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Aza-*closo*-dodecaborane(12): The story of six-coordinate nitrogen

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Abstract: The icosahedron-type *closo*-aza- and *closo*-azametalladodecaboranes $NB_{11}H_{12}$ and $MNB_{10}H_{11}$ and the corresponding neutral and anionic *nido*-azaundecaboranes $NB_{10}H_{13}$, $NB_{10}H_{12}^-$ and $NB_{10}H_{11}^{2-}$ are described. These species are the isoelectronic analogues of the well known dicarbaboranes $C_2B_{10}H_{12}$, $MC_2B_9H_{11}$, $C_2B_9H_{13}$, $C_2B_9H_{12}^-$, $C_2B_9H_{11}^{2-}$. *closo*-Azadodecaboranes are the first examples of nitrogen incorporated in a cluster skeleton with five-fold connectivity and six-fold coordination, including the *exo*-hydrogen atom. Several methods for the synthesis of the *closo*- and *nido*-azaboranes are reported. The structure of $NB_{11}H_{12}$ is discussed. The *nido*-anion $NB_{11}H_{12}X^-$, which is the product of opening *closo*-$NB_{11}H_{12}$ by the action of a base X^-, is interpreted in terms of the related hypothetical 13-vertex polyhedron $NB_{12}H_{13}$.

INTRODUCTION

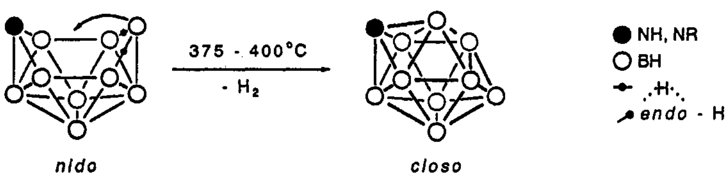
Thirty years ago, the discovery of six-coordinate carbon in dicarba-*closo*-dodecaborane, $C_2B_{10}H_{12}$ (1), made the chemists finally become aware that carbon will not under all circumstances be a good boy who strictly obeys to classical valence bond rules. Carbon once being debunked as a brother of the rascal boron, we became interested in the question, whether nitrogen could also behave in such an unorthodox manner. With the electronic equivalency of a CC and a BN unit in mind, we tried to synthesize the analogues of the *closo*-species $C_2B_{10}H_{12}$ and $MC_2B_9H_{11}$ (M stands for a metal-complex fragment which contributes two cluster electrons) and also of the *nido*-species $C_2B_9H_{13}$, $C_2B_9H_{12}^-$, and $C_2B_9H_{11}^{2-}$. The formulae of the expected analogues would be $NB_{11}H_{12}$, $MNB_{10}H_{11}$, $NB_{10}H_{13}$, $NB_{10}H_{12}^-$, and $NB_{10}H_{11}^{2-}$, respectively. It is well known that carbon has a greater tendency than boron to reduce its connectivity in cluster opening or degradation reactions. One might expect this tendency to continue in the series of increasing electronegativity from boron via carbon to nitrogen. Anyhow, four-fold connectivity of nitrogen within the skeleton, i.e. non-classical five-fold coordination with inclusion of the terminally bonded hydrogen, had been realized years ago in the cluster molecules *nido*-$NC_2B_8H_{11}$ (2) and *closo*-NB_9H_{10} (3); in both molecules the positions of the higher connectivity five are reserved to boron. What about such higher cluster connectivity with nitrogen, including a sixth coordination place for either an electron pair or an *exo*-ligand?

INCORPORATION OF NITROGEN IN B_9 AND B_{10} SKELETONS

closo-, *nido*-, and *arachno*-Azadecaboranes have been the first representatives of larger azaborane clusters. The starting material is the classical $B_{10}H_{14}$ which loses a B atom when treated either with Me_2N-NS (4) or with $NaNO_2$ (5). Poor yields of derivatives of *arachno*-NB_9H_{14} [Eq.(a)] or a 55% yield of *nido*-NB_9H_{12} [Eq. (b)] are obtained, respectively. Concerning the mechanism of these reactions, there is a lack of transparency, whereas the thermal elimination of H_2 from *nido*-NB_9H_{12} gives *closo*-NB_9H_{10} (3) in a most transparent way [Eq. (c)].

$$B_{10}H_{14} \xrightarrow{+\,Me_2N-NS} (Me_2N)NB_9H_{12}^- \xrightarrow{Na} NB_9H_{13}^- \xrightarrow[+\,MeCN]{Br_2} NB_9H_{12}(NCMe) \qquad (a)$$

$$B_{10}H_{14} \xrightarrow[-\,H_2]{+\,NaNO_2} \xrightarrow[-\,HBO_2,\ -\,NaHSO_4]{+\,H_2SO_4} NB_9H_{12} \qquad (b)$$

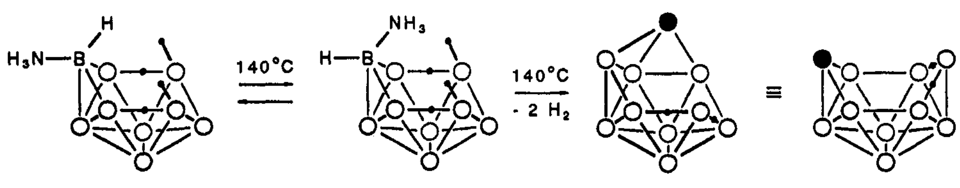


(c)

We started from ethyl instead of sodium nitrite and synthesized NB_9H_{12} in a one-step reaction, which is not yet mechanistically but at least stoichiometrically clear [Eq. (d)] (6).

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

A mechanistically lucid access to NB_9H_{12} is achieved by the thermolysis of the well known *arachno*-$B_9H_{13}(NH_3)$ (7). We suggest an *exo/endo* exchange of the ligands H and NH_3 as the first step, followed by the elimination of H_2 [Eq. (e)] (8).



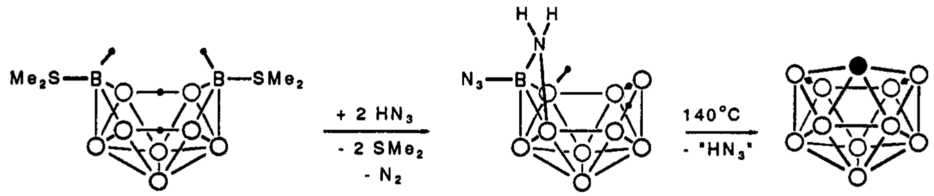
(e)

N-Alkyl derivatives RNB_9H_{11} are available in a similar way by applying RNH_2 instead of NH_3. Starting from *arachno*-$B_9H_{13}(SMe_2)$ (9), two steps are necessary [Eq. (f)] (10).

$$B_9H_{13}(SMe_2) \xrightarrow[-\,SMe_2]{+\,RNH_2} B_9H_{13}(NRH_2) \xrightarrow[-\,2\,H_2]{140°C} RNB_9H_{11} \qquad (f)$$

In order to gain an NB_{10} skeleton we had planned to decompose 6-(azido)decaborane(14), $B_{10}H_{13}(N_3)$, expecting the nitrene intermediate to be arranged to *nido*-azaundecaborane, $NB_{10}H_{13}$. With the synthesis of $B_{10}H_{13}Cl$ from $B_{10}H_{12}(SMe_2)_2$ and HCl in mind (11), we tried to synthesize $B_{10}H_{13}(N_3)$ from $B_{10}H_{12}(SMe_2)_2$ and HN_3. Unexpectedly, we observed a 1:2 reaction with the evolution of 1 mole of N_2. A potential nitrene intermediate added two H atoms and entered into a bridge position, giving the decaborane

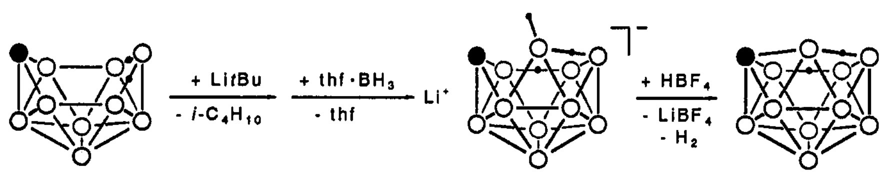
$B_{10}H_{12}(N_3)(NH_2)$. The thermolysis of this product in boiling xylene yielded the desired *nido*-azaborane $NB_{10}H_{13}$ besides as much of the gases N_2 and NH_3 as is equivalent to the decomposition of 1 mole of HN_3. Apparently, the bridging amino-group had been incorporated into the borane skeleton as an NH unit [Eq. (g)]. Unfortunately, the yield of $NB_{10}H_{13}$ was only 5% (12). Nevertheless, *nido*-$NB_{10}H_{13}$ after Eq. (g) had opened the synthesis of *closo*-$NB_{11}H_{12}$ (see below).



(g)

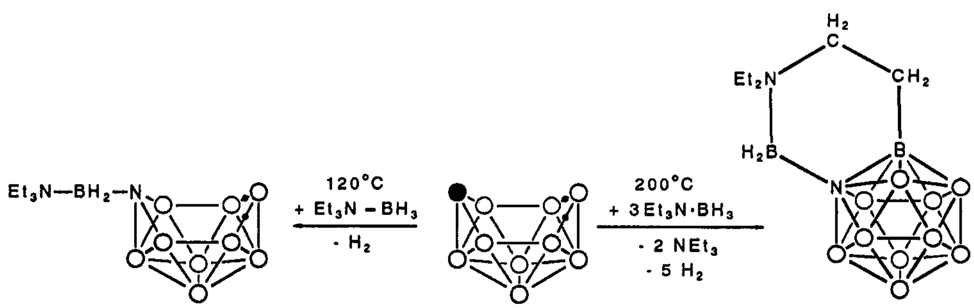
INCORPORATION OF BORON IN THE NB_9 SKELETON

The deprotonation of *nido*-NB_9H_{12} with Li*t*Bu and subsequent addition of thf·BH_3 yields the *arachno*-species Li[$NB_{10}H_{14}$] whose structure is suggested from 2D-NMR ^{11}B-^{11}B evidence. The anion loses a molecule of H_2 upon protonation, allowing quite a convenient access to *nido*-$NB_{10}H_{13}$ [Eq. (h)] (6).



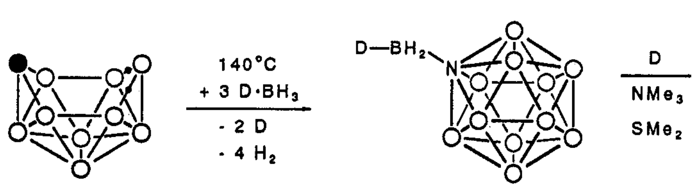
(h)

The successful application of $Et_3N{\cdot}BH_3$ in order to transform $NB_{10}H_{13}$ into $NB_{11}H_{12}$ (13) (see below) prompted us to apply the same borane in order to incorporate boron into the skeleton of *nido*-NB_9H_{12}. Instead of an incorporation, we observed a simple *exo*-borylation of nitrogen at 120°C (8). In a melt of excess $Et_3N{\cdot}BH_3$ at 200°C, however, the NB_9 skeleton adopts even two BH units, thus making the *closo*-NB_{11} skeleton available. The N-borylation remains, and one of the ethyl groups of NEt_3 closes a six-membered ring by ethylating a neighboring B atom [Eq. (i)]. The product crystallizes in the triclinic space group $P\bar{1}$ (6).



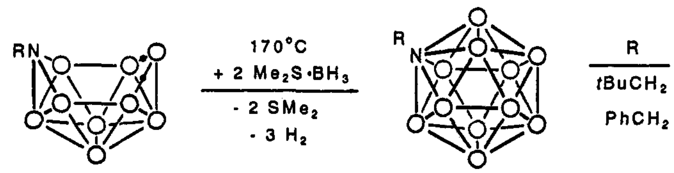
(i)

Could the ring-closure of reaction (i) be avoided by starting from D·BH_3 with bases D different from NEt_3? We found out that Me_2S and NMe_3 are such bases, which permit the closure to the *closo*-NB_{11} skeleton already at 140°C. The N-borylation cannot be avoided [Eq. (j)] (6).



(j)

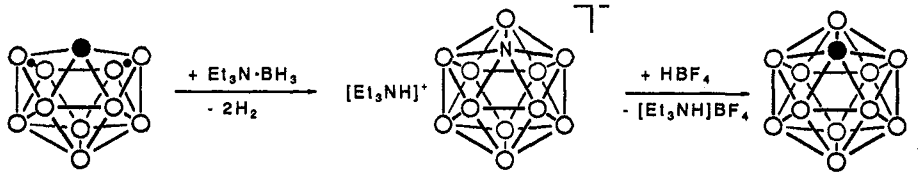
In order to make the N-borylation impossible, we employed N-alkyl boranes RNB_9H_{11}. Two BH units are inserted when an excess of $Me_2S{\cdot}BH_3$ is applied at 170°C in decalin [Eq. (k)] (10).



(k)

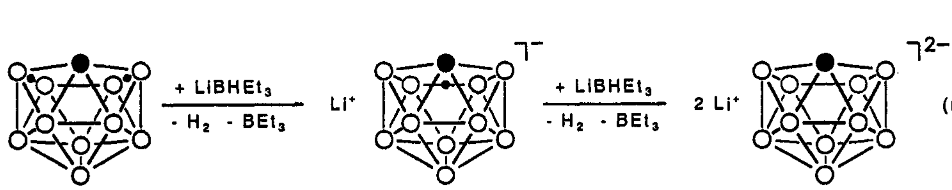
INCORPORATION OF BORON OR METAL IN THE NB_{10} SKELETON

When we had that 5% yield of *nido*-$NB_{10}H_{13}$ [Eq. (g)] in our hands in 1989, we immediately tried to close it by the action of $Et_3N{\cdot}BH_3$. We identified the *closo*-anion $NB_{11}H_{11}^-$ and the corresponding cation $NHEt_3^+$ as the products, from which the neutral *closo*-species $NB_{11}H_{12}$ was available on protolysis with HBF_4 in an overall-yield of 47% [Eq. (l)]. Apparently, $NB_{11}H_{12}$ is a stronger Brönsted acid than $NHEt_3^+$ or $NB_{11}H_{11}^-$ a weaker base than NEt_3. A 5:5:1 set of ^{11}B-NMR signals clearly indicated the C_{5v} structure of $NB_{11}H_{12}$; the ^{1}H-NMR triplet [^1J(HN) = 62.5 Hz] for the N-bonded proton is in accord with the symmetrical charge distribution around the N atom on the C_5 axis (13). $NB_{11}H_{12}$ is the first example for six-coordinate nitrogen incorporated in a cluster skeleton with five-fold connectivity.



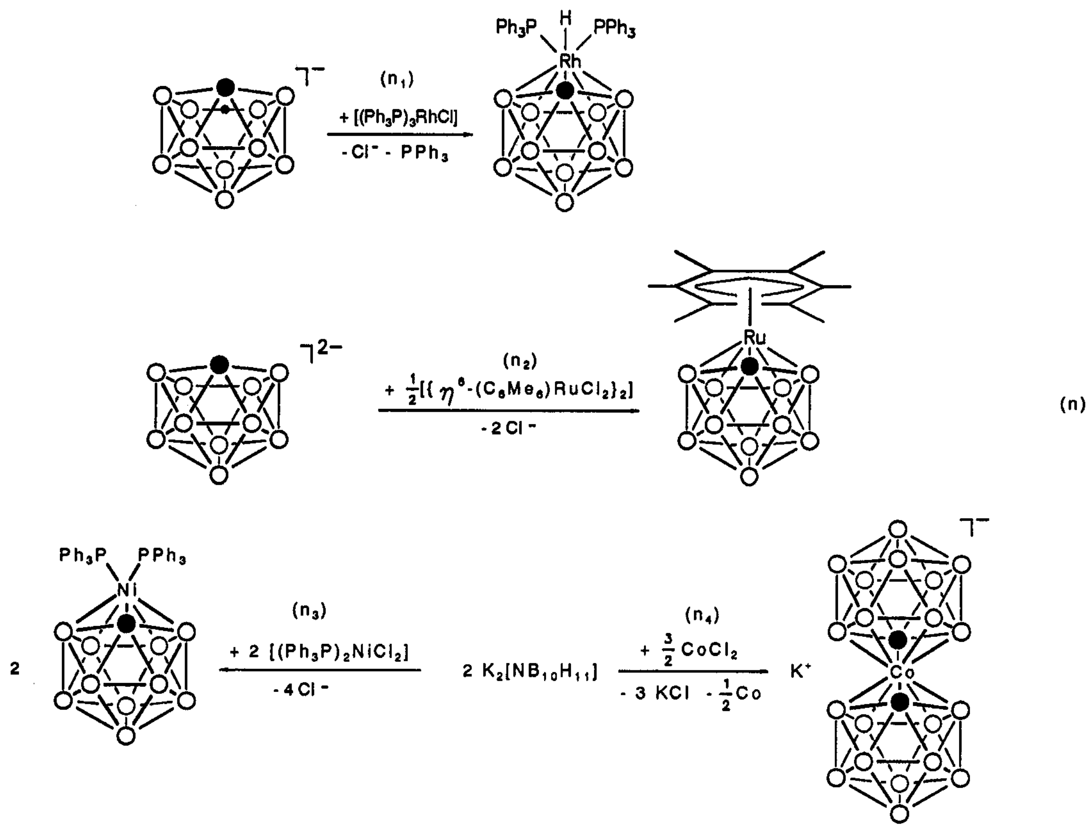
(l)

One usually starts from the *nido*-anions $C_2B_9H_{12}^-$ or $C_2B_9H_{11}^{2-}$ in order to close the nido-C_2B_9 skeleton with a metal-complex fragment. The analogous *nido*-anions $NB_{10}H_{12}^-$ and $NB_{10}H_{11}^{2-}$ are easily formed by the action of an alkali triethylborate on $NB_{10}H_{13}$ in a 1:1 or 2:1 ratio, respectively [Eq. (m)]. The extra-hydrogen atom in $NB_{10}H_{12}^-$ is found in a bridging position on the mirror plane through the molecule, according to NMR evidence. The position of the analogous H atom in $C_2B_9H_{12}^-$ had been discussed for years, but is now confirmed to be chiefly in an *endo*-position, again on a mirror plane (14).



(m)

Chlorotris(tripenylphosphane)rhodium closes *nido*-$NB_{10}H_{12}^-$ in the same way as had been found for *nido*-$C_2B_9H_{12}^-$ (15). The closure is accompanied by the loss of one phosphane molecule and the migration of the extra-H atom from boron to the metal [Eq. (n_1)] (16). The known metallation of the *nido*-anion $C_2B_9H_{11}^{2-}$ by the dimeric dichloro-η^6-(hexamethylbenzene)ruthenium (17) can as well be applied to $NB_{10}H_{11}^{2-}$ [Eq. (n_2)] (6). The N atom adopts a five-fold connectivcity in both azametalladodecaborane skeletons, well established by X-ray analyses. The metallation of $NB_{10}H_{11}^{2-}$ seems to be quite a general reaction. We were able to close $NB_{10}H_{11}^{2-}$ with an $[Ni(PPh_3)_2]^{2+}$ unit [Eq. (n_3)] and also to bind two anions $NB_{10}H_{11}^{2-}$ to a Co^{3+}cation in a sandwich-type product [Eq. (n_4)].



COMMENTS ON THE STRUCTURE OF AZADODECABORANE

Structural evidence comes from an ab initio calculation on $NB_{11}H_{12}$ at an HF/6-31G* level (18), from a gas-phase electron diffraction (GED) study on $NB_{11}H_{12}$ (19), and from a crystal structure determination of $(PhCH_2)NB_{11}H_{11}$ (10). The GED data could be equally well fit by four models with C_{5v} symmetry. As the best model the one was taken which allowed a calculation of the ^{11}B NMR shifts by the IGLO method in the best agreement with our experimental values (13). The thirty skeletal bond lengths can be arranged in five zones of equal distances in the gas phase molecule of C_{5v} symmetry. This symmetry is still present in solutions of $(PhCH_2)NB_{11}H_{11}$ as far as the characteristic 5:5:1 set of ^{11}B NMR chemical shifts is concerned, what is apparently due to a rapidly rotating benzyl group. In crystalline $(PhCH_2)NB_{11}H_{11}$, however, the rigid benzyl group as well as the monoclinic lattice make all thirty edges of the icosahedron-type skeleton different from each other. Nevertheless, the five zones remain such as each zone contains bond distances in a narrow range. In Table 1 the NB_{11} skeleton is looked at as a bicapped pentagonal antiprism with the N atom as the upper capping apex. The X-ray data are mean values from the five or ten individual bond distances, respectively, in each zone.

The BB bond distances in the crystal are smaller than in the free molecule, a general phenomenon. Unexpectedly, the situation is reverse for the BN bond distances. Anyhow, the BN distances are the shortest ones in the skeleton, though they are rather long, if compared to normal aminoboranes (≈ 1.40 Å) or amine-boranes (≈ 1.60 Å). They seem to be determined by the smaller atomic radius of nitrogen, as compared to boron, on the one hand and by the high coordination number of nitrogen on the other hand. Recently, we found a mean bond distance of only 1.516 Å for the BN bonds in the crystal structure of *closo*-NB_9H_{10} in which the boron is six-, but the nitrogen atom five-coordinated (6). Apparently, the increase of the coordination number of N from five to six makes the BN bonds significantly longer. The average BN bond length in the metal complex $[(Ph_3P)_2RhH]NB_{10}H_{11}$ of 1.694 Å with again six-coordinate nitrogen is close to that of $(PhCH_2)NB_{11}H_{11}$ (16).

TABLE 1. Skeletal bond distances (Å) of $NB_{11}H_{12}$ (calculated and from gas-phase electron diffraction) and of $(PhCH_2)NB_{11}H_{11}$ (averaged from X-ray diffraction)

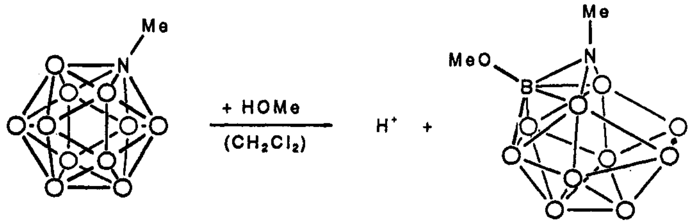
	$NB_{11}H_{12}$ Calcd.	$NB_{11}H_{12}$ GED	$(PhCH_2)NB_{11}H_{11}$ X-ray
Upper pyramidal zone	1.710	1.716	1.719
Upper pentagonal zone	1.821	1.825	1.796
Antiprismatic zone	1.767	1.791[a]	1.745
Lower pentagonal zone	1.808	1.791[a]	1.773
Lower pyramidal zone	1.798	1.791[a]	1.770

[a] Mean value of 20 edges in 3 zones.

The largest BB bond lengths are those in the upper pentagonal zone thus illustrating the chief distortion of the NB_{11} skeleton from icosahedral geometry: The N atom penetrates towards the center of the polyhedron and the adjacent B atoms make way by forming a larger pentagon. Parallel to this situation, the five BH bonds at this pentagon are shifted out of radial direction towards the N atom, thereby shielding the N atom considerably. This shielding effect may be the reason, why we were unable to bind larger alkyl groups, e.g. the *tert*-butyl group, to the N atom of *closo*-azadodecaborane.

OPENING OF THE CLOSED AZADODECABORANE SKELETON

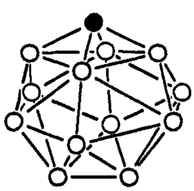
The 1,2-dicarba-*closo*-dodecaborane $C_2B_{10}H_{12}$ can be opened by the attack of bases like NaOEt in EtOH; this opening process is accompanied by the loss of H_2 and of one B atom as $B(OEt)_3$, giving the *nido*-anion $C_2B_9H_{12}^-$ (20). We found out that aza-*closo*-dodecaborane is opened by the attack of mere methanol without degradation. We first started from the *N*-methyl derivative in a solution of CH_2Cl_2 in the presence of an excess of MeOH. We identified the *nido*-anion $[MeNB_{11}H_{11}(OMe)]^-$ as the product in solution, which could be crystallized as $[N(PPh_3)_2][MeNB_{11}H_{11}(OMe)]$ [Eq. (o)] (21). The anion in the crystal exhibited the same structure that had been concluded for the anion in solution from NMR data. The corresponding cation in the primary methanolysis process must be H^+, solvated by excess MeOH or perhaps CH_2Cl_2. It could not be detected by spectroscopic methods. All efforts to isolate the free acid $H[MeNB_{11}H_{11}(OMe)]$, apparently quite a strong acid, ended with the decomposition of the cluster.



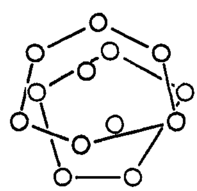
(o)

The structure of the anion can be described to contain an open, non-planar pentagon with nitrogen of three-fold connectivity on a mirror plane and with the methoxy group bonded terminally to the neighboring B atom on the mirror plane. Two B atoms of connectivity 4 are bridged by an H atom. This H atom is the one that had been exchanged by the methoxy group in its original terminal position. Methanol can be excluded as its source since no deuterium is transferred to the bridging position upon methanolysis with CD_3OD, and there is no exchange of that H atom on standing neither with an excess of methanol nor with protons in the medium in the case of any protic solvent. The opening of $MeNB_{11}H_{11}$ apparently proceeds through the attack of the base at a B atom close to the N apex, the opening of two BN bonds, the migration of the terminal H atom to a bridging position and the dissociation at the methanolic OH bond.

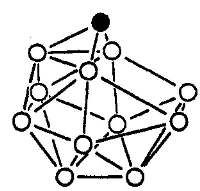
The *nido*-structure of the anion $[MeNB_{11}H_{11}(OMe)]^-$ is related to a hypothetical *closo*-$NB_{12}H_{13}$, which is isoelectronic with the hypothetical anion $B_{13}H_{13}^{2-}$. A favorable structure of the closed 13-vertex polyhedron may be derived from the icosahedron by opening an edge and inserting a vertex with the connectivity 4; this vertex would be the NH unit in the case of $NB_{12}H_{13}$. Such an inserting process lets two vertices have the extreme connectivity 6. The resulting structure of C_{2v} symmetry had been claimed by theory (22). Another way to look at this structure is to have a non-planar hexagon and a pentagon fused together in a kind of antiprismatic manner and to cap both polygons. The capping apex over the hexagon and one vertex in the pentagon adopt the connectivity 6, one in the hexagon 4, all others 5. *closo*-Structures of this type are realized in metallaboranes, e.g. $[(CpCo)C_2B_{10}H_{12}]$ (23), where the three positions with the connectivities 6, 6 and 4 are occupied by Co, B, and one of the C atoms, respectively. Going from *closo*-$NB_{12}H_{13}$ to *nido*-$NB_{11}H_{12}^{2-}$, such a B atom ought to be removed that reduces the extra-connectivities from 6 to 5 and from 4 to 3 and, consequently, the connectivity of two B atoms from 5 to 4. This is exactly the structure formed in the opening process of $MeNB_{11}H_{11}$ with MeOH. *nido*-Structures of that type are known in several heteroboranes. In *nido*-$Et_4C_4B_8H_8$ (24), the connectivity of the four electronegative C atoms can additionally be reduced to values of 3 and 4 by opening a bond. In *nido*-$[(CpCo)Se_2B_9H_9]$ (25), the rather electronegative Se atoms are found in the positions with the low connectivities 3 and 4, and the electropositive Co atom in a position with the higher connectivity 5, coordinated by both the Se atoms.



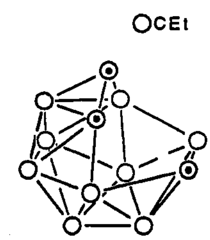
closo - $NB_{12}H_{13}$



hexagon/pentagon, bicapped



nido - $NB_{11}H_{12}^{2-}$



nido - $Et_4C_4B_8H_8$

The opening process according to Eq. (o) can be generalized. The azaboranes $RNB_{11}H_{11}$ may be attacked by $LiBHEt_3$, LiMe, KO*t*Bu, or $[S(NMe_2)_3][Me_3SiF_2]$ instsead of MeOH [Eq. (p)] (6).

$$closo\text{-}RNB_{11}H_{11} + MX \longrightarrow M^+ + nido\text{-}RNB_{11}H_{11}X^- \qquad \text{(p)}$$

R:	H	Me	Me	Me	Me	Me	Et
M:	H	H	Li	K	$S(NMe_2)_3$	Li	H
X:	OMe	OMe	H	O*t*Bu	F	Me	OMe

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