Five- and Six-Coordinate Nitrogen in Azaborane Clusters

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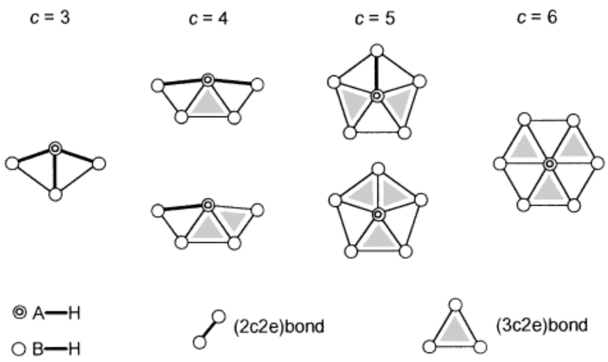
In the majority of known azaboranes $N_aB_bH_c$ and their derivatives, the coordination number of the nitrogen atoms within the cluster does not exceed the classical values of 3 or 4. In the azaboranes *closo*-NB_9H_{10}, *nido*-$NB_{10}H_{13}$, and *closo*-$NB_{11}H_{12}$ and in their derivatives, however, the nitrogen atoms are 5- or 6-coordinate and thus represent a novel bonding situation. The synthesis, structure, and reactivity of these azaboranes are reviewed in this article.

Introduction

Azaboranes $N_aB_bH_c$ are closed deltahedral borane clusters or fragments thereof, in which at least one BH vertex is replaced by an NH vertex. Azaborates are the corresponding anions $[N_aB_bH_c]^{n-}$. Derivatives of azaboranes are formed by the addition of Lewis bases L to give $N_aB_bH_cL_d$ or by the substitution of hydrogen atoms by anionic groups X to give $N_aB_bH_cX_d$ (X = F, OR, NR_2, R etc.). Heteroazaboranes $S_aN_bC_cB_dH_eM_f$ are those azaboranes in which BH vertices have been replaced by S, CH, M etc.; the symbol M in this context means the fragment of a transition-metal complex with the metal atom being incorporated into the cluster skeleton.

If the bonding within borane clusters is described in terms of localized bonds, then electron deficiency makes it necessary to take skeletal three-centre, two-electron [(3c,2e)] bonds into account in addition to the more usual two-centre, two-electron [(2c,2e)] bonds. The skeletal coordination number, called *connectivity* (*c*), may exceed the value $c = 3$; this value would allow a skeletal atom to form four traditional (2c,2e) bonds, including one radial (2c,2e) bond between the skeletal atom and its *exo* ligand. Values of $c = 3-5$ are usually encountered in borane clusters, and $c = 6$ is found in a few cases. With $c > 3$, (2c,2e) bonds are no longer sufficient for the description of bonds. It may be de-

Figure 1. Localized bonds for a skeletal atom A with different connectivities of A



Peter Paetzold, born in 1935, received his doctoral degree on his work with Egon Wiberg at the Ludwig-Maximilians-Universität in Munich in 1961. He became Professor of inorganic chemistry and Director of the Institut für Anorganische Chemie at the Rheinisch-Westfälische Technische Hochschule in Aachen in 1968. He focused his interest on synthetic, structural and mechanistic aspects of boron chemistry. Due to his work, major progress was achieved in the chemistry of azidoboranes (the analogues of carbonic azides), iminoboranes (the analogues of alkynes, presenting a BN triple bond), boron-nitrogen ring compounds (the analogues of cyclobutadiene, benzene, Dewar benzene, and cyclooctatetraene), azadiboriridines (the analogues of cyclopropenyl cations, presenting a BB bond of unexpected basicity), and azaborane clusters (the analogues of dicarbaborane clusters, presenting five- and six-coordinate nitrogen). The analogy of the couples BN and CC, also of the couples BO and CN, is the common thread running through his work.

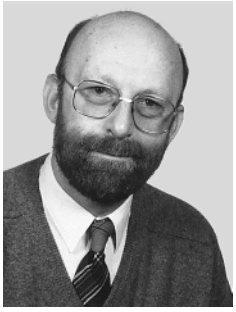


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Table 1. Formal charge $\delta_F(A)$ of skeletal atoms A = B, C, N, depending on the number t of (3c,2e) and y of (2c,2e) bonds at A (see Figure 1)

c t/y	3 0/3	4 1/2	4 2/1	5 2/1	5 3/0	6 3/0
$\delta_F(B)$	−3/3	−2/3	−1/3	−1/3	0	0
$\delta_F(C)$	0	+1/3	+2/3	+2/3	+3/3	+3/3
$\delta_F(N)$	+3/3	+4/3	+5/3	+5/3	+6/3	+6/3

duced from Figure 1 that for c = 4−6 at least one, two or three (3c,2e) bonds are necessarily present, respectively, provided the atom A obeys to the octet rule. (Note that connectivities c = 3−6 correspond to overall coordination numbers of 4−7 by inclusion of the *exo* ligand.)

The discovery in 1963 that carbon atoms within the icosahedral C_2B_{10} skeleton of the carbaborane $C_2B_{10}H_{12}$[1] exhibited a connectivity c = 5 (coordination number = 6) changed the traditional view of the bonding situation of

Figure 2. Azaboranes and azaheteroboranes with a nitrogen connectivity of 2 or 3 (read BR instead of BH in **1−6**)

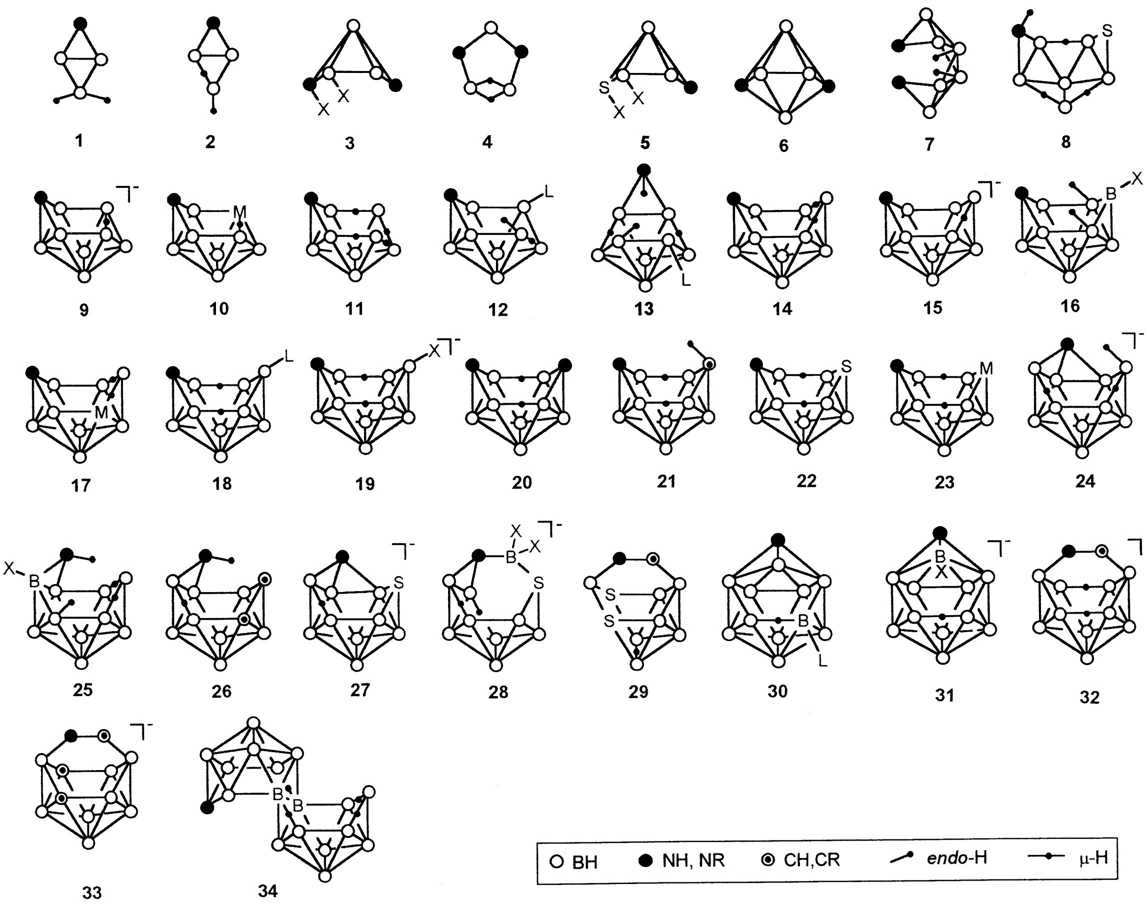


Table 2. Azaboranes and azaheteroboranes with nitrogen connectivity of 2 or 3

Vertices	Type	Skeletal atoms	Number in Figure 2
4	*nido*	NB_3	**1**[5][6] **2**[6]
5	*arachno*	N_2B_3 SNB_3	**3**[6] **4**[7] **5**[8]
6	*nido*	N_2B_4	**6**[9][10]
8	*arachno*	N_2B_6	**7**[11]
8	*hypho*	SNB_6	**8**[12]
9	*nido*	NB_8 NB_7M	**9**[13] **10**[14]
9	*arachno*	NB_8	**11**[15] **12**[13][16]
9	*hypho*	NB_8	**13**[17]
10	*nido*	NB_9 NB_8M	**14**[13][18][19][20][21][22] **15**[23] **16**[23] **17**[24]
10	*arachno*	NB_9 N_2B_8 NCB_8 SNB_8 NB_8M	**18**[21][25][26] **19**[25] **20**[27] **21**[28] **22**[12] **23**[24]
11	*arachno*	NB_{10} NC_2B_8 SNB_9	**24**[20][29][30] **25**[31] **26**[2][32][33] **27**[30]
11	*hypho*	SNB_9 S_2NCB_7	**28**[30] **29**[34]
12	*nido*	NB_{11}	**30**[35] **31**[35][36]
12	*arachno*	NCB_{10} NC_3B_8	**32**[37] **33**[37]
18	*nido*	NB_{17}	**34**[38]

carbon-containing molecules. Whereas the formal charge of boron changes from −1 to the more favourable value of 0 as a result of an increase in its connectivity (Table 1), the formal charge of carbon may become +1 with a connectivity of $c = 6$ or even $c = 5$. Since carbon is more electronegative than boron and its real charge is less positive than that of boron, the B−C skeletal bonds must be highly polarized, and actually the border case $c = 6$ is not observed for carbon. Indeed, there is a strong tendency in the reactions of icosahedral carbaboranes to reduce the connectivity of carbon. The more electronegative nitrogen shows a formal charge of at least +4/3 or +5/3, when incorporated into a cluster skeleton with $c = 4$ or 5, respectively. Hence, a very large bond polarisation must be expected in corresponding azaboranes. Nevertheless, the carbaborane $NC_2B_8H_{11}$ with $c(N) = 4$ was synthesized as early as 1974[2], followed in 1986 by the closed cluster molecule NB_9H_{10}[3], and finally, the icosahedral cluster molecule $NB_{11}H_{12}$ in 1991. The discovery of $NB_{11}H_{12}$, which is isoelectronic with $C_2B_{10}H_{12}$, represented the first observation of the connectivity $c(N) = 5$[4]. Certainly, the reactivity of the highly coordinated azaboranes is governed by their tendency to reduce the connectivity at nitrogen.

A great number of small azaboranes and heteroazaboranes clusters with $c(N) = 2$ and larger ones with $c = 3$ are known. The skeletal nitrogen atoms in these azaboranes are bonded in a way that may be interpreted only in terms of (2c,2e) bonds. A survey is given in Figure 2 and Table 2. In terms of Wade's rules, *nido*, *arachno*, and *hypho* clusters are present, although no *closo* species are found. Note that the same structural pattern, an icosahedral fragment, holds for all the molecules and anions **11**−**34**. Note also that in cases of $c(N) = 2$ (**1**−**5**, **7**, **8**, **13**, **29**, **32**, **33**) π bonds need to be taken into account in order to provide the nitrogen atom with an electron octet.

A much smaller number of azaboranes and heteroazaboranes with $c(N) = 4$, 5 have been described; Table 3 and Figure 3 present a synopsis. All these clusters are derived from three parent azaboranes, all of which are well-characterized: *closo*-NB_9H_{10} (**35**), *nido*-$NB_{10}H_{13}$ (**38**), and *closo*-$NB_{11}H_{12}$ (**43**). It is intended here to review the synthesis, structure, and reactivity of these azaboranes with 5- and 6-coordinate nitrogen centres. Part of this chemistry has already been reviewed[50][51][52][53]. We start with a section about synthetic procedures that still includes all of the azaboranes.

Synthesis

The commercially available decaborane, $B_{10}H_{14}$, is the starting material for the synthesis of the azaboranes **8**−**45**, presented in this section. The synthesis of the azaboranes **1**−**7**, which starts from the azadiboriridine NB_2R_3 or from iminoboranes RB(NR′), will not be discussed here. There are three synthetic possibilities that include a change of skeletal atoms: the addition (*insertion*) or the removal (*degradation*) of a skeletal atom or both (*degradative insertion*). In addition, there are two possibilities that involve a change only in the skeletal *arrangement*, and which go hand in hand with a transformation in the direction *arachno* → *nido* → *closo* (*closure*) or vice versa (*opening*). Changes in the ligand sphere or in the hydrogen bridge area (e.g. deprotonations) are not considered in this section.

Figure 3. Azaboranes and azaheteroboranes with nitrogen of connectivity 4 or 5

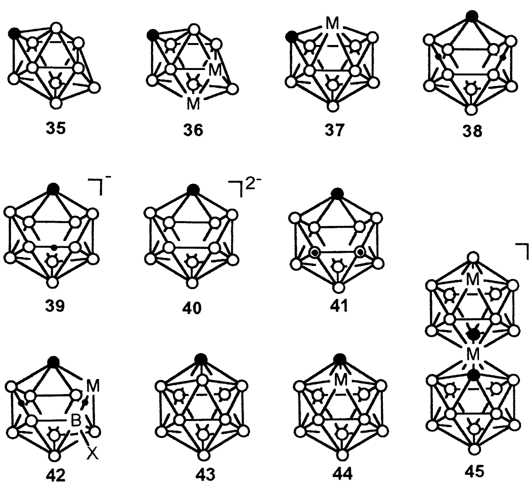


Table 3. Azaboranes and azaheteroboranes with nitrogen connectivity of 4 or 5

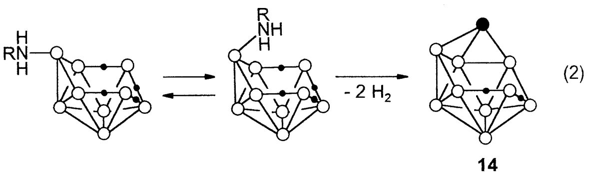
Vertices	Type	Skeletal atoms	Number in Figure 3
10	*closo*	NB_9 NB_7M_2	**35**[3][13][39] **36**[40]
11	*closo*	NB_9M	**37**[19][41]
11	*nido*	NB_{10} NC_2B_8 NB_9M	**38**[31][42] **39**[43][44] **40**[43][44] **41**[2][32][33][45] **42**[46]
12	*closo*	NB_{11} $NB_{10}M$	**43**[4][21][36][47][48][49] **44**[43][44] **45**[44]

Insertion

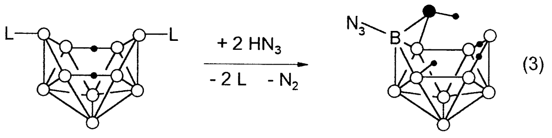
We describe here the insertion of sulphur S (into azaboranes), nitrenes NH or NR (into boranes), metal-complex fragments M (into azaboranes), and borylenes BH (into azaboranes). The insertion of elemental sulphur transforms the *nido* anion **15** into the *arachno* anion **27**, the sulphur atom contributing four electrons to the cluster [Eq. (1)]. The anion **15** is easily available from RNB_9H_{11} (**14**) by applying the base 1,8-bis(dimethylamino)naphthalene (*proton sponge*)[30].

$$[RNB_9H_{10}]^- + 1/8\ S_8 \rightarrow [S(RN)B_9H_{10}]^- \qquad (1)$$

The insertion of a nitrene unit NR into a B_9 skeleton can be achieved by first transforming $B_9H_{13}(SMe_2)$ into $B_9H_{13}(NH_2R)$ followed by a dehydrogenation in boiling xylene to give products of type **14** [Eq. (2)][13][21]. [Note the identity of the structures **14** given in Eq. (2) and in Figure 2].



The insertion of a unit NH (from HN_3) into $B_{10}H_{12}L_2$ (L = SMe_2) to give **25** with a bridging NH_2 group [c(N) = 2] is accompanied by an H/N_3 ligand exchange [Eq. (3)][31].



25

The reaction of CB_8H_{14} first with $NaNO_2$ and then with hydrochloric acid yields NCB_8H_{13} (**21**); the stoichiometry of this insertion of an NH vertex is unknown[28]. The insertion of metal cations into azaboranes, on the other hand, follows a clear cut stoichiometry. The 10-vertex *nido* species NB_9H_{12} (**14**) is transformed into an 11-vertex species either of the *closo* type [**37**; M = CpCo[19], (cymene)Ru[41]; Eq. (4)] or the *nido* type (**42**; X = Cl, M = Cp*Ir[46]). The 11-vertex *nido* species $[NB_{10}H_{12}]^-$ (**39**) and $[NB_{10}H_{11}]^{2-}$ (**40**) are transformed into the 12-vertex *closo* species $NB_{10}H_{11}M$ [**44**; M = $(Ph_3P)_2HRh$[43], $(C_6Me_6)Ru$, $(Ph_3P)_2Ni$[44]; Eqs. (5), (6)] or $[M(NB_{10}H_{11})_2]^-$ (**45**; M = Co[44]). The *arachno* 9-vertex species NB_8H_{13} (**11**), finally, gives the *nido* species $NB_8H_{11}M$ [**23**; M = $(Me_2PhP)_2Pt$[24]; Eq. (7)].

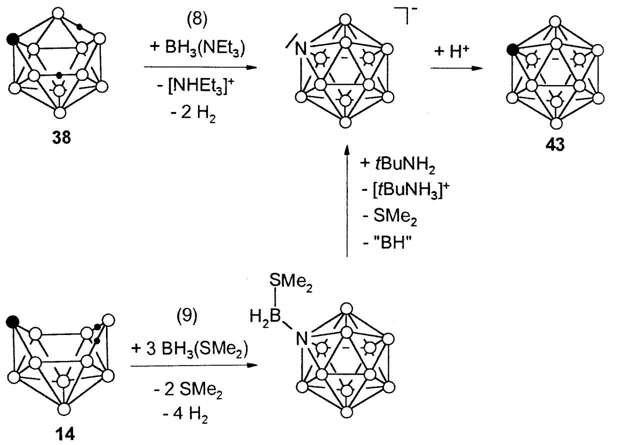
$$NB_9H_{12} + 1/2\ [(C_{10}H_{14})RuCl_2]_2 \rightarrow NB_9H_{10}[Ru(C_{10}H_{14})] + 2\ HCl \tag{4}$$

$$[NB_{10}H_{12}]^- + (Ph_3P)_3RhCl \rightarrow NB_{10}H_{11}[RhH(PPh_3)_2] + PPh_3 + Cl^- \tag{5}$$

$$[NB_{10}H_{11}]^{2-} + 1/2\ [(C_6Me_6)RuCl_2]_2 \rightarrow NB_{10}H_{11}[Ru(C_6Me_6)] + 2\ Cl^- \tag{6}$$

$$NB_8H_{13} + [(PhMe_2P)_2PtCl_2] \rightarrow NB_8H_{11}[Pt(PMe_2Ph)_2] + 2\ HCl \tag{7}$$

The insertion of a BH unit into azaboranes plays an important role in the synthesis of the icosahedral species $NB_{11}H_{12}$ (**43**). It is possible to start from the *nido* clusters $NB_{10}H_{13}$ (**38**) or NB_9H_{12} (**14**) and insert one or two BH units, respectively [Eq. (8)[4] and (9)[48]]. The thermal dehydrogenation (140°C) of **38** or **14** in the presence of BH_3 yields the *closo* anion $[NB_{11}H_{11}]^-$, either directly [Eq. (8)[4]] or via *closo*-$(Me_2SBH_2)NB_{11}H_{11}$ [Eq. (9)[48]; the anion can then easily be protonated to give **43**.



38 **43** **14**

The synthesis of the *N*-organo *closo* 12-vertex derivative $RNB_{11}H_{11}$ can be achieved in one step from RNB_9H_{11} (**14**) [Eq. (10)][21].

$$RNB_9H_{11} + 2\ BH_3(SMe_2) \rightarrow RNB_{11}H_{11} + 2\ SMe_2 + 3\ H_2 \tag{10}$$

The insertion of a molecule BH_3 without loss of H_2 should transform a *nido* into an *arachno* species, exemplified by the formation of the anion **24** from the anion **15** [Eq. (11)][29][30].

$$[RNB_9H_{10}]^- + BH_3(thf) \rightarrow [RNB_{10}H_{13}]^- + thf \tag{11}$$

Both a carbyne unit and a nitrene unit are inserted when nitriles R′CN are added to the anions $[B_{10}H_{13}]^-$ or $[C_2B_8H_{11}]^-$ to give the 12-vertex *arachno* clusters $[N(R'C)B_{10}H_{13}]^-$ (**32**) and $[NC_2(R'C)B_8H_{11}]^-$ (**33**), respectively[37].

Degradation

The *nido* cluster NB_9H_{12} (**14**) is sensitive towards protic agents. One boron atom is removed by the attack of water in the presence of an acid to give *arachno*-NB_8H_{13} (**11**) [Eq. (12)][15].

$$NB_9H_{12} + 3\ H_2O \rightarrow NB_8H_{13} + B(OH)_3 + H_2 \tag{12}$$

One boron vertex is removed from *closo*-RNB_9H_9 and recovered in the borazine $(HBNR')_3$, when primary amines are applied, either according to Eq. (13) in polar THF or according to Eq. (14) in less polar, noncoordinating dichloromethane giving the *nido* anion **9** or the *arachno* species **12**, respectively[13].

$$RNB_9H_9 + 2\ R'NH_2 \rightarrow [R'NH_3][RNB_8H_9] + 1/3\ (HBNR')_3 \tag{13}$$

$$RNB_9H_9 + 2\ R'NH_2 \rightarrow RNB_8H_{10}(NH_2R') + 1/3\ (HBNR')_3 \tag{14}$$

The elimination of a BH_3 unit from the anions $[NB_{10}H_{14}]^-$ and $[NB_{10}H_{13}(N_3)]^-$ (**24**) on protonation may be accompanied by a cluster closure and is therefore mentioned in a later section.

Degradative Insertion

The first production of an azaborane with c(N) = 3 dates back to 1967, when two products, including the *arachno* cluster **19** (X = H)[25], were isolated from the reaction of decaborane and a thionitrosyl amine [Eq. (15)]. The fate of the expelled B atom is not known.

$$B_{10}H_{14}/Me_2NNS \rightarrow [SB_{10}H_{11}]^-/[(Me_2N)NB_9H_{12}]^- \tag{15}$$

Going from thionitrosyl to nitrosyl made a series of azaboranes available by the application of $NaNO_2$ in acidic media[54]. The transformation of the carbaborate $[C_2B_9H_{12}]^-$ into a mixture of $NC_2B_8H_{13}$ (**26**) and $NC_2B_8H_{11}$ (**41**) marked the starting point for this method in 1974[2], followed by the synthesis of NB_9H_{12} (**14**) in 1975;

the workup can be done with conc. H_2SO_4 [Eq. (16)][15] or with iodine, giving a 57% yield[19].

$$B_{10}H_{14}/NaNO_2/H_2SO_4 \rightarrow NB_9H_{12} \qquad (16)$$

The diazaborane $N_2B_8H_{12}$ (**20**) can be prepared from NB_9H_{12} (**14**) by the same method. More stoichiometric clarity is achieved when the ionic nitrite is replaced by alkylnitrites [Eq. (17)][39]. The expelled boron vertex is then identified as trialkoxyborane.

$$B_{10}H_{14} + 3\ EtONO \rightarrow NB_9H_{12} + B(OEt)_3 + H_2 + NO + NO_2 \qquad (17)$$

The thiaborane SB_9H_{11} was transformed by the action of BuONO into a mixture of SNB_6H_{11} (**8**) and SNB_8H_{11} (**22**)[12], and $B_{18}H_{22}$ into $NB_{17}H_{20}$ (**34**)[38].

We formally consider the nitrogen atoms of bridging amino groups to be skeletal atoms with $c = 2$ throughout this review article; the alternative position would be to view such groups as having the same functionality as two skeletal ligands, one of which contributes one and the other two electrons. The very first synthetic route to a larger azaborane was by the degradative insertion of an NHEt vertex by reacting $B_9H_{13}(SEt_2)$ with NH_2Et. The *hypho* cluster **13** (L = NH_2Et) was synthesized by this method in 1962[55] and was structurally identified in 1963[17]. The expelled boron vertex was presumably incorporated into a borazine [Eq. (18)].

$$B_9H_{13}(SEt_2) + 3\ NH_2Et \rightarrow (EtHN)B_8H_{11}(NH_2Et) + SEt_2 + 2\ H_2 + 1/3\ (HBNEt)_3 \qquad (18)$$

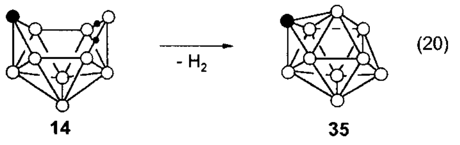
The 10% yield of NB_7H_9M [**10**; M = $Ir(PMe_3)_3$] from the action of N_2H_4 on $B_8H_{12}M'$ [M' = $Ir(CO)(PMe_3)_2$] is formally the result of a degradative insertion[14].

A metal rather than a nitrogen vertex may be inserted under expulsion of a boron vertex. For example, $NB_8H_{11}M$ [**17**; M = $(C_6Me_6)Ru$] may be formed from NB_9H_{12} (**14**) and $[MCl_2]_2$[24] and azadirhoda-*closo*-decaborane **36** (M = Cp*Rh) from the *hypho*-borane **13** and $[MCl_2]_2$ [Eq. (19)][40].

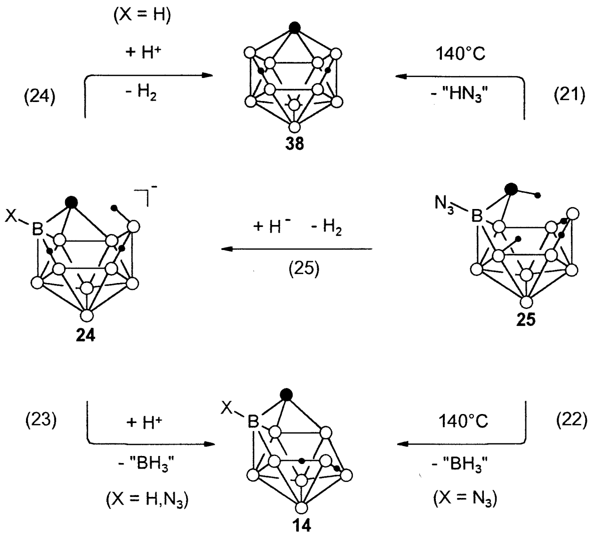
$$(EtHN)B_8H_{11}(NH_2Et) + [Cp^*RhCl_2]_2 + 4\ NaH \rightarrow (EtN)B_7H_7(RhCp^*)_2 + BH_3(NH_2Et) + 4\ NaCl + 3\ H_2 \qquad (19)$$

Closure

Thermal dehydrogenation of *nido*-NB_9H_{12} at 375–400 °C makes *closo*-NB_9H_{10} available [Eq. (20)][3], and the dehydrogenation of RNB_9H_{11} follows the same pattern to give RNB_9H_9[13].



The *arachno* species $NB_{10}H_{14}(N_3)$ (**25**) undergoes an elimination of HN_3 in boiling xylene to give the *nido* cluster **38** [Eq. (21)]; the degradation product **14**, however, is the predominant product component [Eq. (22)][31]. Upon protolysis, the 11-vertex *arachno* anions of type **24**, $[RNB_{10}H_{13}]^-$ [from **15** by the insertion of BH_3, Eq. (11)] or $[NB_{10}H_{13}(N_3)]^-$ (from **25** by deprotonation[20]), are also predominantly degraded to give products of type **14** [Eq. (23)][20][29][30]; in the case of $[NB_{10}H_{14}]^-$, the *nido* species **38** is the concurrent closure product [Eq. 24)][29]. The deprotonation of **25**, according to Eq. (25)[20], represents a closure process that transforms one *arachno* structure (**25**) into another (**24**). Note that the skeleton of **24** can formally be derived from the corresponding *nido* skeleton of **30** or **31** by the removal of a vertex with $c = 4$, thus increasing the pentagonal aperture of **30** and **31** by one vertex; a vertex of $c = 5$ needs to be removed in order to transform **30** or **31** formally into **25** with a heptagonal aperture.



Opening

The opening of the *closo* species RNB_9H_9 (**35**) and $RNB_{11}H_{11}$ (**43**) by protic agents HX, neutral bases L, or anionic bases X^- gives *nido* products of the type $RNB_9H_{10}X$ (**16**), $RNB_{11}H_{11}L$ (**30**), or $[RNB_{11}H_{11}X]^-$ (**31**), respectively, as discussed in a later section. The *nido* clusters RNB_9H_{11} (**14**) are transformed into the *arachno* clusters $RNB_9H_{11}L$ (**18**) by the addition of Lewis bases L; the term "opening" has only an electronic meaning in this case, since the topology of the 10-vertex cluster skeleton is the same for *nido* and *arachno* species.

Structure

The geometry of the parent aza-*closo*-boranes NB_9H_{10} (**35**) and $NB_{11}H_{12}$ (**43**) have been determined from Hartree-Fock SCF calculations with 3-21G an 6-31G* basis sets as well as from X-ray (**35**) and electron diffraction work (**43**) (Table 4). The structures represent a C_{4v} distorted bicapped tetragonal antiprism and a C_{5v} distorted icosahedron, respectively, as expected from Wade's cluster rules. We denote the three types of symmetrically equivalent boron atoms as *ortho*, *meta*, and *para* with respect to their distance from the nitrogen vertex. Typically, the nitrogen vertex of

NB_9H_{10} is in one of the two capping positions with $c = 4$. The highly symmetric structures, calculated for NB_9H_{10} and $NB_{11}H_{12}$ and observed for $NB_{11}H_{12}$ in the gas phase, are also present in solution, according to NMR data; they are slightly distorted in crystalline NB_9H_{10} and in two crystalline derivatives of $NB_{11}H_{12}$ (Table 4). Although the skeletal distances of the free molecules are in general longer than those in the crystal, the sequence is the same when going through the five zones of equivalent distances for C_{4v} or C_{5v} symmetry. The BN bonds, the shortest in both *closo* clusters, are distinctly shorter in the NB_9 than in the NB_{11} skeleton, a phenomenon that is apparently related to the different connectivity of the nitrogen atom. A smaller effect of the same type and origin is observed for the boron atoms in the *antipodal* position, i.e. the apex opposite to the nitrogen atom.

A typical feature of both polyhedra is the short distance between the nitrogen atom and the polyhedral centre, if compared to the boron atoms. The penetration of the nitrogen atom into the cluster widens the B−B distances in the upper pyramidal basis making them the largest in the skeleton. In addition, the four (five) B−H bonds in the upper pyramidal basis are shifted away from the radial direction towards the nitrogen atom, thereby shielding it considerably.

Table 4. Calculated and experimental distances in *closo*-NB_9 and -NB_{11} skeletons[a]

	NB_9H_{10} calcd.[56][57]	NB_9H_{10} X-ray[39]	$NB_{11}H_{12}$ calcd.[56]	$NB_{11}H_{12}$ GED[47]	$RNB_{11}H_{11}$[b] X-ray[21]	$NB_{11}H_{10}Y$[c] X-ray[48]
Upper pyramid (B−N)	157.7	152	171.0	171.6(9)	171.9	172.2
Upper pyramidal basis	187.4	181	182.1	182.5(6)	179.6	179.7
Antiprismatic zone	180.6	175	176.7	179.1(5)	174.5	175.2
Lower pyramidal basis	186.9	177	180.8	179.1(5)	177.3	178.3
Lower pyramid	171.1	163	179.8	179.1(5)	177.0	178.1

[a]Average of four (five) slightly different values in the four pyramidal zones and of eight (ten) values in the antiprismatic zone in the NB_9 (NB_{11}) skeleton in the case of crystal data − [b] R = $PhCH_2$ − [c] Group Y represents a $-BH_2-NEt-CH_2-CH_2-$ chain, bridging N and B2

The structures of the azametalla-*closo*-boranes $NB_7H_8(RhCp^*)_2$ (**36**)[40], $NB_{10}H_{11}[RhH(PPh_3)_2]$[43], and $NB_{10}H_{11}[Ru(C_6Me_6)]$ (**44**)[44] have also been investigated in the crystalline phase and represent typical 10- or 12-vertex *closo* structures, respectively.

The azametallaboranes **37**, $NB_9H_{10}(CoCp^*)$[19] and $NB_9H_{10}[Ru(cymene)]$[41], represent the rare case of a 11-vertex *closo* species for which the structure has been confirmed. Typically, the metal atom is in the unique position with $c = 6$; this position is unfavourable for boron and impossible for nitrogen.

The *nido* 11-vertex molecules $RNB_{10}H_{12}$ (R = NB_2HtBu_3; **38**), $NC_2B_8H_{11}$ (**41**), and $NB_9H_{11}Cl(IrCp^*)$ (**42**) can be described as the expected icosahedral fragment structures with a pentagonal aperture, which is confirmed by crystal structure analysis[42][45][46].

There is no doubt that five-coordinated nitrogen atoms ($c = 4$) are incorporated into the borane cluster skeletons of the *closo* 10-, *closo* 11- and *nido* 11-vertex species and six-coordinated nitrogen atoms ($c = 5$) into the skeletons of the *closo* 12-vertex species.

Although the formal charge of the nitrogen atom is highly positive, the real atomic charge is expected to be most negative at the electronegative nitrogen atom of NB_9H_{10} or $NB_{11}H_{12}$, whereas the most positive positions should be the nitrogen-bound hydrogen atom and the boron atoms adjacent to the nitrogen atom (*ortho* position, *o*-B). This is confirmed by ab initio calculations of the atomic charges, which are quantitatively different depending on whether calculated according to the methods of either Mulliken or Löwdin (Table 5). Qualitatively, however, the results of the two calculations are in accord and indicate that the boron atoms in the *meta* position (*m*-B) are the most negatively charged ones, the antipodal boron atoms (*para* position, *p*-B) range between *o*-B and *m*-B, and the least positively charged hydrogen atoms are the antipodal ones. The large calculated dipole moments of ca. 5.1 (**35**) and 4.6 D (**43**) are oriented with their positives ends towards the negatively charged nitrogen atoms, demonstrating that all the 20 (24) atoms and particularly the hydrogen atoms on the symmetry axis contribute to the dipole moment.

The sequence $m > p > o$ for the charge densities at the boron atoms (Table 5) does not parallel the ^{11}B-NMR chemical shifts, which form a series $m > o > p$ with decreasing field [in CD_2Cl_2, standard $BF_3(OEt_2)$]: −21.7, −5.6, 62.4 (NB_9H_{10})[39] and −11.9, −9.8, 2.7 ($NB_{11}H_{12}$)][4]. The downfield shift of *p*-B, particularly with NB_9H_{10}, is called the *antipodal effect*. It has been compared to the corresponding antipodal effect exhibited by the isoelectronic species XB_9H_9 and $XB_{11}H_{11}$ with X = AlH^{2-}, BH^{2-}, CH^-, S etc. The antipodal effect for NB_9H_{10} has been described as greatly influenced by the paramagnetic part of the chemical shielding; the HOMO−LUMO energy difference is also an important factor, as are the tangential p_x, p_y orbitals at the *p*-B atom, which are called *NMR-active*[57][58][59]. Since precise calculated geometrical data are available, computational methods such as IGLO allow the calculation of ^{11}B-NMR data which are in good accord with experimental results[47].

An analysis of the charge distribution in clusters should provide an understanding of which vertices will be attacked by electrophiles and which by nucleophiles. The products of ligand substitution, opening, and even degradation reac-

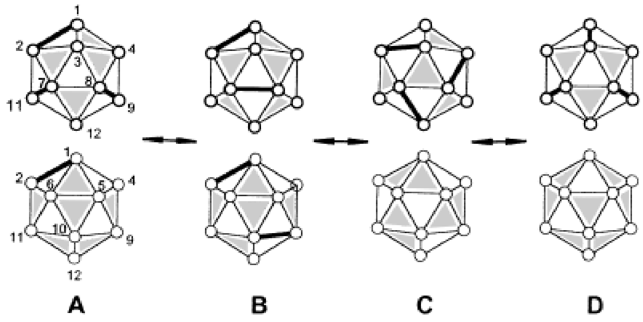
Table 5. Mulliken (a) and Löwdin (b) atomic charges of NB_9H_{10} and $NB_{11}H_{12}$[56]

		N	*o*-B	*m*-B	*p*-B	1-H	*o*-H	*m*-H	*p*-H
NB_9H_{10}	(a)	−1.073	0.184	−0.068	0.092	0.434	0.000	0.027	−0.024
	(b)	−0.234	0.062	−0.135	−0.077	0.291	0.030	0.040	0.031
$NB_{11}H_{12}$	(a)	−1.065	0.097	−0.054	0.009	0.443	0.037	0.037	0.029
	(b)	−0.222	0.027	−0.123	−0.078	0.295	0.040	0.048	0.038

tions may be predicted, provided that the first step of the reaction determines the products and that the ground-state polarities determine the transition state of that first step. In the case of NB_9H_{10} and $NB_{11}H_{12}$, one would expect nucleophiles to attack the *ortho* position and electrophiles the *meta* position. Such an expectation is met for nucleophiles, which exclusively attack at the *ortho* belt, whereas electrophiles attack either in the *para* or in the *meta*, but never in the *ortho* position (see following sections).

The binding electrons in closed boranes are delocalized over the whole skeleton in a way that is strongly suggestive of the π electrons in benzene-type molecules, and closed boranes have therefore been denoted as aromatic systems. In this context, azaboranes may be compared to pyridine. In the old-fashioned valence-bond description of benzene, the delocalization of the π electrons is achieved by introducing resonance between structures built up by localized (2c, 2e) π bonds. Such a procedure can also be applied to boranes, where the resonating structures are built up by localized (2c,2e) and (3c,2e) bonds[60]. The icosahedral dodecaborate $[B_{12}H_{12}]^{2-}$ is given as an example. This anion may be built up by y (2c,2e) bonds and t (3c,2e) bonds. The 24 atoms contribute 60 valence orbitals and 50 valence electrons. From the balances $60 = 3t + 2y$ and $50 = 2t + 2y$, we find $y = 15$ and $t = 10$. There are twelve B−H (2c,2e) bonds leaving three (2c,2e) and ten (3c,2e) bonds to build up the cluster skeleton. Four resonance structures of different energy can be constructed (Figure 4). Each of the structures **A** and **B** of C_1 symmetry is related to 120 degenerate resonance structures, the structure **C** (C_3 symmetry) allows 40 and the structure **D** (C_{3v} symmetry) 20 degenerate structures, which altogether sum up to 300 resonating structures. (Note that the number of degenerate structures is equal to the ratio of the order of the group I_h to the order of the corresponding subgroup.) The number of structures would be increased if we allowed those which (a) contain also open instead of only closed (3c,2e) bonds, (b) contain edges without bonding interaction, (c) contain vertices not obeying the octet rule. In going from $[B_{12}H_{12}]^{2-}$ to the isoelectronic $NB_{11}H_{12}$ the degeneracy decreases and structures in which the nitrogen atom adopts one of the (2c,2e) bonds become favourable.

Figure 4. Resonance formulae **A**−**D** of $[B_{12}H_{12}]^{2-}$, front and rear side of the icosahedral structure being shown for each



Reactivity

Little is known about the reactivity of the azametalla-*closo*-boranes with either an NB_7M_2 (**36**), NB_9M (**37**), or $NB_{10}M$ skeleton (**44**, **45**). The same is true for the reactivity of the *nido* 11-vertex clusters $NC_2B_8H_{11}$ (**41**) and $NB_9H_{11}ClM$ (**42**). More is known about the reactivity of *closo*-NB_9H_{10} (**35**), *closo*-$NB_{11}H_{12}$ (**43**), and *nido*-$NB_{10}H_{13}$ (**38**).

Redox Reactions

The *N*-alkyl derivatives RNB_9H_9 and $RNB_{11}H_{11}$ are stable towards iodine and bromine, even if dissolved in liquid bromine[49]. A mixture of $RNB_{11}H_{11}$ and liquid chlorine may be kept for a while at low temperature, but can undergo a spontaneous violent reaction. No doubt BN, $BHal_3$ and HHal are the thermodynamically stable products from a mixture of $NB_{11}H_{12}$ and excess Hal_2, but such a mixture is more or less metastable. Strong reduction agents like alkali metals do not react with $RNB_{11}H_{11}$.

Brønsted Acid/Base Reactions

The skeleton of the *closo* species RNB_9H_9 and $RNB_{11}H_{11}$ is stable if dissolved in strong acids such as triflic acid F_3CSO_3H[49]; a proton/proton exchange cannot be excluded, however. The nitrogen-bound protons of the parent molecules NB_9H_{10} and $NB_{11}H_{12}$ can be easily removed by bases, in the case of $NB_{11}H_{12}$ even with the weak base NEt_3, to give the anions $[NB_9H_9]^-$ and $[NB_{11}H_{11}]^-$. These anions can easily be alkylated by RI and RO_3SCF_3, respectively, if R represents an α-unbranched alkyl group[3][21][36]; bulky alkyl and aryl groups R cannot be fixed to the nitrogen atom of the anions, but such derivatives RNB_9H_9 and $RNB_{11}H_{11}$ are available from RNB_9H_{11} by either dehydrogenation [Eq. (20)] or insertion of two BH units [Eq. (10)], respectively.

The *nido* cluster $NB_{10}H_{13}$ (**38**) can be deprotonated once or twice by hydride bases, depending on the stoichiometric amount of base. The protons are removed from the bridging positions, not from the NH group. The corresponding anions $[NB_{10}H_{12}]^-$ (**39**) and $[NB_{10}H_{11}]^{2-}$ (**40**) are isoelectronic with the anions $[C_2B_9H_{12}]^-$ and $[C_2B_9H_{11}]^{2-}$ and, like these, they offer a pentagonal open face which is isolobal with $C_5H_5^-$ and is ready, therefore, to form pentahapto bonds with transition-metal species M^{2+}. A third proton cannot be removed from $[NB_{10}H_{11}]^{2-}$. Interestingly, the *nido*-azadicarbaborane $NC_2B_8H_{11}$ (**41**) which is isoelectronic with $NB_{10}H_{13}$ can be deprotonated at the nitrogen atom, since bridging hydrogen atoms are absent; applying K_2CO_3 and MeI consecutively gives the corresponding *N*-

methyl derivative[32][45]. Nevertheless, the terminal nitrogen atom and not one of the bridging protons becomes active when $NB_{10}H_{13}$ is added to the azadiboriridine NB_2tBu_3 to yield $(NB_2HtBu_3)NB_{10}H_{12}$[42].

Electrophilic Substitution

The *closo* clusters RNB_9H_9 (R = p-ClC_6H_4) and $RNB_{11}H_{11}$ (R = Me) react neither with triflic acid (as mentioned above) nor with methyl triflate. A mixture of one of the clusters, with methyl triflate as the solvent and triflic acid as a catalyst, however, results in a five- and six-fold methylation after four hours [Eqs. (26), (27)][49].

$$NB_9H_9 + 5\ MeOTrf \rightarrow RNBH_4Me_5 + 5\ HOTrf \qquad (26)$$

$$RNB_{11}H_{11} + 6\ MeOTrf \rightarrow RNB_{11}H_5Me_6 + 6\ HOTrf \qquad (27)$$

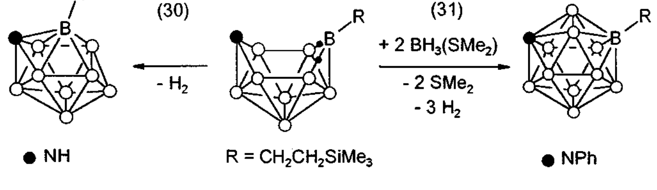
As expected from the cluster charge distribution, the *ortho* positions remain unattacked by the electrophile, whereas the *meta* and *para* positions are completely substituted. The same procedure transforms the *ortho*-dicarbaborane $C_2B_{10}H_{12}$ into $C_2B_{10}H_2Me_{10}$; all boron vertices in this product carry methyl groups, even those adjacent to carbon[61]. If the methylation of the aza-*closo*-boranes is prolonged by 16 hours, one of the methyl groups in each of the products is replaced by a triflate group [Eqs. (28), (29)].

$$RNB_9H_4Me_5 + HOTrf \rightarrow RNB_9H_4Me_4(OTrf) + CH_4 \qquad (28)$$

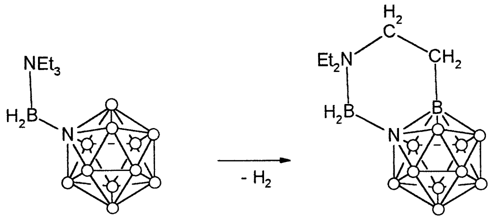
$$RNB_{11}H_5Me_6 + HOTrf \rightarrow RNB_{11}H_5Me_5(OTrf) + CH_4 \qquad (29)$$

The triflate group is fixed to a *meta* position in the 10-vertex product, but to a *para* position in the icosahedral species. An electrocyclic mechanism via a six-membered cyclic transition state has been proposed for the reactions (28) and (29)[49].

Although *ortho*-alkyl derivatives of NB_9H_{10} are not available by electrophilic alkylation, they are available, if one starts from $NB_9H_{11}R$ with the group R in the 9 position. The thermal dehydrogenation yields NB_9H_9R with R in *ortho* position [Eq. (30)]. The starting material can be synthesized from NB_9H_{12} and the corresponding alkenes by hydroboration[22]. As expected, the 9-alkyl derivative $PhNB_9H_{10}R$ gives the *meta*-alkyl derivative $PhNB_{11}H_{10}R$ on ring closure with $BH_3(SMe_2)$ [Eq. (31)][30].



A singular alkylation at the *ortho* belt of the closed NB_{11} skeleton is observed when the synthesis of $NB_{11}H_{12}$ from NB_9H_{12} is performed with $BH_3(NEt_3)$ instead of $BH_3(SMe_2)$, according to Eq. (9). At 200°C the product, expected from Eq. (9), is apparently not stable, and undergoes a further dehydrogenation; a B−C bond is formed from a CH_3 and a BH moiety [Eq. (32)][48]. An intermolecular dehydrogenation of this type has never been observed; the loss in entropy would be too great.



(32)

The bromination of the same *closo* species that were used for the methylation, yields either a fivefold-brominated or a monobrominated product when $AlBr_3$ acts as a Friedel−Crafts catalyst [Eqs. (33), (34)][49].

$$RNB_9H_9 + 5\ Br_2 \rightarrow RNB_9H_4Br_5 + 5\ HBr \qquad (33)$$

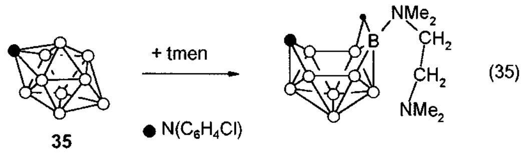
$$RNB_{11}H_{11} + Br_2 \rightarrow RNB_{11}H_{10}Br + HBr \qquad (34)$$

As expected, the bromination takes place in the *meta* and *para* position of the NB_9, but exclusively in the *para* position of the NB_{11} skeleton. Iodination in the presence of $AlCl_3$ stops at the diiodination to give $RNB_9H_7I_2$, with iodine in the *meta* and *para* position, or at the moniiodation to give the *para* product $RNB_{11}H_{10}I$.

There is some similarity in the halogenation of the azaboranes RNB_9H_9 and $RNB_{11}H_{11}$ on the one hand and of the isoelectronic thiaboranes SB_9H_9 and $SB_{11}H_{11}$ on the other; these can be halogenated once, twice or three times, preferably in the *meta*, also in the *para*, but not in the *ortho* position[62][63][64]. The isoelectronic carbaborates $[CB_9H_{10}]^-$ and $[CB_{11}H_{12}]^-$ also undergo a similar electrophilic halogenation to give $[CB_9H_9Hal]^-$ (Hal = Cl, Br, I, in the *meta* position) or $[CB_9H_5Hal_5]^-$ (Hal = Cl, Br, in the *meta* and *para* positions)[65][66][67] and to give $[CB_{11}H_{11}Hal]^-$ (Hal = Cl, Br, I, in the *para* position) or $[CB_{11}H_{10}I_2]^-$ (I in the *meta* and *para* position) or $[CB_{11}H_6Hal_6]^-$ (Hal = Cl, Br, in the *meta* and *para* position)[68][69][70].

Cluster Opening by Bases

The 10-vertex aza-*closo*-borane RNB_9H_9 (**35**) can be opened by amines. Whereas simple tertiary amines like NEt_3, $NiBu_3$ do not react with RNB_9H_9 (R = p-ClC_6H_4), the bifunctional tertiary amine $Me_2N{-}CH_2{-}CH_2{-}NMe_2$ (tmen) gives a 1:1 adduct via one of the basic nitrogen atoms, which attacks one of the *ortho* positions. The *closo* species is transformed into a *nido*-NB_9 skeleton that contains an unsymmetric hydrogen bridge without fluxional behaviour, according to NMR data at room temperature [Eq. (35)][23]. The same type of hydrogen bridge is present in the anions $[RNB_9H_{10}]^-$ (**15**; R = Ph, $PhCH_2$), which are formed from RNB_9H_{11} (**14**) by the addition of $R'NH_2$ (R′ = tBu) and subsequent deprotonation of the adduct (**18**) by hydride [Eq. (36)][23]. The difference in reactivity between ordinary tertiary amines and tmen is not understood.



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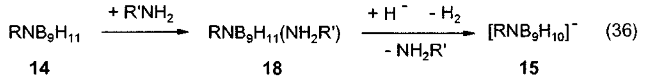
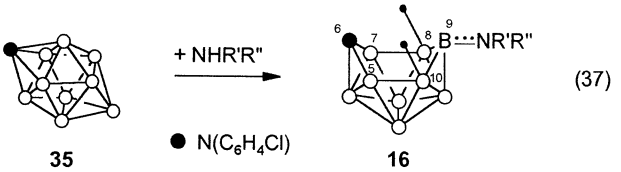


$$\underset{\mathbf{14}}{RNB_9H_{11}} \xrightarrow{+\,R'NH_2} \underset{\mathbf{18}}{RNB_9H_{11}(NH_2R')} \xrightarrow[-\,NH_2R']{+\,H^-\quad -\,H_2} \underset{\mathbf{15}}{[RNB_9H_{10}]^-} \qquad (36)$$

The *closo* species RNB_9H_9 is degraded when an excess of primary or secondary amine is applied. A secondary amine like $NHEt_2$ or $NH\textit{i}Pr_2$ and even a primary amine with a bulky group like $NH_2\textit{t}Bu$ simply opens RNB_9H_9 without degradation, when an excess of amine is avoided. The hydrogen atoms of the reacting moieties BH and NH are found in the open face of the product [Eq. (37)]. Bridging positions B8−B9 and B10−B9 would be expected if the product $RNB_9H_{10}(NR'R'')$) was a *nido* cluster, whereas bridging positions B5−B10 and B7−B8 would indicate an *arachno* cluster. An electron count, according to Wade's rules, predicts a *nido* product $RNB_9H_{10}X$ (**14**) if the ligand X behaved like a hydrogen atom, but would give an *arachno* product if X acted as a three-electron ligand, forming a σ and a dative π bond, due to a lone pair of X. The two non-*exo*-hydrogen atoms of the product, Eq. (37), were found by NMR methods to be predominantly in an *endo* position at B8 and B10, i.e. a position inbetween those typical for *nido* and *arachno* 10-vertex clusters. Such an electronic-hybrid situation was also concluded from the ^{11}B-NMR data[23] apparently because of weak BN π bonding between the amino ligand and the cluster.

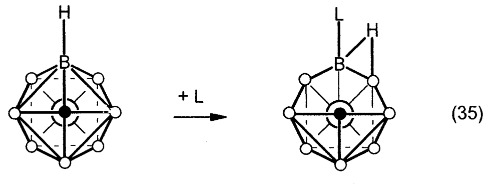


35 **16**

In the case of the *closo*-borane $RNB_{11}H_{11}$ (**43**), simple tertiary amines such as NEt_3 are added to the *ortho* position to give the *nido* cluster **30** by the migration of the former terminal hydrogen atom into a neighbouring bridge position in the open pentagonal face (R = Ph) [Eq. (38)][35].

$$PhNB_{11}H_{11} + NEt_3 \rightarrow PhNB_{11}H_{11}(NEt_3) \qquad (38)$$

The similarity of the steric course of reactions (35) and (37) is elucidated by observing the *closo* clusters along the main axes. The reduction of the connectivity at the nitrogen atom to *c* = 3 involves the opening of one B−N bond in reaction (35), but of two B−N bonds in reaction (38). No B−B bond is opened during reaction (38), whereas three B−B bonds are opened and one B−B bond is closed during reaction (35), which can be considered to be the reverse of the dehydrogenation, Eq. (30), with respect to the skeletal changes.



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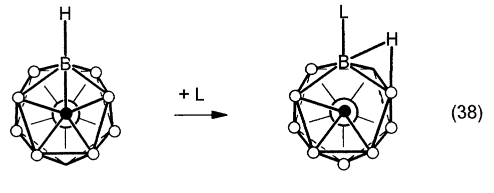


43 **30**

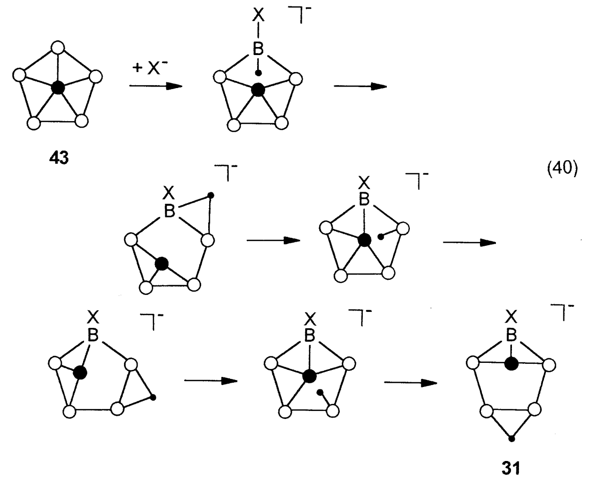
nido products of type **31** are formed when anions X^- are added to *closo*-$RNB_{11}H_{11}$ [Eq. (39)][35]. Substances MX as different as LiMe, LiBu, $K[O\textit{t}Bu]$, $[N(PPh_3)_2]Cl$, $[S(NMe_2)_3]$-$[Me_3SiF_2]$ (X = F by elimination of Me_3SiF), and $K[BHEt_3]$ (X = H by elimination of BEt_3) have been allowed to react with $MeNB_{11}H_{11}$.

$$MeNB_{11}H_{11} + MX \rightarrow M[MeNB_{11}H_{11}X] \qquad (39)$$

In the case of protic agents such as HOMe, the anion MeO^- is added to $RNB_{11}H_{11}$ (R = H, Me, Et, Ph), and the proton, the corresponding cation, is dissolved in the organic medium, e.g. CH_2Cl_2. Efforts to isolate the free acid $H[RNB_{11}H_{11}(OMe)]$ resulted in a complete degradation of the cluster. The cluster anion can be precipitated, however, from solutions of the free acid by adding salts such as $[N(PPh_3)_2]Cl$, leaving HCl in the solvent[36]. No deuterium is incorporated into the cluster if DOMe instead of HOMe is applied, proving that the bridging hydrogen atom in the anion **31** is one of the hydrogen atoms of the starting material **43** and that there is no hydrogen/deuterium exchange between the anion **31** and DOMe[36]. A secondary amine such as the protic agent $HNEt_2$ yields the salt-type product $[H_2NEt_2][RNB_{11}H_{11}(NEt_2)]$[35].

We assume that the mechanism of the formation of anions **31** from **43** is best described by the reaction sequence (40), which starts with the addition of X^- to **43**, followed by a series of rearrangements of a hydrogen atom from an *endo* into a bridging position and vice versa. The second intermediate in this sequence corresponds to the isolated neutral adduct $RNB_{11}H_{11}(NEt_3)$ (**30**). [Only the 6-vertex upper halves of the 12-vertex polyhedral anions are drawn in sequence (40).]

The anions $[RNB_{11}H_{11}X]^-$ (**31**) are remarkably stable in protic media including aqueous acids and bases. Efforts have failed to deprotonate the anion $[PhNB_{11}H_{11}(OH)]^-$ in order to study the oxo-ligand in the expected dianion $[PhNB_{11}H_{11}O]^{2-}$, even though the strongest bases have



(40)

been applied. A degradation of the anions **31** has never been observed.

To summarize the findings on cluster opening: The closed NB_9 and NB_{11} skeletons of **35** and **43** are stable toward oxidation and reduction and toward Brønsted and Lewis acids. The *closo*-NB_{11} skeleton is opened by anionic or neutral bases to give a *nido*-NB_{11} skeleton with a nonplanar pentagonal aperture; this *nido* skeleton is stable towards degradation by bases. This is in striking contrast to the behaviour of the isoelectronic C_2B_{10} skeleton, which undergoes a degradative opening with bases to give the *nido*-C_2B_9 skeleton, whose planar pentagonal aperture is the basis for the synthesis of so many dicarbametalla-*closo*-dodecaboranes. The isoelectronic *nido*-NB_{10} clusters are not available from *closo*-NB_{11} systems and have to be synthesized by an alternative method. The *closo*-NB_9 skeleton can be opened by amines, if no excess is applied, but will be opened and degraded by protic bases in excess.

Degradative Opening of *closo*-RNB_9H_9

The *closo*-NB_9 skeleton is transformed into the *nido*-NB_8 skeleton in a sufficiently polar, aprotic medium such as thf as has been shown for RNB_9H_9 with R = *p*-ClC_6H_4, *p*-MeC_6H_4, $PhCH_2$[13]; the *nido* anion $[RNB_8H_9]^-$ (**9**) is the product. The expelled boron atom is found in a borazine molecule ($(HBN\textit{i}Pr)_3$), if *i*$PrNH_2$ is the attacking base [Eq. (13)], but will be detected in the anion BF_4^-, if fluorides such as $[NBu_4]F$ or $[S(NMe_2)_3][Me_3SiF_2]$ are the degrading agents, according to reactions of unknown stoichiometry. The reaction of RNB_9H_9 with *i*$PrNH_2$ or other primary amines in the less polar solvent CH_2Cl_2, on the other hand, yields the *arachno*-NB_8 species $RNB_8H_{10}(NH_2R')$ [**12**; Eq. (14)][13].

Applications of Azaboranes

The nitrogen-bound amino group in the anion $[(Me_2N)NB_9H_{12}]^-$ [**19**; Eq. (15)] can be treated with MeI to form $(Me_3N)NB_9H_{12}$[25]. This product and similar ones are reported to be useful as blowing agents, in electrical resistors, and as reducing agents[71].

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