2$ (320.0): calcd. H 13.54, N 8.75; found H 13.15, N 8.82.

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[295/94]