

## New perspectives in boron-nitrogen chemistry—I

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**Abstract** - New perspectives in boron-nitrogen chemistry result from molecules  $RB=NR$  with two-coordinate boron atoms (iminoboranes) and from boranes  $N_xB_yH_z$  with nitrogen atoms of coordination number 4, 5, or 6 in the skeleton (azaboranes). - The structure, stabilization, and reactivity of iminoboranes  $RB=NR$  and the isoelectronic alkynes  $RC=CR$  are compared. Iminoboranes are building blocks of molecules  $(RBNR)_n$  ( $n = 2, 3, 4, \infty$ ) which are isoelectronic with cyclobutadiene, benzene, Dewar benzene, cyclooctatetraene, or polyacetylene. Acyclic and cyclic additions to the triple bond of  $RB=NR$  are described with a stress on transition metal complexes as reaction partners. - The formation of new azaboranes is reported, which are more or less organo-derivatives of nido- $NB_3H_6$ , arachno- $N_2B_3H_7$ , nido- $N_2B_4H_6$ , arachno- $NB_6H_{13}^-$ , nido- $NB_{10}H_{13}$ , and closo- $NB_{11}H_{12}$ .

### NEW PERSPECTIVES IN THE LIGHT OF A CLASSIFICATION OF BORON NITROGEN CHEMISTRY

Numerous boron compounds being notorious examples for electron-deficiency, a useful classification of boron chemistry may start from distinguishing between classically and non-classically bonded boron atoms. In this context, the attributes "classical" and "non-classical" mean that the two-center-two-electron approximation either describes the skeletal bonding situation sufficiently well or does not, respectively; delocalized  $\pi$  bonds, as in boron fluoride or borazine, or hyperconjugation, as possibly in trialkylboranes, are not in consideration for the purpose of this classification. The general distinction between a molecular and a solid-state structure may be superimposed, establishing four classes of compounds: classical molecular species (e.g. triethylborane, ether-trifluorborane, etc.) and classical solid-state species (e.g. boron oxide, colemanite etc.), on the one hand, and non-classical molecular species (e.g. diborane, dicarbadodecaborane etc.) and non-classical solid-state species (e.g. elementary boron, calcium hexaboride etc.), on the other hand. Classical boron compounds are structurally governed by three- and four-coordinate, non-classical boron compounds by four-, five-, and six-coordinate boron atoms.

The diversity of traditional boron nitrogen chemistry is dominated by classical molecules. The basic types are represented by aminoboranes,  $X_2B=NR_2$ , and amine-boranes,  $X_3B-NR_3$ , with the coordination numbers 3 and 4, respectively. The diversity comes from the variation of the ligands X and R, comprising chains like  $X_2B-NR-BX_2$  or  $R_2N-BX-NR_2$  or even larger BN aggregates, comprising also cyclic aggregates of BN units, the most common ones being benzene-analogous borazines, and comprising, moreover, ions of the type  $[R_3N-BX_2-NR_3]^+$  etc. - Classical solids in BN chemistry seem to be restricted to boron nitride until quite recently. - Non-classical molecules in BN chemistry are restricted to those that contain one or more nitrogen atoms in the electron-deficient skeleton. Such azaboranes have been investigated for more than two decades, e.g. the species  $NB_6H_{13}^-$ ,  $NC_2B_8H_{11}$ ,  $NB_8H_{13}$ ,  $NB_8H_{12}$ ,  $NB_8H_{10}$ , all of which were synthesized via the action of  $Me_2NNS$  or  $NaNO_2$  on  $B_{10}H_{14}$ . - Non-classical borides, finally, that contain nitrogen are not well known, with the exception of nitrogen incorporated in so-called tetragonal boron.

A new perspective in the field of classical BN molecules came up in 1975, when the first iminoborane with two-coordinate boron,  $C_6F_5-B=N-tBu$  had been isolated as a substance that could be stored and handled at low temperature (ref. 1). Meanwhile, more than 50 iminoboranes  $X-B=N-R$  have been synthesized and well characterized, those with organic ligands X mostly in our laboratory, those with amino groups as the ligands X mostly in Nöth's laboratory at the University of Munich. Reviews appeared in 1987 and 1988 (ref. 2). What remains for the following section is a brief survey on the structure and reactivity of iminoboranes, including some unreviewed recent results in this field.

New perspectives of BN containing solids ought to be taken into consideration, when recent efforts of several groups to obtain well-defined mixed crystals of hexagonal boron nitride and graphite, BC<sub>x</sub>N, or also of cubic boron nitride and diamond will have brought more structural clarity than had been necessary for testing some refractory properties of such materials under the aspects of technical application.

Azaborane chemistry has mainly been restricted, hitherto, to the larger clusters mentioned above. Some recent contributions of our group concerning smaller azaborane cluster compounds will be reported in two of the following sections. Finally, a novel access to larger azaboranes is introduced, which makes nido-NB<sub>10</sub>H<sub>13</sub> and closo-NB<sub>11</sub>H<sub>12</sub> available.

### A SURVEY ON THE STRUCTURE AND REACTIVITY OF IMINOBORANES INCLUDING RECENT RESULTS

The structure of alkyl(imino)boranes R-B=N-R' is characterized by a linear C-B-N-C chain and by a BN triple bond (ref. 2). Experimental evidence comes from crystal structure and vibrational analyses and is confirmed by ab initio calculations. A comparison of average BN and CC bond lengths and force constants (Fig. 1) demonstrates the same proportionate progress going from the single via the double to the triple bond. It is also clear from this comparison that a CC bond is stronger than the corresponding isoelectronic BN bond.

$\diagup$ -B-N- $\diagdown$	$\diagup$ B=N $\diagdown$	-B≡N-	$\diagup$ -C-C- $\diagdown$	$\diagup$ C=C $\diagdown$	-C≡C-	
158	140	124	154	133	118	pm
3.7	7.5	13.0	4.5	9.4	15.7	N/cm

Fig. 1. Comparison of BN and CC bonds: bond lengths and force constants.

Small dipole moments, calculated as well as observed (0.20 D for tBuB=NtBu), prove iminoboranes to be rather unpolar. The small real charges seem to be distributed with δ<sup>+</sup> on boron and δ<sup>-</sup> on nitrogen, according to electronegativity, in contrast to the formal charges connected with four covalent bonds at each of these atoms. Though small, the polarity is great enough, relatively, to make iminoboranes kinetically unstable at room temperature and rather reactive towards a lot of substances even at low temperature, provided the BN bond is not sterically overcrowded by the ligands R and R'. Unpolar alkynes, on the other hand, are kinetically stable at room temperature, though oligomeric products (RCCR)<sub>n</sub> would be thermodynamically more stable, e.g. cyclobutadiene (n = 2), benzene (n = 3), Dewar benzene (n = 3), cyclooctatetraene (n = 4), or polyacetylene (n = ∞). The catalytic oligomerization of alkynes has been well explored, whereas raising the temperature seems not to be a synthetically valuable attempt to overcome the activation barrier. Polar alkynes, however, tend to be unstable at room temperature, like iminoboranes; fluoroalkynes RC≡CF are examples.

The relative stability of iminoboranes RB=NR' distinctly depends on the steric demand of R and R' (ref. 2). tBuB=NtBu, e.g., may be stored at 0°C, but MeB=NMe not above -110°C. The stabilization process gives oligomeric products (RBNR')<sub>n</sub> that are isoelectronic to those mentioned above for alkynes (Fig. 2).

The non-catalytic stabilization generally favours borazines (n = 3), but a set of large ligands R,R' makes diazadiboretidines (n = 2) more favourable, expectedly; Dewar borazines mark a borderline. Thus, iminoboranes RB=NtBu will give the borazine or the Dewar borazine or the diazadiboretidine, respectively, if the steric demand of R increases in the sequence CH<sub>2</sub>Me/CHMe<sub>2</sub>/CMe<sub>3</sub>. If R and R' are α-unbranched alkyl groups, poly(iminoborane) will be found as a byproduct, easily separable from the corresponding borazine because of its insolubility. - There are several catalysts that transform iminoboranes into cyclodimers instead of cyclotrimers. The isonitrile CNtBu, e.g., cyclodimerizes iminoboranes RB=NtBu, whose non-catalytic stabilization gives borazines. With MeB=NtBu, in particular, the catalytically synthesized cyclodimer and the cyclooctatetraene-analogous cyclotetramer undergo a reversible equilibrium.

A reaction of a certain substrate with an iminoborane will only be possible, of course, if the oligomerization of the iminoborane proceeds slower. The typical reaction of an iminoborane is a 1,2-addition of a molecule to the BN triple bond, transforming it into a double bond of the aminoborane type (ref. 2). Protic agents HX are rapidly added at low temperature (X = Cl, OR, NR<sub>2</sub> etc.; e.g. HX = HO*i*Pr in Fig. 3) and several chlorides of the elements B, Si, Ge, Sn, P, As, Sb as well. Even unpolar bromine adds to iminoboranes, an unstable NBr bond being formed. - (2+1)Cycloadditions were developed recently. The addition of dimethylsilylene to tBuB=NtBu (Fig. 3) is an example. - Iminoboranes easily undergo (2+2)cycloadditions. Among several nicely reacting components, hexafluoroacetone is picked out in Fig. 3. - Whereas (2+2)cycloadditions are rare with alkynes,

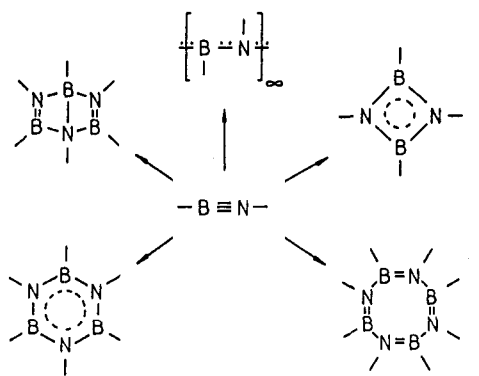


Fig. 2. Stabilization of Iminoboranes.

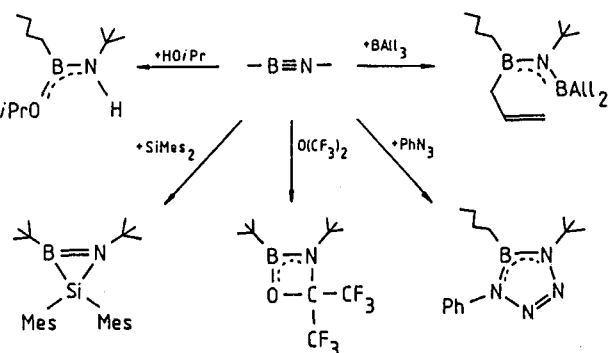


Fig. 3. Five typical reactions of iminoboranes.

(2+3)cycloadditions are very common with both, iminoboranes and alkynes. Covalent azides are typical 1,3 dipolar compounds that react readily with iminoboranes (Fig. 3). (2+4)Cycloadditions are notoriously slow. Well known for the metastable alkynes, they are not easily found for the unstable iminoboranes. Reactions, however, that proceed through a six-membered cyclic transition state, are possible for iminoboranes and alkynes, e.g. the allyloboration with  $B(C_3H_5)_3$  (Fig. 3).

Typical reactions of alkynes in the coordination sphere of transition metals are the side-on coordination, the formation of a bridge between two metal atoms, and the cyclodimerization at a metal. In spite of trying to reproduce nearly all known side-on coordinations of alkynes, only one complex could be synthesized with iminoboranes:  $[Cp_2NbH(\underline{t}BuBN\underline{t}Bu)]$ ; the BN bond length of  $\underline{t}BuB=N\underline{t}Bu$  (126 pm) increases by only 3 pm by complexation (ref. 3). The same iminoborane may bridge two Co atoms in  $[(OC)_6Co_2(\underline{t}BuBN\underline{t}Bu)]$  (ref. 2); no further examples of such a tetrahedrane-type complex have been found. The cyclodimerization of iminoboranes at a metal, however, is a common reaction (ref. 2,4). Different from alkynes, iminoboranes prefer the early transition metals; no complex of a diazadiboretidine with Ni could be synthesized. The products are nido-clusters with a four-membered BNBN-ring as the basis and metal as the top of a tetragonal pyramid. The distance between metal and nitrogen is 10 - 15 pm longer than between metal and boron, in accord with the difference in the atomic radii of B and N. The bonding situation may be qualitatively described by two coordinative bonds from nitrogen to metal and two donative back bonds from metal to boron. Without these back bonds, the boron nuclei would be expected to suffer a distinct deshielding effect, when the  $\pi$  electrons of the free diazadiboretidine are shifted towards the metal. In fact, however, there is a shielding effect: The  $^{11}B$  NMR signal of  $(PrBN\underline{t}Bu)_2$ , e.g., is shifted from 43.9 ppm to the high-field values 15.7, 11.7, and 8.0 ppm by bond formation with  $Cr(CO)_4$ ,  $Fe(CO)_3$ , and  $CoCp$ , respectively; this is the direction of increasing availability of metal d-electrons.

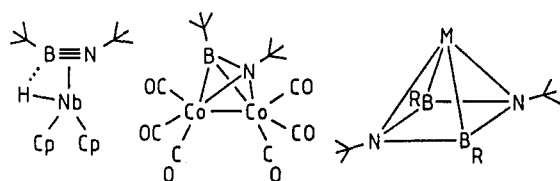


Fig. 4. Iminoboranes side-on bonded to Nb, in a bridging position between two Co atoms, and cyclodimerized at several metals.

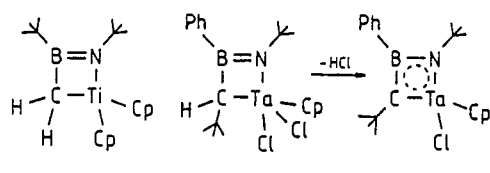


Fig. 5. Products from the (2+2)cycloaddition of iminoboranes and carbene complexes.

Like alkynes, iminoboranes may undergo a (2+2)cycloaddition with carbene-metal complexes of the Schrock type. The highly reactive  $H_2C=TiCp_2$  and the more stable  $\underline{t}BuCH=TaCl_2Cp$  are useful starting compounds (ref. 2,5). At higher temperature or by the addition of  $NEt_3$ , one molecule HCl can be eliminated from the Ta complex, giving a kind of cyclic carbene species (Fig. 5). Amino groups instead of organic ligands at boron provoke a metathetical ring-opening of the (2+2)cycloadducts, with an alkylidenoaminoborane as one of the products, e.g.  $Me_3Si(\underline{t}Bu)N=B-CH\underline{t}Bu$  (ref. 6).

Reactive molecules like the adducts of benzyne or butadiene to zirconocene can react with iminoboranes in a kind of (2+3)cycloaddition (ref. 2,7; Fig. 6).

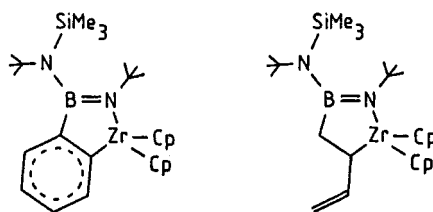
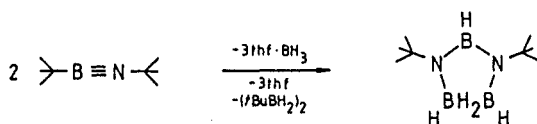


Fig. 6. Products from the (2+3)cycloaddition of iminoboranes and the complexes  $\text{Cp}_2\text{Zr}(\text{C}_6\text{H}_4)$  and  $\text{Cp}_2\text{Zr}(\text{C}_4\text{H}_6)$ .

### AZABORANES FROM IMINOBORANES

The iminoborane  $\text{tBuB=NtBu}$  readily reacts with tetrahydrofuran-borane at  $-78^\circ\text{C}$  to form 1,3-di-*tert*-butyl-1,3-diazacyclopentaborane, which may be considered to be an *arachno*-derivative of a pentagonal bipyramid. The same product is formed from the corresponding diazadiboretidine,  $(\text{tBuBNtBu})_2$ , and  $\text{thf}\cdot\text{BH}_3$  at  $25^\circ\text{C}$ . Starting from diazadiboretidines  $(\text{RBNtBu})_2$  ( $\text{R} = \text{Et}, \text{Pr}, \text{Bu}$ ), the reaction with 1 - 3 mol of  $\text{thf}\cdot\text{BH}_3$  gives successively the 4,5-dialkyl derivative of  $\text{N}_2\text{B}_3\text{H}_5\text{tBu}_2$ , the 4-alkyl derivative, and  $\text{N}_2\text{B}_3\text{H}_5\text{tBu}_2$  itself (ref. 8).



The reaction of pentaborane(9) with alkynes  $\text{C}_2\text{R}_2$  in the presence of lutidine is well known to give *nido*- $\text{C}_2\text{B}_4\text{H}_6\text{R}_2$  (Fig. 7). Attempts to transfer this reaction to iminoboranes results in a different product. Instead of  $\text{BH}_3$ , the base only takes away a proton from  $\text{B}_5\text{H}_9$ , and the iminoborane forms an *arachno*-cluster anion with  $\text{B}_5\text{H}_8^-$ , which is derived from the tricapped trigonal prism by removing two of the caps (ref. 9, Fig. 7).

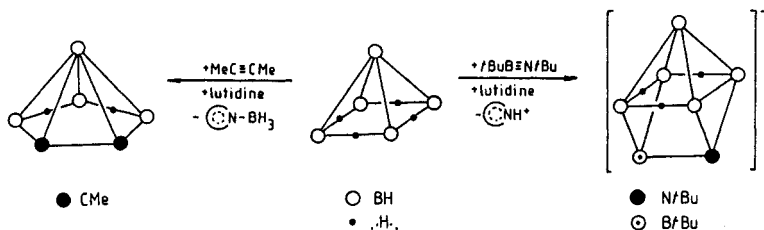
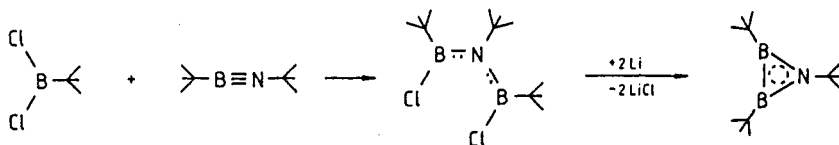


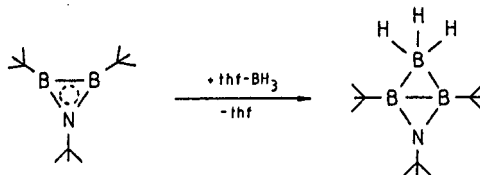
Fig. 7. Formation of *arachno*- $\text{NB}_6\text{H}_8(\text{tBu})_2^-$ .

### AZABORANES FROM AZADIBORIRIDINES

Tri-*tert*-butylazadiboriridine is available in two steps from the corresponding iminoborane (ref. 10):



Unexpectedly, this molecule adds the Lewis acid  $\text{BH}_3$  across the  $\text{BB}$  bond (ref. 11); the ring  $\text{N}$  atom does not show any basicity in this reaction.



The product exhibits  $C_s$  symmetry in solution. The  $\text{BH}_3$  group is rigid with respect to the NMR time-scale, even at  $90^\circ\text{C}$ , with one H atom lying on the mirror plane. The X-ray structural analysis reveals the three  $\text{BB}$  bonds to be of comparable lengths (175 - 178 pm) and the two  $\text{BN}$  bonds as well (141 - 142 pm). The two triangles of the bicyclobutane structure are bent at  $37^\circ$  against each other. Wade's cluster electron counting rules are obeyed for a *nido*-derivative of a trigonal bipyramid. A high-level ab initio calculation shows the parent molecule  $\text{NB}_3\text{H}_6$  to be more basic by 17 kcal than ammonia towards the acid  $\text{BH}_3$ .

By the same procedure as for  $\text{NB}_2(\text{tBu})_3$ , an azadiboriridine with one methyl group less,  $\text{NB}_2(\text{tBu})_2\text{iPr}$ , may be synthesized at  $-78^\circ\text{C}$  (Fig. 8). The addition of  $\text{BH}_3$  at this low temperature again gives the corresponding triorgano-derivative of nido- $\text{NB}_2\text{H}_6$ . By heating the compound  $\text{NB}_2(\text{tBu})_2\text{iPr}$ , however, two molecules of it are fused to a nido-cluster unit, derived from a pentagonal bipyramid by removing an atom from the basis. Out of three potential distributions of the boron ligands  $\text{iPr}$  and  $\text{tBu}$ , the fusing mechanism only permits the distribution of symmetry  $\text{C}_1$  and excludes the  $\text{C}_{2v}$  versions. Proceeding to the synthesis of azadiboriridines with a set of smaller ligands at B1, B2, and N, the addition of Li to the well characterized intermediate boranes,  $\text{Cl-B(R)-N(R'')-B(R')-Cl}$ , gives eight further cluster products  $\text{N}_2\text{B}_4\text{R}_2\text{R}'_2\text{R}''_2$ , without the corresponding azadiboriridines being detectable by their NMR signals at  $-78^\circ\text{C}$  (Fig. 8).

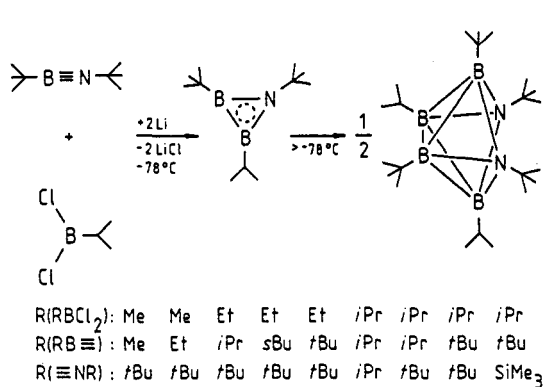


Fig. 8. Formation of 9 derivatives of nido- $\text{N}_2\text{B}_4\text{H}_6$ .

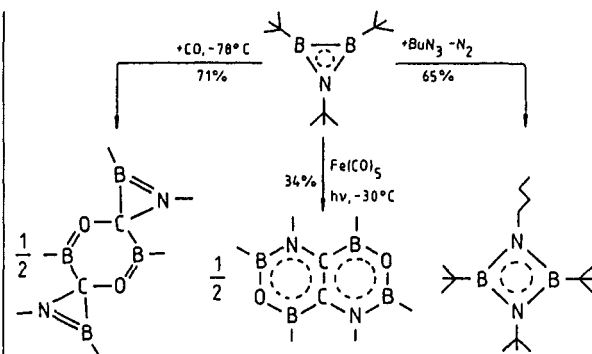


Fig. 9. Reactions of the azadiboriridine  $\text{NB}_2(\text{tBu})_3$  with CO and  $\text{BuN}_3$ .

Away from opening an unexpected path into azaborane cluster chemistry, azadiboriridines may also behave unexpectedly in a reaction with the carbene analogue CO (ref. 12). The tri-tert-butylazadiboriridine adds CO at  $-78^\circ\text{C}$ , giving a 71% yield of a spirocyclic product (Fig. 9), the BN double bonds of which are the shortest ever found (133 pm). If the photolysis of  $\text{Fe}(\text{CO})_5$  at  $-30^\circ\text{C}$  is taken as a source of CO, a product will be formed the structure of which, though non-planar, reminds of naphthalene and demonstrates the complete opening of the CO triple bond, apparently by the catalytic aid of a species containing iron (Fig. 9). - The product formed with  $\text{BuN}_3$  (Fig 9) is not so unexpected. The formal incorporation of a nitrene into the three-membered  $\text{NB}_2$  ring may be of the same type as the yet unidentified, but reasonable primary product during the reaction of the  $\text{NB}_2$  ring with CO.

## AZABORANES FROM DECABORANE

The action of  $\text{HN}_3$  on  $(\text{Me}_2\text{S})_2\text{B}_{10}\text{H}_{12}$  gives azido- $\mu$ -aminodecaborane  $\text{B}_{10}\text{H}_{12}(\text{N}_3)(\text{NH}_2)$ , the structure of which has been elucidated by a 2D- $^{11}\text{B}$ - $^{11}\text{B}$  NMR spectrum and by an X-ray structural analysis (ref. 13, Fig. 10).

This substance turned out to be a useful synthon for the preparation of azaboranes. Whereas the hydrolysis gives a deboration to the known arachno- $\text{B}_9\text{H}_{13}(\text{NH}_3)$ , the deprotonation with  $\text{LiBHEt}_3$  with subsequent protonation with  $\text{HBF}_4$  makes the 5-azido derivative of the known nido- $\text{NB}_9\text{H}_{12}$  available (Fig. 11).

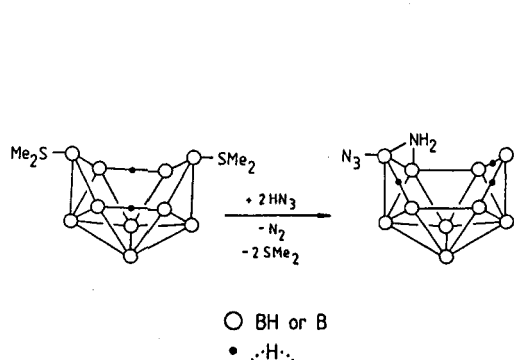


Fig. 10. Formation of  $\text{B}_{10}\text{H}_{12}(\text{N}_3)(\text{NH}_2)$ .

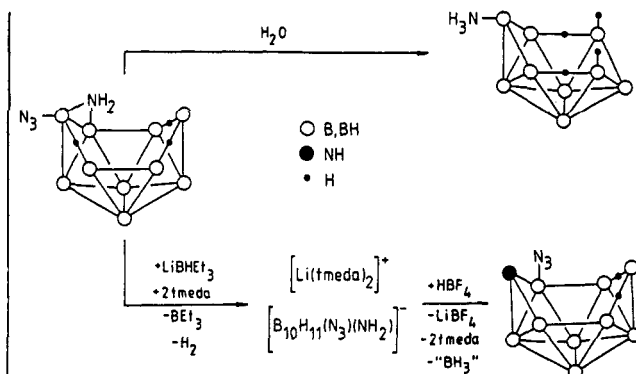


Fig. 11. Hydrolysis and deprotonation/protonation sequence of  $\text{B}_{10}\text{H}_{12}(\text{N}_3)(\text{NH}_2)$ .

The thermolysis of  $B_{10}H_{12}(N_3)(NH_2)$  depends on the solvent. In boiling diglyme, the known nido- $NB_{10}H_{12}$  is formed, from boiling xylene, on the other hand, nido- $NB_{10}H_{13}$  can be isolated and characterized by its NMR spectra, including the  $2D\text{-}^{11}B\text{-}^{13}B$  NMR spectrum (ref. 13, Fig. 12).

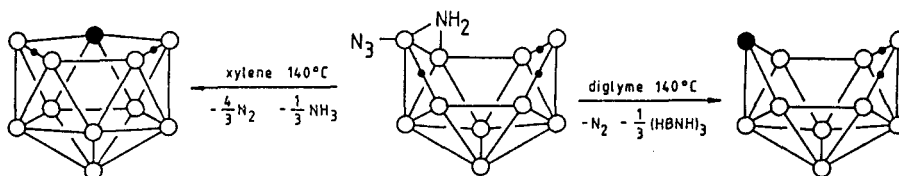


Fig. 12. Formation of two nido-azaboranes from the thermolysis of  $B_{10}H_{12}(N_3)(NH_2)$ .

The open cage of nido- $NB_{10}H_{13}$  can readily be closed to closo- $NB_{11}H_{12}$  by adding  $Et_3N \cdot BH_3$  (Fig. 13). This reaction proceeds via  $[NEt_3H][NB_{11}H_{11}]$  which finally is transformed into  $NB_{11}H_{12}$  by  $HBF_4$ . This closo-cluster is isoelectronic with  $C_2B_{10}H_{12}$  and  $B_{12}H_{12}^{2-}$ . Our earlier attempts to gain  $NB_{11}H_{10}R_2$  by closing the open skeleton of arachno- $B_{10}H_{12}(SMe_2)_2$  with an iminoborane  $RB=NR$  had failed, because the oligomerization of iminoboranes is faster than a potential cage closure reaction. closo- $NB_{11}H_{12}$  seems to be the first molecule that contains a six-coordinate nitrogen atom in a non-classical bonding situation.

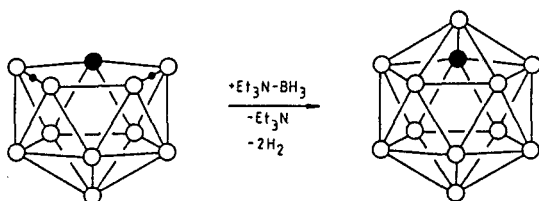


Fig. 13. Formation of closo- $NB_{11}H_{12}$  from nido- $NB_{10}H_{13}$ .

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