OPENING OF CLOSED AZADECABORANES RNB_9H_9 BY AMINES

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Dedicated to Professor Jaromir Plesek on the occasion of his 70th birthday in recognition of his outstanding contributions to organic, borane and carborane chemistry.

The aza-*closo*-decaborane RNB_9H_9 (**4a**; R = 4-ClC_6H_4) is opened to give the *nido*-cluster RNB_9H_9(tmeda) (**7a**) by the addition of $Me_2N(CH_2)_2NMe_2$ (tmeda). The cluster **7a** contains the same type of asymmetric hydrogen bridge as is present in the isoelectronic *nido*-anion $[RNB_9H_{10}]^-$ (**10b**, **10c**; R = Ph, $PhCH_2$), obtained by the action of $KBHEt_3$ on the corresponding *arachno*-cluster $RNB_9H_{11}(NH_2t\text{-Bu})$ (**9b**, **9c**). Secondary amines HNR^1R^2 yield the azaboranes $RNB_9H_{10}(NR^1R^2)$ (**11a–11c**; R^1/R^2 = H/*t*-Bu, Et/Et, i-Pr/i-Pr). From 2D-$^1H/^{11}B$ NMR correlations, concerning the two non-terminal H atoms, and from the ^{11}B NMR shifts, a *nido/arachno* hybrid structure is deduced for **11a–11c**, governed by the contribution of π-bonding between the lone pair of the amino group and the neighbouring B atom. Amines, like nucleophiles generally, attack the *closo*-boranes RNB_9H_9 at one of the B atoms adjacent to the N atom, as expected.
Key words: Azadecaboranes; Cluster opening; *nido/arachno* Hybrids.

It is well known that aza-*closo*-dodecaboranes $RNB_{11}H_{11}$ (**1**) can be opened by amines to give either amine-aza-*nido*-undecaboranes $RNB_{11}H_{11}(NR'_3)$ (**3**) in the case of tertiary amines (Eq. (*1*)) or aminoaza-*nido*-undecaborates $[RNB_{11}H_{11}(NR'_2)]^-$ (**2**) in the case of secondary amines (Eq. (*2*)). The products **2** and **3** are stable against the attack of bases and are soluble in protic media without decomposition[1]. Aza-*closo*-decaboranes RNB_9H_9 (**4**), on the other hand, are attacked by primary amines under opening and degradation of one BH vertex to give either aza-*nido*-nonaborates $[RNB_8H_9]^-$ [**5**; Eq. (*3*)] or amine-aza-*arachno*-nonaborane $RNB_8H_{10}(NR'H_2)$ [**6**; Eq. (*4*)], depending on the polarity of the solvent. The products **5** and **6** are not stable against complete degradation by protic agents[2] (Scheme 1).

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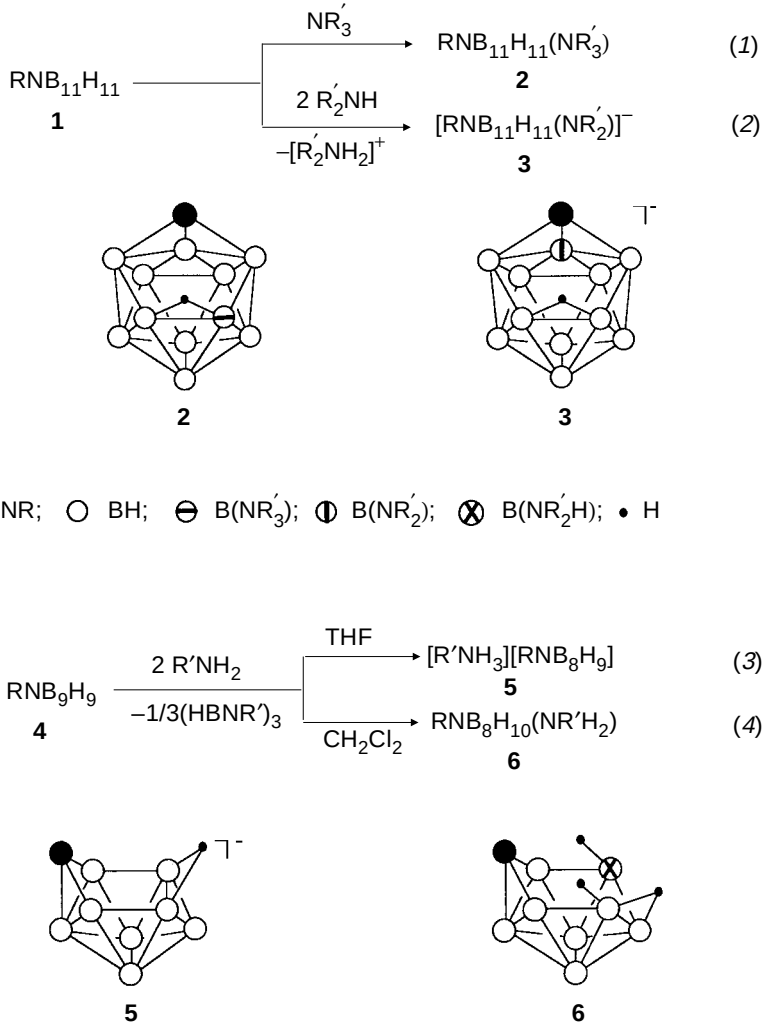
The question arises whether simple opening of aza-*closo*-decaboranes without degradation would be possible by avoiding any excess of amine beyond the 1 : 1 ratio.

EXPERIMENTAL

[1,2-Bis(dimethylamino)ethane]-[6-(4-chlorophenyl)-6-aza-*nido*-decaborane(10)] (1/1) (**7a**)

Bis(dimethylamino)ethane (tmeda; 0.079 ml, 0.51 mmol) is added to **4a** (ref.[2]) (120 mg, 0.51 mmol) in CH_2Cl_2 (10 ml) at –78 °C. The reaction mixture is brought to room temperature and stirred (12 h).



SCHEME 1

After filtration, all volatiles are removed *in vacuo*. The residue is again dissolved in a minimal amount of CH_2Cl_2. Hexane is added. The product (167 mg, 94 %) is precipitated at –40 °C as a colourless solid. For $C_{12}H_{29}B_9ClN_3$ (348.1) calculated: 41.4% C, 8.4% H, 12.1% N; found: 41.3% C, 9.1% H, 12.0% N.

tert-Butylamine-[6-phenyl-6-aza-*arachno*-decaborane(12)] (1/1) (**9b**)

A solution of *t*-$BuNH_2$ (0.115 ml, 1.09 mmol) and *nido*-$PhNB_9H_{11}$ (ref.[1]) (210 mg, 1.05 mmol) in CH_2Cl_2 (10 ml) is stirred at room temperature (10 min). The colourless product (250 mg, 87%) is obtained in the same way as described for **7a**. For $C_{10}H_{27}B_9N_2$ (272.6) calculated: 44.1% C, 10.0% H, 10.3% N; found: 43.8% C, 10.3% H, 10.2% N.

tert-Butylamine-[6-benzyl-6-aza-*arachno*-decaborane(12)] (1/1) (**9c**)

The colourless product **9c** (545 mg, 83%) is obtained from *t*-$BuNH_2$ (0.250 ml, 2.40 mmol) and *nido*-$(PhCH_2)NB_9H_{11}$ (ref.[3]) (490 mg, 2.30 mmol) in the same manner as **9b**. For $C_{11}H_{29}B_9N_2$ (286.7) calculated: 46.1% C, 10.2% H, 9.8% N; found: 46.1% C, 10.7% H, 9.9% N.

(18-Crown-6)potassium[6-phenyldecahydro-6-aza-*nido*-decaborate] (**10b**)

A 1.0 molar solution of $KBHEt_3$ in THF (0.77 ml) is added dropwise to a solution of **9b** (210 mg, 0.77 mmol) in THF (8 ml). A gas is evolved. After stirring (3 h), 18-crown-6 (210 mg, 0.80 mmol) is added. All volatile materials are removed *in vacuo*. The residue is dissolved in CH_2Cl_2 (15 ml) and stirred (3 days). The same further procedure as for **7a** gives colourless crystals of **10b** (240 mg, 62%).

(18-Crown-6)potassium[6-benzyldecahydro-6-aza-*nido*-decaborate) (**10c**)

As described for **10b**, the reaction of $KBHEt_3$ (0.50 ml of 1.0 molar solution in THF), **9c** (145 mg, 0.51 mmol), and 18-crown-6 (130 mg, 0.50 mmol) gives colourless **10c** (100 mg, 38%, after repeated recrystallization).

9-(*tert*-Butylamino)-6-(4-chlorophenyl)-6-azadecaborane(12) (**11a**)

A solution of *t*-$BuNH_2$ (0.04 ml, 0.35 mmol) in CH_2Cl_2 (5 ml) is added dropwise to a solution of **4a** (ref.[2]) (94 mg, 0.41 mmol) in CH_2Cl_2 (30 ml) at –78 °C. The solution is stirred at ambient temperature (3 h). The solvent is removed *in vacuo* and excess **4a** is sublimated off at 80 °C/0.1 Pa. The residue is dissolved in hexane, the solution is filtered, and the filtrate is concentrated to a volume of 5 ml. Colourless product crystallizes at –80 °C (95 mg, 89%).

6-(4-Chlorophenyl)-9-diethylamino-6-azadecaborane(12) (**11b**)

As described for **11a**, Et_2NH (0.054 ml, 0.52 mmol) and **4a** (136 mg, 0.58 mmol) are transformed into **11b** (104 mg, 68%).

6-(4-Chlorophenyl)-9-diisopropylamino-6-azadecaborane(12) (**11c**)

In the same manner, i-Pr_2NH (0.045 ml, 0.35 mmol) and **4a** (96 mg, 0.41 mmol) give **11c** (103 mg, 76%). For $C_{12}H_{28}B_9ClN_2$ (333.1) calculated: 43.3% C, 8.5% H, 8.4% N; found: 43.1% C, 8.4% H, 8.4% N.

p-Toluidine-[6-(4-tolyl)-6-aza-*arachno*-decaborane(12)] (1/1) (**9d**)

A mixture of the aza-*nido*-decaborane **8d** (ref.[2]) (125 mg, 0.59 mmol), THF (15 ml) and methanol (5 ml) is refluxed (12 h). Solvents are removed *in vacuo*. The colourless product (93 mg, 98%) is precipitated from CH_2Cl_2/hexane at –40 °C.

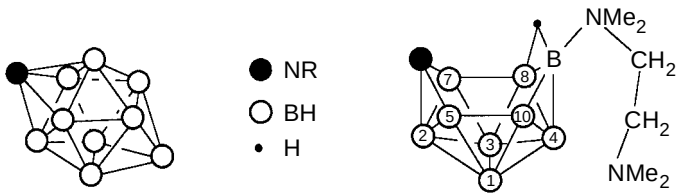
Neopentylamine-[6-neopentyl-6-aza-*arachno*-decaborane(12)] (1/1) (**9e**)

The product **9e** (115 mg, 99%) is obtained from the aza-*nido*-decaborane **8e** (160 mg, 0.83 mmol) by the same procedure.

RESULTS

The aza-*closo*-decaboranes RNB_9H_9 (R = 4-ClC_6H_4 (**4a**), 4-MeC_6H_4, $PhCH_2$) do not react with tertiary amines like NEt_3, $N(i\text{-}Bu)_3$, even not in boiling toluene. The tertiary amine $Me_2NCH_2CH_2NMe_2$ (tmeda), on the other hand, adds to the azaborane **4a** under opening of the *closo*-skeleton at –30 °C, giving *nido*-RNB_9H_9(tmeda) (**7a**; Eq. (*5*)). We ascribe the unexpected difference in reactivity of the amines NR_3 and tmeda to a catalytic effect, that the second NMe_2 group performs on the irreversible opening procedure after the loose reversible addition of the first NMe_2 group to one of the B atoms adjacent to the N atom of **4a** (Scheme 2); we do not understand, however, how this opening proceeds in detail.

$$\underset{\textbf{4a}}{RNB_9H_9} \xrightarrow[R = p\text{-}ClC_6H_4]{\text{tmeda}} \underset{\textbf{7a}}{RNB_9H_9(\text{tmeda})} \qquad (5)$$



SCHEME 2

The structure of **7a** can be deduced from the NMR spectra. Though the unsymmetry of the hydrogen bridge between B8 and B9 does not differentiate the ^{11}B NMR signals of the couples B1/B3 and B5/B7, the signals of B8 and B10 are different (Table I), and the ^1H NMR signal of the μ-H atom gives correlations with B8 and B9, but not with B10, in the 2D-$^1H/^{11}B$ HMQC NMR spectrum. The assignment of the ^{11}B NMR signals is in accord with a 2D-$^{11}B/^{11}B$ COSY NMR spectrum; cross peaks between the pairs B2/B5, B2/B7, B8/B9, and B7/B8 are not found, expectedly, because of the influence of the neighbouring N and the bridging H atom, and because of the weakness of the

bond B7–B8, often observed in decaborane structures. The ligand tmeda gives only the two ^{1}H NMR signals of CH_3 and CH_2 at ambient temperature; at –50 °C, however, six signals are observed at δ 1.23, 1.64, 2.15 (3 s), 1.30, 1.51, 2.42 (3 m) (6 : 3 : 3 : 1 : 2 : 1; in toluene-d_8), which is in accord with structure RNB_9H_9(NMeMe′–CHH′–CH_2''–NMe_2''). We assume that a dynamic intramolecular B–N bond rupture and closure, including both N atoms of tmeda, makes both halves of the base equivalent. This dynamic process becomes slow with respect to the NMR time scale at –50 °C. The half of tmeda, which is adjacent to the azaborane cluster, correlates with the unsymmetric cluster structure, whereas the other half of tmeda is too far away for such correlation.

The structural identification of **7a** is confirmed by an independent synthesis of the aza-*nido*-decaborate anions $[RNB_9H_{10}]^-$ (R = Ph, $PhCH_2$), which also contain a bridging H atom in a rigid unsymmetric position. The synthesis starts from the known aza-*nido*-decaboranes RNB_9H_{11} (**8b**, **8c**) (refs[1,3]). These boranes can easily be transformed into the aza-*arachno*-decaboranes $RNB_9H_{11}(NH_2t\text{-Bu})$ (**9b**, **9c**) by the addition of *t*-$BuNH_2$ (Eq. (*6a*)). Deprotonation by $KBHEt_3$ in the presence of 18-crown-6 (L′) gives the colourless solids [KL′][RNB_9H_{10}] (**10b**, **10c**; Eq. (*6b*), see Scheme 3).

Lewis base adducts RNB_9H_{11}·L of the type **9**, in particular with isonitriles as bases, are well known[3,4]. The NMR data of **9b**, **9c** (Table II) fit well into the known pattern, and the 2D-^{11}B/^{11}B COSY NMR spectrum of **9c** confirms the structural assignment.

TABLE I
^{11}B and ^{1}H NMR shifts[a] of RNB_9H_9(tmeda) (**7a**) and [KL′][RNB_9H_{10}] (**10b**, **10c**)

Compound	Nucleus	1	2	3	4	5	7	8	9	10	μ-H[b]
7a	^{11}B[c]	–9.7	–31.1	–9.7	–19.7	9.3	9.3	–21.3	36.0	–9.7	–
10b		–11.6	–30.6	–9.7	–19.9	6.4	8.9	–20.8	28.7	–8.1	–
10c		–11.0	–32.4	–9.6	–21.7	6.5	8.4	–21.0	28.9	–9.0	–
7a	^{1}H[d]	2.15	1.35	2.15	1.16	2.64	3.70	1.60	–	1.35	–2.78
10b		1.80	1.55	2.08	0.67	2.73	3.59	1.63	4.50	2.01	–4.12
10c		1.80	1.19	2.02	0.48	2.68	3.50	1.43	4.38	1.83	–4.33

[a] 160.4 MHz, BF_3·Et_2O (^{11}B); 499.8 MHz, $SiMe_4$ (^{1}H); in THF-d_8 (**7a**), CD_2Cl_2 (**10b**, **10c**). [b] 2D-H/B correlations with B8 and B9. [c] Assignment **7a**, **10c** by 2D-^{11}B/^{11}B COSY NMR, **10b** by analogy; no cross-peaks observable, if B/B is part of triangles BNB or BHB, also not B7/B8 (**7a**), B4/B9, B9/B10 (**10b**); accidental degeneracy B1/B3/B10 and B5/B7 (**7a**). [d] ^{1}H{^{11}B} peaks observed; assignment by 2D-^{1}H/^{11}B HMQC NMR (H5, H7 of **7a** by analogy).

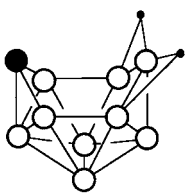
Additional signals of **7a**: 2.02 s, 12 H (CH_3); 3.05 s, 4 H (CH_2); 7.21–7.28 m, 4 H (C_6H_4); **10b**: 3.60 s, 24 H (L′); 7.09–7.22 m, 5 H (C_6H_5); **10c**: 3.62 s, 24 H (L′); 4.25, 4.31 2 d, 2 H, ^2J = 13.7 (NCHH′C_6H_5); 6.95–7.22 m, 5 H (C_6H_5).

The anions $[RNB_9H_{10}]^-$ give nine different ^{11}B NMR signals, which can be assigned in the way given in Table I by the 2D-$^{11}B/^{11}B$ NMR data of **10c**. The ^1H NMR signals of nine different terminal H atoms can be assigned using a 2D-$^1H/^{11}B$ NMR spectrum of **10c**. The bridging H atom gives correlations with B8 and B9, but not with B10, proving that this atom does not fluctuate, at least not with respect to the NMR time scale. As expected, the ^{11}B and ^1H NMR shift pattern of **10b**, **10c** fits nicely to that of **7a**, with the exception of the atom B9.

$$\underset{\textbf{8b, 8c}}{RNB_9H_{11}} \xrightarrow{t\text{-}BuNH_2} \underset{\textbf{9b, 9c}}{RNB_9H_{11}(NH_2t\text{-}Bu)} \qquad (6a)$$

$$\textbf{9b, 9c} \xrightarrow[-H_2\ -BEt_3\ -NH_2t\text{-}Bu]{KBHEt_3\ \ 18\text{-crown-6 (L')}} \underset{\textbf{10b, 10c}}{[KL'][RNB_9H_{10}]} \qquad (6b)$$

8, 9, 10	R
b	Ph
c	$PhCH_2$



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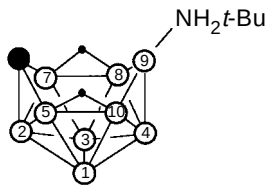

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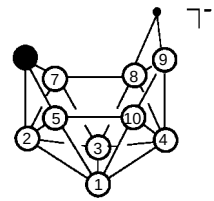

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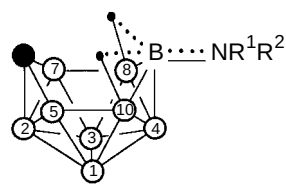
SCHEME 3

Different from tertiary amines, secondary amines HNR^1R^2 do react with the aza-*closo*-decaborane **4a**. If an excess of amine is strictly avoided, the borane will be aminohydrogenated under opening of the closed structure, according to Eq. (*7*) (Scheme 4), but is not degraded in a way known for primary amines (Eqs (*3*), (*4*)).

$$\underset{\textbf{4a}}{RNB_9H_9} \xrightarrow{NHR^1R^2} \underset{\textbf{11a–11c}}{RNB_9H_{10}(NR^1R^2)} \qquad (7)$$

11	R^1	R^2
a	H	*t*-Bu
b	Et	Et
c	i-Pr	i-Pr



SCHEME 4

The structure of the 9-amino-6-azadecaboranes **11a–11c** is again deduced from the NMR spectra. The assignment of the ^{11}B and ^{1}H NMR signals could be achieved by 2D NMR measurements. The equivalence of the BH pairs in the positions 1/3, 5/7 and 8/10 clearly indicates a mirror plane through the B atoms 2, 4 and 9. Though the shift patterns of all the three products coincide nicely, there is a difference concerning the couplings of the two extra H atoms: A correlation of these atoms with B8/B10 and with B9 in observed in the case of **11a**, whereas these atoms give cross peaks in the 2D-$^{1}H/^{11}B$ HMQC NMR spectrum with B8/B10, but not with B9 in the case of **11b**, **11c**. One may conclude that the extra H atoms have more or less bridging character in **11a** and more or less endo character in **11b**, **11c**.

In order to elucidate the degradation of the aza-*nido*-boranes RNB_9H_{11} in more detail, we refluxed **8d**, **8e** (R = *p*-MeC_6H_4, *t*-$BuCH_2$) in an excess of methanol and recovered half of the starting material as undegraded aza-*arachno*-decaborane $RNB_9H_{11}(NH_2R)$ (**9d**, **9e**); the other half had been completely degraded to give $B(OMe)_3$, apparently in addition to RNH_2; this base in turn adds rapidly to undegraded RNB_9H_{11} to give **9d**, **9e** (Eq. (*8*), Scheme 5). The *arachno*-clusters **9d**, **9e** are unaffected by boiling methanol. Their structural identification is possible in a straightforward way by comparing the NMR data to those of **9b**, **9c** (Table II).

$$\underset{\textbf{8d, 8e}}{2\ RNB_9H_{11}} \xrightarrow[-\ 9\ B(OMe)_3\ -\ 18\ H_2]{27\ MeOH} \underset{\textbf{9d, 9e}}{RNB_9H_{11}(NH_2R)} \qquad (8)$$

8, 9	R
d	*p*-MeC_6H_4
e	*t*-$BuCH_2$

SCHEME 5

DISCUSSION

The opening of the aza-*closo*-boranes $RNB_{11}H_{11}$ (**1**, Eq. (*1*)) and RNB_9H_9 (**4**, Eq. (*5*)) by neutral bases L have three features in common: (i) The connectivity *c* of the N atom is reduced from *c* = 5 (**1**) and *c* = 4 (**4**) to *c* = 3 by the opening of two B–N bonds (**1**) or one B–N bond (4); (ii) the base L attacks one of the B atoms adjacent to the N atom of **1** or **4**; (iii) the H atom at the attacked B atom is shifted from a terminal into a bridging position in the neighbourhood. Differences, on the other hand, in the opening reactions concern the number of opened B–B bonds: none in the case of **1**, but two in the case of **4**, which means a net reduction by one B–B bond, since one B–B bond is closed on the way from **4** to **7** (the bond B4–B9 in **7**). The skeletal aperture of the opened *nido*-clusters is a five-membered (**2**) or a six-membered ring (**7**). With respect

to the skeletal changes, reaction (*5*) (Scheme 6) is the reversal of the formation of **4** by thermal dehydrogenation of RNB_9H_{11} (refs[2,4]).

The connectivity reduction of the N atom gives the main contribution to the driving force of the opening reactions (*1*) and (*5*). This conclusion can qualitatively be understood by considering the formal charges at the cluster N atom in the picture of localized

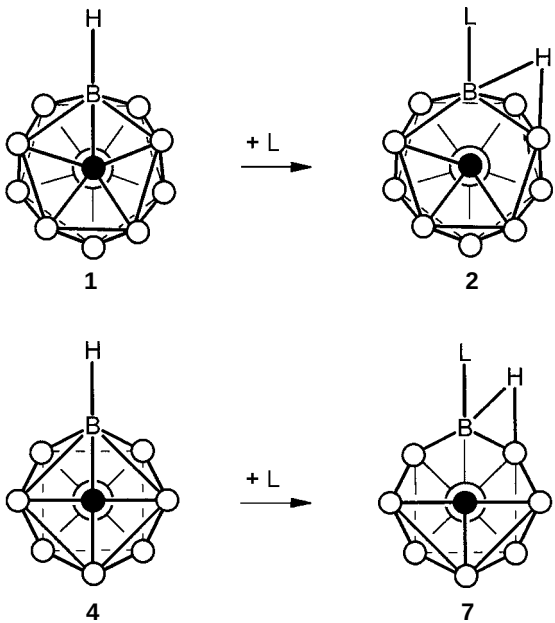
TABLE II
^{11}B and ^{1}H NMR shifts[a] of $RNB_9H_{11}(NH_2R')$ (**9b**–**9e**) and $RNB_9H_{10}(NR^1R^2)$ (**11a**–**11c**), ^{11}B NMR data of **8a** for comparison[2]

Compound	Nucleus	1/3	2	4	5/7	8/10	9	μ-H[b]
8a	^{11}B[c]	–1.2	–27.0	–27.0	14.6	–12.9	15.3	–
9b		–40.6	–14.3	1.6	–8.3	–37.4	–17.8	–
9c		–41.2	–15.7	0.4	–8.8	–38.5	–18.0	–
9d		–41.1	–15.1	1.3	–8.2	–38.1	–12.7	–
9e		–40.9	–18.4	0.0	–7.5	–40.1	–13.8	–
11a		–23.9	–24.5	–7.2	8.9	–39.4	36.3	–
11b		–25.4	–24.0	–6.8	7.9	–40.4	36.5	–
11c		–23.1	–23.9	–6.5	9.2	–40.1	37.3	–
9b	^{1}H[d]	0.49	2.70	2.70	2.53	0.49	1.70	–1.93
9c		0.36	2.20	2.53	2.40	0.36	1.24	–2.29
9d		0.44	–	2.83	2.33	0.50	1.76	–2.10
9e		0.31	–	–	2.27	0.31	1.72	–2.37
11a		1.54	1.87	2.82	3.54	0.55	–	–1.17
11b		1.51	1.89	2.88	3.53	0.46	–	–1.18
11c		1.45	1.92	2.83	3.48	0.52	–	–1.21

[a] See footnote [a], Table I; in $CDCl_3$ (**9b**, **9c**), THF-d_8 (**9d**, **9e**), CD_2Cl_2 (**11a–11c**). [b] 2D-H/B correlations with B5(7) and B10(8) (**9c**); B8(10) and B9 (**11a**); B8(10) (**11a–11c**). [c] Assignment **9c**, **11a–11c** by 2D-$^{11}B/^{11}B$ COSY NMR, **9b**, **9d**, **9e** by analogy; no cross peaks observable with B1/B10 (B3/B8), B5/B10 (B7/B8) (**9c**), B4/B9, B8(B10)/B9, B5/B10 (B7/B8) (**11a–11c**), B2/B5(B7) (**9c–11c**); **11a–11c**: B8(B10) gives d/d, ^{1}J = 146/48 Hz (**11a**), 143/53 Hz (**11b**), 146/46 Hz (**11c**). [d] $^{1}H\{^{11}B\}$ peaks observed; assignment by 2D-$^{1}H/^{11}B$ HMQC NMR (**9b**, **9d**, **9e** by analogy).

Additional signals of **9b**: 1.52 s, 9 H ($C(CH_3)_3$); 4.13 s, 2 H (NH_2); 7.05–7.27, 5 H (C_6H_5); **9c**: 1.42 s, 9 H ($C(CH_3)_3$); 3.88 s, 2 H (CH_2); 4.02 s, 2 H (NH_2); 7.07–7.13, 5 H (C_6H_5); **9d**: 2.19 s, 3 H (CH_3); 2.34 s, 3 H (CH_3); 6.80–7.25, 8 H (C_6H_4), 7.95 s, 2 H (NH_2); **9e**: 0.81 s, 9 H ($C(CH_3)_3$); 0.99 s, 9 H ($C(CH_3)_3$); 2.47 s, 2 H (CH_2); 2.80 s, 2 H (CH_2); 5.34 s, 2 H (NH_2); **11a**: 1.36 s, 9 H ($C(CH_3)_3$); 5.39 s, 1 H (NH); 7.23–7.35, 4 H (C_6H_4); **11b**: 1.21 t, 6 H (CH_3); 3.42 q, 4 H (CH_2); 7.62–7.95, 4 H (C_6H_4); **11c**: 1.29 d, 12 H (CH_3); 3.96 sept, 2 H (CH); 7.22–7.35, 4 H (C_6H_4).

(2c2e) and (3c2e) bonds, as pointed out by Williams[5]. A (2c2e) bond contributes 1 e, a (3c2e) bond 2/3 e to each of the partners; the sum $y + t$ of the y (2c2e) bonds and t (3c2e) bonds must be four at each cluster vertex (octet rule). The difference between the electrons of an unbonded N atom (5 e) and the sum of the four electron contributions of the bonded N atom defines the formal charge. The relation between the formal charge and the cluster connectivity of an N atom is described in Table III. (Note that the terminal N–R bond must be taken into account.)



(*1*)

(*5*)

SCHEME 6

The real charge of the N atom in the *closo*-clusters NB_9H_{10} and $NB_{11}H_{12}$ is certainly negative in the neighbourhood of four or five semimetallic B atoms, as confirmed by *ab initio* calculations[6]. Formal charges follow from the unreal assumption of an equal charge distribution between the partners of a bond. The larger the difference between formal and real charges is, the more the charge density of the binding electrons is shifted towards the more electronegative partner in reality, thus weakening the bond strength. A formal charge of 5/3 to 6/3 of the N atom of *closo*-$RNB_{11}H_{11}$ or a formal charge of 4/3 to 6/3 of the N atom of *closo*-RNB_9H_9 are reduced during the opening process to a formal charge of 3/3 in the opened *nido*-species $RNB_{11}H_{11}L$ (**2**), $[RNB_{11}H_{11}X]^-$ (**3**) or RNB_9H_9L (**7a**), respectively, *i.e.*, to the formal charge of the familiar ammonium-type N atom (L: neutral base; X^-: anionic base, ref.[1]). Thus, the opening process strengthens the remaining B–N bonds.

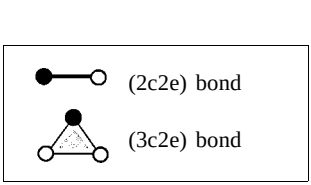
The boron belt adjacent to the N atom of NB_9H_{10} and $NB_{11}H_{12}$ is more positively charged than the B atoms in the second belt and the B atom in antipodal position, according to calculated charge densities[6]. Nucleophiles are expected, therefore, to attack one of the B atoms in the first belt, as observed for **1** and **4**. Electrophiles, on the other hand, are expected from theory to attack B atoms away from the first belt, in accord with experience[7].

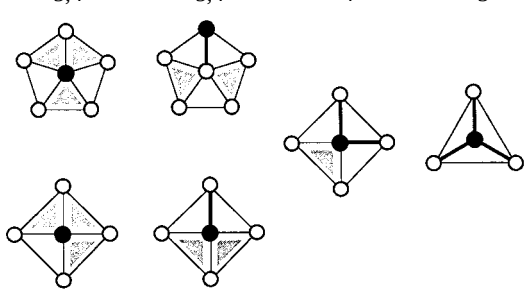
A comment is necessary on the cluster structure of the products **11a–11c**. Formal electron count of $RNB_9H_{10}(NR^1R^2)$ will give a *nido*-structure, if the amino group is taken like an H atom as a one-electron donator, but will give an *arachno*-structure, if the amino group acts as a three-electron donator, *i.e.*, if a BN-π bond between the amino group and the atom B9 is present in addition to the σ-bond. One experimental criterion for the *nido/arachno*-assignment would be the position of the two extra H atoms. They are expected in a bridging position between the atoms B8/B9 and B9/B10 in the case of a *nido*-cluster, RNB_9H_{11} (**8**) being a typical example; in the case of an *arachno*-cluster, $RNB_9H_{11}(NH_2R')$ (**9**) as a typical example, the extra H atoms bridge the atoms B7/B8 and B5/B10. The endo position of these H atoms at the atoms B8 and B10, found for **11b** and **11c**, marks a border position between a *nido*- and *arachno*-cluster structure. A *nido*-structure is indicated by the corresponding 2D-$^1H/^{11}B$ correlations, found for **11a**, but the cross peak for the correlation of the extra H atoms with B9 is distinctly weaker than the one with B8/B10.

Another experimental criterion for the *nido/arachno*-alternative are the ^{11}B NMR shifts, which are distinctly different for the *nido*-cluster (*p*-$ClC_6H_4)NB_9H_{11}$ **8a**, ref.[2]) and the *arachno*-clusters **9b–9e**, which we pick out as typical examples (Table II). Apart from the atoms B8, B9 and B10, which are structurally most different in the

TABLE III
Relation between formal charge and cluster connectivity of the N atom[a]

t + *y*	3 + 1	2 + 2	1 + 3	0 + 4
formal charge	6/3	5/3	4/3	3/3
connectivity	5,4	5,4	4	3





[a] Number of (3c2e)/(2c2e) bonds: *t*/*y*.

compared clusters of type **8**, **9** and **11**, it is apparent that the ^{11}B NMR shifts of **11a–11c** are settled in the range between the signals of *nido*-**8** and *arachno*-**9**.

Altogether, the azaboranes **11** seem to be hybrids in between a *nido*- and an *arachno*-cluster. This corresponds to the assumption of a B–N π-bond, which is distinctly weaker than in simple aminoboranes. This is also in accord with only one ^{1}H NMR doublet for the four Me groups of the amino group i-Pr$_2$N (**11c**). The two i-Pr groups are equivalent because of the mirror plane through **11c**, and the two Me groups of each i-Pr group are equivalent because of the easy rotation of the amino group around the B–N bond, which allows the N–C bonds of the amino group to be situated on the mirror plane, provided the N atom is planarly configurated. At low temperature, however, the one doublet for i-Pr is split into four doublets (τ_{coal} = –40 °C). This means a restriction of the free rotation as well as a particular conformation of the amino group, nonsymmetric with respect to a hypothetical mirror plane. The ^{11}B NMR signals, however, are not affected at low temperature in a way that would indicate loss of C_s symmetry.

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