APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 227–239 (1996)

REVIEW

Nitrogen Incorporation into Boron Hydride Clusters*

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Keywords: heteroborane; cluster; nitrogen

INTRODUCTION

This review is a survey of research in the area of heteroborane cluster chemistry involving nitrogen as a heteroatom. The incorporation of heteroelements into boron hydride clusters has been an active area of research for many years, as evidenced by the wealth of information on carborane species, in particular. However, reported heteroboranes incorporating nitrogen, either as a cluster atom or in a substituent, have until recently remained relatively scarce.

The criteria for inclusion of a species in this review are as follows.

(1) The species must be a cluster. For the purposes of this review, a cluster is defined as a polyhedral unit of the type discussed by Wade[1] and Lipscomb[2] containing at least one vertex which is at least three coordinate with respect to the cluster framework. This criterion limits the review to species which, but for the heteroatoms, may be thought of as 'classical' deltahedral boron hydride clusters.

(2) The species must contain at least one nitrogen atom bonded to at least one boron cluster vertex in a non-dative sense. The criterion disqualifies species in which the only boron–nitrogen interaction(s) are of the Lewis acid–base type.

(3) Upon (hypothetical) removal of all cluster vertices that are *not* boron or nitrogen from a species, the resulting structure must still fall within the guidelines outlined by the above criteria. This criterion excludes species which exist as clusters only by virtue of multi-site metal coordination to a boron–nitrogen ring system.

(4) While the scope of this review includes reactivity of nitrogen-containing boron hydrides when this reactivity results in species which themselves fall within the above criteria, the discussion is representative, rather than exhaustive, vis-à-vis nitrogen-containing boron hydrides.

The species described are divided into four basic classifications, to each of which a separate section is dedicated.

Section 1: Azaboranes
This section reviews literature describing the preparation and chemistry of species incorporating one nitrogen into the cluster framework. To be considered part of the cluster framework, the nitrogen atom must be at least three-coordinate with respect to the cluster, excepting four- and five-vertex clusters.

Section 2: Diazaboranes
This section reviews the literature describing the preparation and chemistry of species incorporating two nitrogen atoms into the cluster framework.

Section 3: Azaboranes containing other heteroatoms
This section summarizes literature on the preparation and chemistry of azaborane clusters containing additional heteroatoms along with boron and nitrogen.

Section 4: Other nitrogen-containing boron hydride clusters
This section includes boron hydride clusters containing nitrogen in non-vertex positions, such as

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* Dedicated to Professor Peter Paetzold on the occasion of his birthday.

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CCC 0268-2605/96/030227-13

Received 8 June 1995
Accepted 11 August 1995

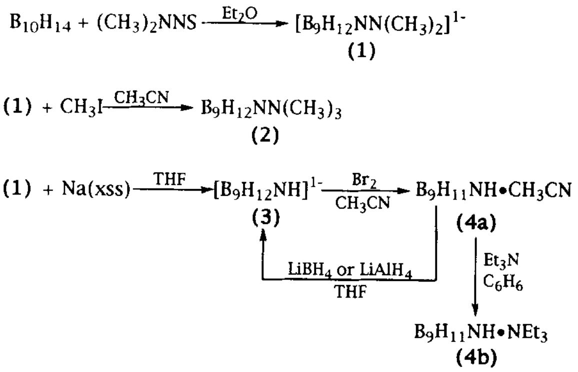
bridging between two boron atoms or as a terminal substituent on the boron cluster framework, the purpose being to encompass species which fall within the scope of this review but do not fall within the classifications delineated for the above three sections.

AZABORANES

The first reported preparation of an azaborane cluster was by Muetterties and co-workers in 1967.[3] Reaction of decaborane(14), $B_{10}H_{14}$, with thionitrosodimethylamine, $(Me)_2NNS$, in diethyl ether solution produced $(B_9H_{12}NNMe_2)^-$ (**1**), along with a thiaborane product. The nitrogen-containing cluster **1** undergoes partial decomposition upon recrystallization from ethanol. Compound **1** can be converted to the inner salt $B_9H_{12}NNMe_3$ (**2**) by reaction with methyl iodide. The nitrogen–nitrogen bond in **1** can be cleaved by reaction with excess sodium in THF to yield the azaborane anion *arachno*-$[6\text{-}HNB_9H_{12}]^-$ (**3**) in low yield. Anion **3** is isolated as the tetramethylammonium salt by recrystallization from aqueous acetic acid and can be converted to the cesium salt. Characterization of **3** was made on the basis of ^{11}B and ^{1}H NMR, infrared spectroscopy and elemental analysis. Based on these analytical data, an *arachno* structure derived from the *arachno*-$[B_{10}H_{14}]^{2-}$ dianion was proposed.

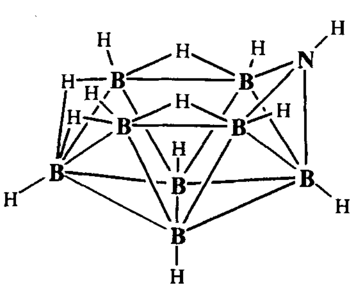
Despite the low yield of **3**, some derivative chemistry was carried out. Reaction of **3** with bromine in acetonitrile yielded the acetonitrile adduct *arachno*-9-(MeCN)-6-HNB_9H_{11} (**4a**) as a sublimable solid. Adduct **4a** is converted back to **3** upon treatment with $LiAlH_4$ or $LiBH_4$ in THF and can be converted to the triethylamine adduct *arachno*-9-(Et_3N)-6-HNB_9H_{11} (**4b**) by reaction with triethylamine in benzene. This azaborane chemistry is summarized in Scheme 1

The first uncharged azaborane cluster free of any coordinated Lewis base, 4-HNB_8H_{12} (**5**) was reported in 1975 by Plesek and Schaefer.[4] The azaborane **5** was formed in *ca* 30% yield by addition of sodium nitrite to $B_{10}H_{14}$ in THF, followed by acidification with HCl. Compound **5** was characterized by single-crystal X-ray diffraction analysis. The X-ray study solved an apparent discrepancy between ^{11}B NMR data, which suggested an eight-boron structure, and mass-spectrometric data, which showed a nine-boron species that had apparently formed within the spectrometer. Further decaborane–sodium nitrite chemistry was reported some years later by Base and co-workers.[5,6] The initial product from the reaction of $B_{10}H_{14}$ with $NaNO_2$ was proposed to be $Na[B_{10}H_{12}NO_2]$ (**6**). Reaction intermediate **6** is reported to be converted, as described above,[4] to **5** by action of dilute HCl, or to a *nido*-6-azadecaborane(12), 6-HNB_9H_{11} (**7**), upon treatment with concentrated sulfuric acid. Azaborane (**7**) was characterized by infrared and ^{11}B NMR spectroscopy and mass spectrometry.

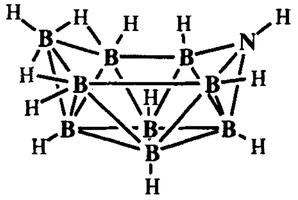


Scheme 1

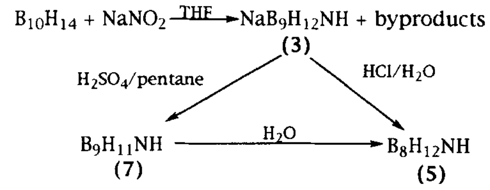
Both reaction pathways are rationalized in terms of degradative insertion of nitrogen into the $B_{10}H_{14}$ framework. Hydrolysis of **7** also produces **5** in high yield. One molecule of Lewis base can be added to the azaborane **7** to obtain *arachno*-9-L-6-HNB_9H_{11} derivatives (**4a**, **4c**, **4d**) where L = MeCN (**4a**), Me_2S (**4c**) or PPh_3 (**4d**). In solution, these adducts exist in equilibrium with free azaborane **7**, as evidenced by NMR. Reaction of adduct **4a** with $LiAlH_4$ in THF produced the *arachno*-$[6\text{-}HNB_9H_{12}]^-$ anion (**3**). The ^{11}B NMR



(**5**)



(**7**)



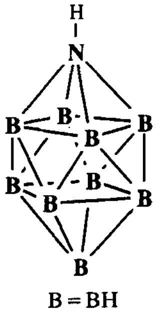
Scheme 2

data for **3** of Base *et al.* appears to confirm the *arachno* structure proposed earlier by Muetterties.[3]

The decaborane–sodium nitrite system has been further investigated by Todd *et al.*, who published a detailed investigation of the reaction in 1986.[7] An ^{11}B NMR spectrum of the product mixture after three days did not show evidence of significant amounts of $Na[B_{10}H_{12}NO_2]$ (**6**), though this species may exist as a transient intermediate. The spectrum did show the presence of *arachno*-$[6\text{-}HNB_9H_{13}]^-$ (**3**), *arachno*-$[B_9H_{14}]^-$, *arachno*-$[B_{10}H_{15}]^-$ and borates as major products, along with a small amount of *nido*-$[B_9H_{12}]^-$. Clearly, the total reaction mechanism is quite complex.

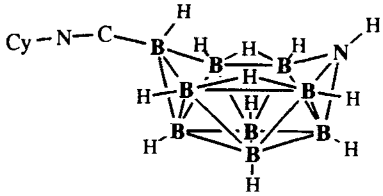
The solvent-free sodium salts from this reaction were treated with concentrated sulfuric acid under a layer of dry pentane, forming mainly $B_{10}H_{14}$ and the neutral azaborane *nido*-6-NHB_9H_{11} (**7**). Reaction chemistry derived immediately from the decaborane–sodium nitrite system is summarized in Scheme 2.

Though compound **7** proved to be unstable with respect to hydrolysis, its Lewis base adducts were quite resistant to attack by water or air. The anionic azaborane *arachno*-$[6\text{-}HNB_9H_{12}]^-$ (**3**), which can be thought of as an adduct of **7**, where H^- functions as the base, was reported to be air-stable for months. Slow passage of **7** through an evacuated hot tube at 375–400 °C formed *closo*-HNB_9H_9 (**8**), which represents the first synthesis of a *closo*-azaborane species. Compound **8** was structurally characterized by ^{11}B and ^1H NMR spectra, which are consistent with axial placement of an NH unit in a bicapped Archimedian antiprism structure of C_{4v} symmetry. A crystal structure of **8** has been published very recently by Paetzold and co-workers[8] as the $[Ph_3P{=}N{=}PPh_3]^+$ salt. ^{11}B NMR spectra were reported at higher fields than in previous studies.[3,5,6] Other base adducts formed were *arachno*-9-(tBuCN)-6-HNB_9H_{11} (**4e**), *arachno*-9-py-6-HNB_9H_{11} (**4f**; py = pyridine) and *arachno*-9-$((C_6H_{11})CN)$-6-HNB_9H_{11} (**4g**). A single-crystal X-ray analysis was performed on **4g**.



(**8**)

B = BH

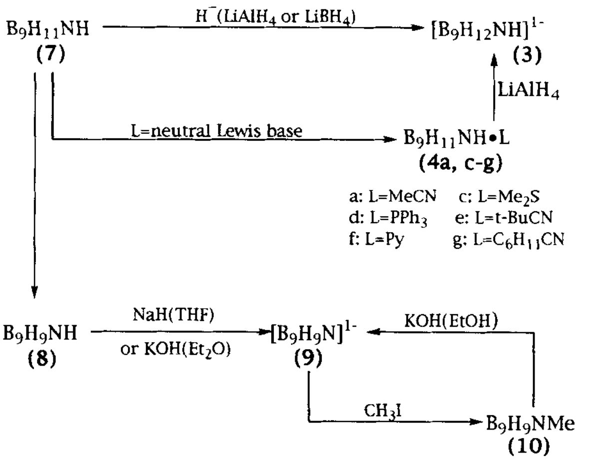


(**4g**)

Cy = cyclohexyl

Treatment of **8** with sodium hydride in THF or with KOH in ethanol gave the *closo*-$[NB_9H_9]^-$ anion (**9**), isolated as the tetramethylammonium salt.[7] Reaction of **9** with methyl iodide in THF produced *closo*-$MeNB_9H_9$ (**10**), which can be converted back to **9** by reaction with KOH in ethanol. Further synthetic studies of the azaborane **7**, in which the yield of pure **7** has been improved to 58%, have been published by Todd and co-workers.[9] Previous synthetic procedures[7] resulted either in samples of **7** that were contaminated with a trace of decaborane, or very low yields of pure compound **7**. In the new procedure, the crude sodium salt mixture from the reaction of $B_{10}H_{14}$ and $NaNO_2$ was treated with iodine in acetonitrile, resulting in the formation of a mixture of the adducts $B_9H_{11}NH \cdot MeCN$ (**4a**) and $B_{10}H_{12} \cdot MeCN$. Gentle heating of this mixture at 60 °C caused dissociation of the azaborane adduct. This allowed for separation of pure **7** by vacuum sublimation from the $B_{10}H_{12}$ adduct, which does not dissociate and is non-volatile. Pure **7** was reported to be much more stable toward hydrolysis than had been believed earlier. A two-dimensional COSY ^{11}B–^{11}B NMR spectrum of azaborane (**7**) was published which unambiguously confirms the assignment of the one-dimensional spectrum. A summary of synthetic chemistry deriving from species **7** appears in Scheme 3.

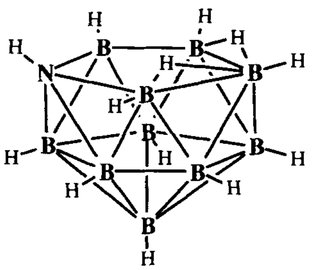
A novel access to azaboranes by way of reaction of $B_{10}H_{12}(SMe_2)_2$ and hydrazoic acid, HN_3, was published in 1990 by Paetzold and



Scheme 3

co-workers.[10] The initial product of the reaction is the *arachno*-μ-(5,6-NH_2)-6-(N_3)-$B_{10}H_{12}$ (**11**), a species containing a bridging amino (NH_2) group and a terminally bonded azido function. Compound **11** has been isolated in 60% yield and characterized by single-crystal X-ray diffraction.

The two-dimensional COSY ^{11}B–^{11}B NMR spectrum of **11** is in accord with the crystal structure. Compound **11** can be transformed into a 5-azido derivative of *nido*-6-HNB_9H_{11} (**7**) by a deprotonation/protonation sequence. Deprotonation of **11** with $LiBH(Et)_3$ in THF yields the *arachno* anion $[NB_{10}H_{13}(N_3)]^-$ (**12**). Subsequent reprotonation with CF_3COOH and accompanying loss of a formal BH_3 moiety results in 5-azido-*nido*-azadecaborane(12), 5-N_3-6-HNB_9H_{10} (**13**). The structure of **13**, determined by two-dimensional COSY ^{11}B–^{11}B NMR, is the same as that for compound **7**, but for the substitution of an azido group at the 5-position on the cluster. Thermolysis of **11** in boiling xylene results in a mixture of products including *nido*-7-azaundecaborane, 7-$HNB_{10}H_{12}$ (**14**). Azaborane (**14**) is isolated from the product mixture in 5% yield by sublimation and has been structurally characterized by NMR methods, including a two-dimensional ^{11}B–^{1}H correlation experiment.



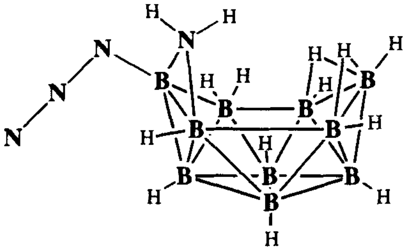
(14)

The NMR-determined structure of **13** was confirmed by a single-crystal X-ray diffraction study in a later paper.[11] Thermolysis of **11** in diglyme at 140 °C was reported at that time to result in quantitative conversion to **7**. The same paper also reported the formation of **7** in 11% yield by thermolysis of the *arachno* nonaborane adduct $B_9H_{13}(NH_3)$ in xylene, along with the formation of three new derivatives of **7**. Reaction of **7** with $Et_3N \cdot BH_3$ proceeds with the evolution of hydrogen to give the 6-$BH_2 \cdot NEt_3$ derivative of **7**, 6-($BH_2 \cdot NEt_3$)-6-NB_9H_{11} (**15**). Both species, **15** and **13**, add the isonitrile (tBu)NC at the 9-position to form the *arachno* adducts 9-(tBuCN)-6-($BH_2 \cdot NEt_3$)-6-NB_9H_{11} (**16**) and 5-N_3-9-(tBuCN)-6-HNB_9H_{10} (**17**).

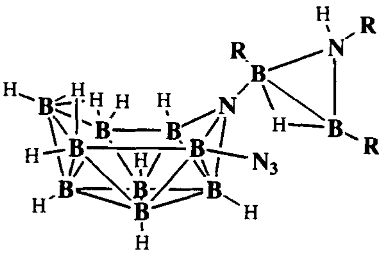
Reaction of **13** with the three-membered ring azadiboriridine [(tBu)B—B(tBu)—N(tBu)] produces an adduct in which one of the ring boron atoms connects to the cluster nitrogen by a hydroboration reaction and the other ring boron interacts in a dative sense with the azido group on the cluster: 5-azido-6-[1,2,3-tri(t-butyl)azoniabora-borata-3-cyclopropyl]-6-aza-*nido*-decaborane(12) (**18**).

Reactions of **7** with azides RN_3 proceed with formation of a coordinate B–N bond between B(9) and N(1) of RN_3 and addition of the B(4)–H bond of **7** to the N(3) atom of RN_3.[12] The products (**19a**, R = H; **19b**, R = CH_2Ph) then contain an azaborane skeleton and a five-membered unsaturated B_2N_3 ring with a common B–B edge.

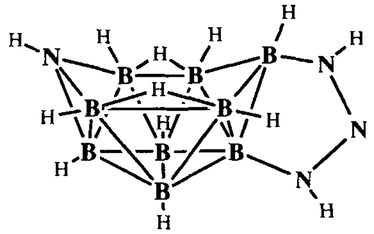
Soon after the first report of the azaborane **14**, there appeared a paper on the preparation of the first *closo* 12-vertex azaborne cluster.[13] Treatment



(11)



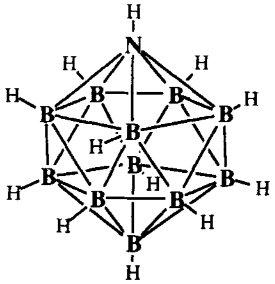
(18)



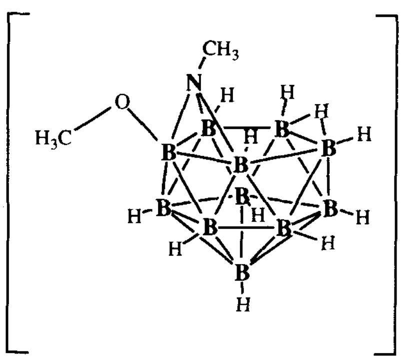
(19a)

of **14** with $Et_3N \cdot BH_3$ at 140 °C formed a compound of formula $Et_3NH[NB_{11}H_{11}]$ (**20**) in quantitative yield. Reaction of **20** with HBF_4 gave *closo*-azadodecaborane, $HNB_{11}H_{11}$ (**21**) as a sublimable colorless solid. No single-crystal X-ray diffraction study on **21** has yet appeared in the literature. However, an optimized structure determined by correlation of gas-phase electron diffraction data with *ab initio* structural calculations and IGLO ^{11}B NMR chemical shift calculations has been published.[17] Compound **21** is the first cluster molecule to contain a six-fold coordinated nitrogen atom in the cluster framework.

More recently, Paetzold and co-workers have reported a route by which the aza-*closo*-dodecaborane skeleton may be opened to an aza-*nido*-dodecaborate.[14] Reaction of the salt **20** with the strong methylating agent methyl triflate, MeO_3SCF_3, gives the *N*-methyl derivative of compound **21**, $MeNB_{11}H_{11}$ (**22a**). In a later paper, Paetzold reported analogous reactions with other alkyl triflates, resulting in the formation of $iPrNB_{11}H_{11}$ (**22b**) and $iBuNB_{11}H_{11}$ (**22c**).[15] Also reported was a new *N*-alkylating reaction of **20** with triethyloxonium tetrafluoroborate, $[Et_3O]BF_4$, to produce $EtNB_{11}H_{11}$ (**22d**). Treatment of the methylated azaborane **22a** with methanol results in the formation of the acid $H[MeNB_{11}H_{11}(OMe)]$ (**23**),[14] which dissociates completely in dichloromethane in the presence of excess methanol. Treatment of a solution of acid **23** with $[N(PPh_3)_2]Cl$ gives a product of formula $[N(PPh_3)_2][MeNB_{11}H_{11}(OMe)]$ (**24**). The anions in **23** and **24** appear to be identical on the basis of their identical NMR spectra and constitute *nido* derivatives of the hypothetical 13-vertex *closo*-tridecaborate anion, $[B_{13}H_{13}]^{2-}$.[16]



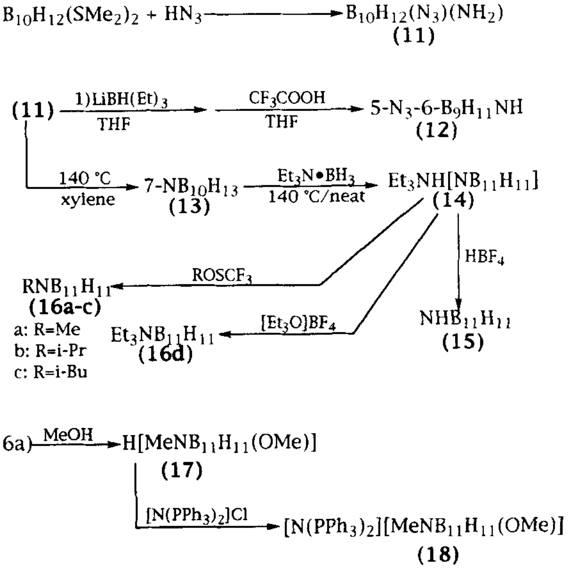
(21)



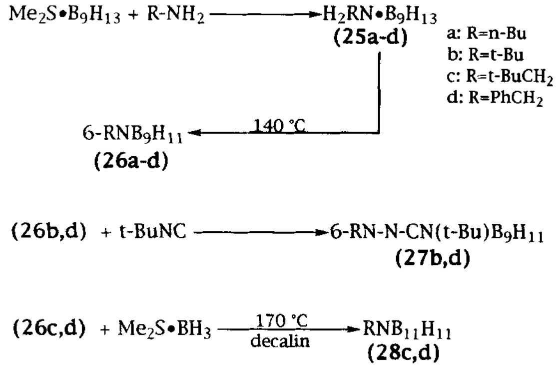
(24)

A summary of reaction chemistry deriving from the decaborane–hydrazoic acid reaction appears in Scheme 4.

Newer routes to the icosahedral NB_{11} skeleton have appeared recently in the literature. Paetzold and co-workers have reported preparation of the *closo* NB_{11} framework starting from dimethyl sulfide–*arachno*-nonaborane(13), $Me_2S \cdot B_9H_{13}$.[15] Treatment of this adduct with a series of primary amines results in substitution of the sulfane ligands and production of the amine adducts $H_2RN \cdot B_9H_{13}$ (**25a–25d**), where R = nBu (**25a**), tBu (**25b**), $tBuCH_2$ (**25c**) and $PhCH_2$ (**25d**). Thermolysis of **25a–25d** at 140 °C causes elimination of hydrogen and incorporation of the NR moiety into the cluster framework, thus producing the corresponding *nido*-6-alkyl-6-azadeca-



Scheme 4

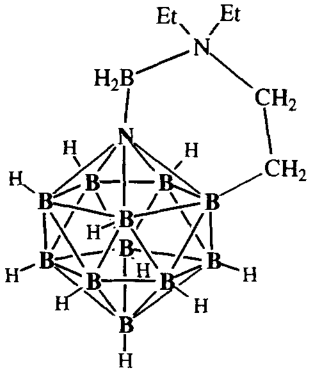


Scheme 5

boranes, 6-RNB_9H_{11} (**26**–**26d**) in moderate (18–24%) yields. These are the first *N*-alkyl derivatives of compound **7**. The *N*-(tBu) derivative (**26b**) and the *N*-CH_2Ph derivative (**26d**) add t-butyl isocyanide, thus forming the *arachno* adducts 6-RN-9-CN(tBu)B_9H_{11} (**27b**) and (**27d**), respectively. Products **25**–**27** were structurally characterized by NMR methods.

Closure of the *nido*-azadecaboranes (**26c**, **26d**) is effected by reaction with excess $Me_2S \cdot BH_3$ in decalin at *ca* 170 °C, resulting in *closo*-azadodecaboranes of formula $RNB_{11}H_{11}$ (**28c**, **28d**). [Note the compound numbering change: compounds **28c** and **28d** are isostructural with $MeNB_{11}H_{11}$ (**22a**) but have been so numbered to preserve continuity in the letters corresponding to the various alkyl groups within this section.] Reaction of compound **26b** with $Me_2S \cdot BH_3$ resulted in a mixture of products from which no *closo*-azaborane could be isolated. Closure of compound **26a** was not attempted. A summary of the azaborane synthetic chemistry starting from dimethyl sulfide-*arachno*-nonaborane(13) is shown in Scheme 5.

Also from the Paetzold group, routes to the icosahedral NB_{11} framework starting from the azaborane **7** have recently appeared in the literature.[18] Reaction of three equivalents of $Et_3N \cdot BH_3$ with **7** gives closure to the icosahedral skeleton $NB_{11}H_{10}Y$ (**29**), where Y = —BH_2—NE_2—CH_2—CH_2—, forming a ring connecting adjacent cluster atoms N1 and B2. Reaction of **7** with $Me_3N \cdot BH_3$ or $Me_2S \cdot BH_3$ effects transformation into the *closo*-azaboranes (Me_3NBH_2)$NB_{11}H_{11}$ (**30a**) and (Me_2SBH_2)-$NB_{11}H_{11}$ (**30b**) at 140 °C. Treatment of **30b** with $tBuNH_2$ causes removal of the N-bonded ligand Me_2SBH_2 with formation of the *closo*-azadodecaborate (t-$BuNH_3$)$NB_{11}H_{11}$ (**31**). Routes to the icosahedral NB_{11} framework starting from **7** are summarized in Scheme 6.



(29)

Recently, the field of macro-polyhedral boron–nitrogen chemistry has been opened by Jelinek, Kennedy and Stibr with the discovery of the 18-vertex azaborane *anti*-[9-$NB_{17}H_{20}$] (**32**).[19] Reaction of *anti*-$B_{18}H_{22}$ with a threefold excess of n-butyl nitrite (n-BuONO), either in diethyl ether at room temperature or in benzene at reflux temperature, results in moderate yields of **32**, whose proposed structure is based on ^{11}B and ^{1}H NMR spectroscopy.

Recently, new routes to azaboranes involving assembly of small boron- and nitrogen-containing units have begun to appear. These are in contrast to the routes discussed above, which for the most part involve incorporation of a nitrogen-containing moiety into a pre-existing cluster framework. The non-classical acid–base adduct product, *nido*-$NB_2(tBu)_3BH_3$ (**33a**), is formed in the reaction of $BH_3 \cdot THF$ with the three-membered azadiboriridine ring of general formula $\overline{NR—BR'—BR''}$, where R = R′ = R″ = tBu.[20] An X-ray diffraction structure has been determined for **33a**. Compound **33a** is also a product in the reaction of tri(t-butyl)azadiboriridine and $B_3H_7 \cdot THF$,[21] and though formed via an

$$(7) + 3Et_3N \cdot BH_3 \rightarrow \underset{(\mathbf{29})}{NB_{11}H_{10}Y}$$

$$(Y = -BH_2—MEt_2—CH_2—CH_2—)$$

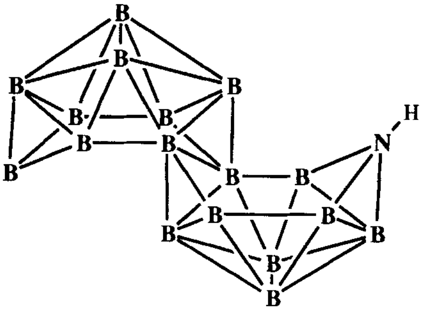
$$(7) + Me_3N \cdot BH_3 \rightarrow \underset{(\mathbf{30a})}{(Me_3MBH_2)NB_{11}H_{11}}$$

$$(7) + Me_2S \cdot BH_3 \rightarrow \underset{(\mathbf{30b})}{(Me_2SBH_2)NB_{11}H_{11}}$$

$$\downarrow tBuNH_2$$

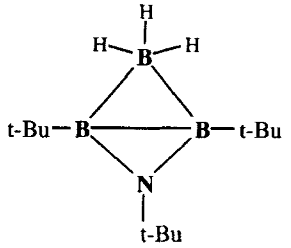
$$\underset{(\mathbf{31})}{(tBuNH_3)MB_{11}H_{11}}$$

Scheme 6



(32)

B = BH; bridge hydrogens are omitted



(33a)

Structure 33

initial Lewis acid–base interaction, these are clearly *nido* cluster compounds in which the nitrogen is bound in the cluster framework in a non-dative sense.

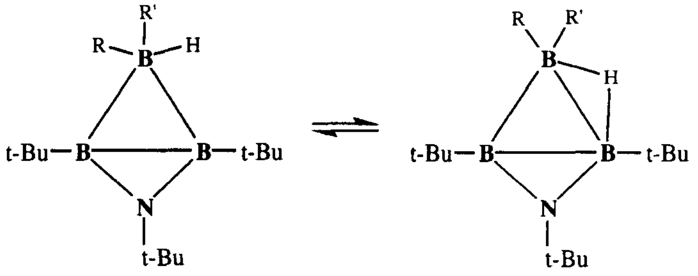
Further cluster assembling reactions leading to azaboranes have been published very recently. A series of *nido*-azatetraboranes have been synthesized by the reaction of tri-(*t*-butyl)azadiboriridine, $NB_2(tBu)_3$, with monoboranes BH_2R[22] to produce *nido*-$NB_2(tBu)_3BH_2R$ with R = H (**33a**), R = Me (**33b**), R = tBu (**33c**), R = $CMe_2(iPr)$ (**33d**), R = Ph (**33e**) and R = sBu (**33f**). With the exception of compound **33a**, these compounds exist in equilibrium with structural isomers in which one of the hydrogen atoms from the R—BH_2 group takes up a bridging position between two adjacent boron atoms. [Eqn [1]). Reaction of tri(t-butyl)azadiboriridine with $(BHEt_2)_2$ produces *nido*-$NB_2(tBu)_3BHEt_2$ (**33g**), while reaction of the same azadiboriridine with 9-borabicyclononane (9-BBN) yields a *nido* azatetraborane of formula *nido*-$NB_2(tBu)_3BH(BBN)$ (**33h**). Compounds **33f** and **33h** exist exclusively as the hydrogen-bridged isomers; no equilibrium is evident by NMR.

DIAZABORANES

A new class of heteroborane appeared with the report of the first diaza-*nido*-hexaboranes by Paetzold in 1987.[23] Iminoboranes of general formula RBN(tBu) are haloborated by $R'BX_2$ to give diborylamines X—(R)B—N(tBu)—B(R')—X, which can then be dehalogenated by Na/K alloy, forming the *nido*-diazahexaboranes of formula $(BR)_2(BR')_2(tBuN)_2$ (**34a–34c**), where R = R' = Me (**34a**), R = R' = iPr (**34b**), or R = tBu, R' = iPr (**34c**).

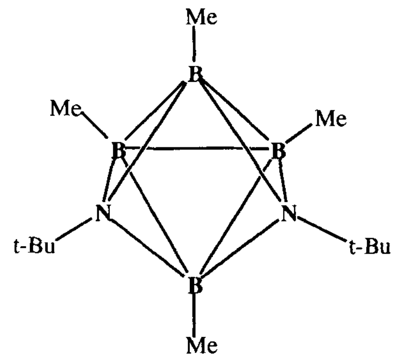
This series has been extended in a more recent paper.[24] Iminoboranes of the formula RBNR'' are haloborated by dihaloboranes $R'BX_2$. Subsequent reduction of the resulting bis(haloboryl)amines with lithium produces *nido*-diazahexaboranes $(BR)_2(BR')_2(NR'')_2$ (**34d–34j**), where R/R'/R'' = Et/iPr/tBu (**34d**), Et/sBu/tBu (**34e**), iPr/iPr/iPr (**34f**), iPr/tBu/iPr (**34g**), tBu/Me/·tBu (**34h**), tBu/Et/tBu (**34i**), and tBu/iPr/$SiMe_3$ (**34j**).[25] In some cases, azadiboriridines are isolated or shown to be intermediates in the mechanism of conversion of the bis(haloboryl)amines to *nido*-diazahexaboranes. In the cases (**34g–34j**), the substituents R and R' are unsymmetrically distributed to axial and equatorial positions in the *nido* structure, which is derived from the pentagonal bipyramid.

Another route to the *nido*-azahexaborane skeleton has appeared recently.[22] Treatment of (t-butyl)azadiboriridine with trialkylboranes BR_3,

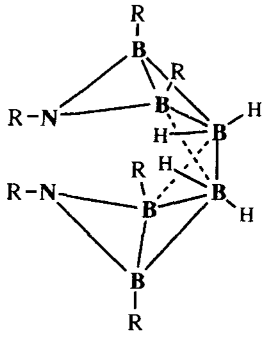


[1]

(33a–33e)
R is identified in text



(34a)



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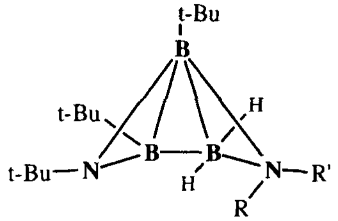
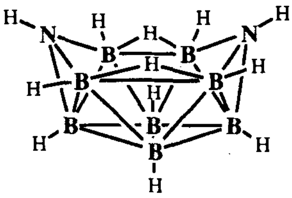


(36)

where R = Me or Et, appears to result in the formation of intermediate azadiboriridines of formula N(tBu)—B(tBu)—B(R), which dimerize to give the new unsymmetrically substituted *nido*-diazahexaboranes $(tBuN)_2(B(tBu))_2(BR)_2$ where R = Me (**34k**) or R = Et (**34l**). A new diazaborane synthesis has been reported by the reaction of tri(t-butyl)azadiboriridine with the THF adduct of B_3H_7.[21] Products include **33a** and the new $(NB_2(tBu)_3)_2B_2H_4$ (**35**), described as an *arachno*-diazaoctaborane derivative.

Reaction of tri(t-butyl)azadiboriridine with the aminoboranes of formula $H_2B{=}NRR'$ results in



(37)

$$RBNR'' + R'BX_2 \rightarrow X{-}BR{-}NR''{-}BR'{-}X$$

$$2X{-}BR{-}NR''{-}BR'{-}X + 4M \xrightarrow{M=Na/K\ or\ Li} (BR)_2(BR')_2(NR'')_2 \quad (\mathbf{34a\text{–}j})$$

R/R'/R''

a: Me/Me/tBu
b: Pr/iPr/tBu
c: tBu/iPr/tBu
d: Et/iPr/tBu
e: Et/sBu/tBu
f: iPr/iPr/iPr
g: iPr/tBu/iPr
h: tBu/Me/tBu
i: tBu/Et/tBu
j: tBu/iPr/SiMe₃

$$(tBu)_3NB_2 + BR_3 \xrightarrow[(reflux)]{THF} (B(tBu))_2(BR)_2(N(tBu))_2 \quad (\mathbf{34k, l})$$

k: R = Me
l: R = Et

$$(tBu)_3NB_2 + B_3H_7 \cdot THF \rightarrow (\mathbf{33a}) + (NB_2(tBu)_3)_2B_2H_4 \quad (\mathbf{35})$$

$$(tBu)_3NB_2 + H_2B{=}NRR' \rightarrow (tBu)N(B(tBu))_2BH_2NRR' \quad (\mathbf{36a\text{–}35d})$$

a: R = nPr, R' = H
b: R = tBu, R' = H
c: R = R' = Me
d: R = R' = Et

$$NaNO_2 + (\mathbf{4a}) \rightarrow 6,9{-}N_2B_8H_{12} \quad (\mathbf{37})$$

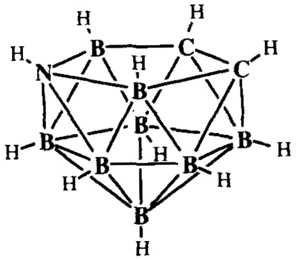
Scheme 7

the formation of *arachno*-diazapentaboranes $(tBu)N(B(tBu))_2BH_2NRR'$ (**36a–36d**).[22] Products have been characterized for R = nPr, R' = H (**36a**); R = tBu, R' = H (**36b**); R = R' = Me (**36c**); and R = R' = Et (**36d**).

A larger diazaborane, the *arachno*-6,9-diazadecaborane(12), 6,9-$N_2B_8H_{12}$ (**37**), is formed in the reaction of $NaNO_2$ and either *arachno*-9-(MeCN)-6-NHB_9H_{11} (**4a**) or *nido*-6-HNB_9H_{11} (**7**) in THF solution.[26] A summary of diazaborane syntheses is presented in Scheme 7.

AZABORANES CONTAINING OTHER HETEROATOMS

The first boron hydride cluster containing both nitrogen and some other heteroatom in cluster positions was the *nido*-azadicarbaborane



(38)

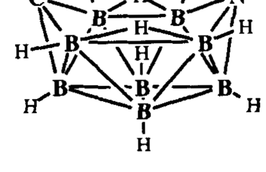
$HNH_2C_2B_8H_8$ (**38**).[27] Compound **38** is a product in the reaction of the carborane anion $[7,8\text{-}H_2C_2B_8H_{10}]^-$ with nitrous acid, HNO_2, in water. This azacarborane was formed in 15% yield and structurally characterized by IR and NMR (^1H and ^{11}B) spectroscopy. The reaction is described as a degradative insertion, as a BH_2^- unit is formally replaced by a NH moiety.

Methylation of **38** at nitrogen is also reported, resulting in $NMeC_2B_8H_{11}$ (**39**). The *N*-benzyl derivative of **38**, $7\text{-}PhCH_2\text{-}7\text{-}N\text{-}9,10\text{-}C_2B_8H_{10}$ (**40**) is formed in the reaction of **38** with $PhCH_2Br$ in Et_2O in the presence of KOH.[28] A crystal structure for **40** has been obtained.

An *arachno* azacarborane species, $6\text{-}H_2C\text{-}9\text{-}HNB_8H_{10}$ (**41**), is produced upon treatment of the monocarborane *arachno*-$4\text{-}CB_8H_{14}$ with a threefold excess of aqueous sodium nitrite in the presence of triethylamine, followed by acidification of the product mixture.[29] The *arachno* structure of **41** was deduced from ^{11}B and ^1H NMR spectra.

The first azaborane with a non-nitrogen heteroatom other than carbon, *arachno*-$6\text{-}S\text{-}9\text{-}HNSB_8H_{10}$ (**42**), has been synthesized from the reaction of n-butyl nitrite with *nido*-$6\text{-}SB_9H_{11}$ in benzene.[30] This azathiaborane has been structurally characterized by ^{11}B and ^1H NMR.

There are several examples of azaboranes containing transition metals as cluster atoms. The first of these was the azaplatinaborane *arachno*-$9\text{-}(PPh_3)_2Pt\text{-}6\text{-}HNB_8H_{10}$ (**43**).[31,32] Metal insertion was accomplished by reaction of $4\text{-}HNB_8H_{12}$ (**5**) with $Pt(PPh_3)_4$. Compound **43** was structurally characterized by X-ray diffraction.



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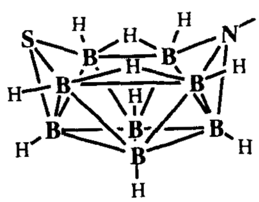

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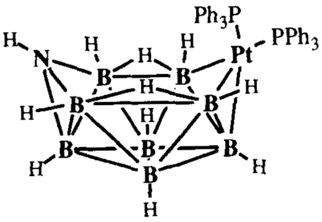

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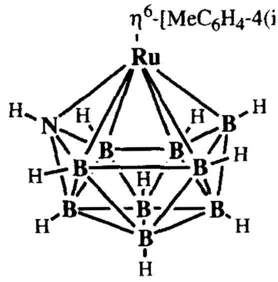


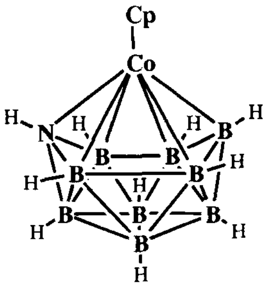
(44)

The first azaruthenaborane species is represented by the 11-vertex *closo*-$1\text{-}[\eta^6\text{-}MeC_6H_4\text{-}4\text{-}(iPr)]Ru\text{-}2\text{-}HNB_9H_9$ (**44**).[33] Azaruthenaborane **44** is one of many ruthenaborane products reported to be formed in the reaction of *nido*-$6\text{-}HNB_9H_{11}$ (**7**) with $[\{\eta^6\text{-}MeC_6H_4\text{-}4\text{-}(iPr)\}]RuCl_2$ in THF in the presence of *N,N,N′,N′*-tetramethylnaphthalene-1,8-diamine. The other reaction products were not fully characterized. The structure of air-stable compound **44** has been determined crystallographically.[33]

Another azametalloborane, the cobaltaborane *closo*-$1\text{-}(\eta^5\text{-}C_5H_5)Co\text{-}2\text{-}HNB_9H_9$ (**45**), has been prepared from *nido*-$6\text{-}HNB_9H_{11}$ (**7**).[9] Treatment of **7** with NaH results in removal of an acidic hydrogen. Subsequent reaction with $CoCl_2$ in the presence of cyclopentadiene yields the *closo* compound **45**, the structure of which has been crystallographically determined.[9]

An 11-vertex *nido* azairidaborane has been prepared by reaction of **7** with $[(\eta^5\text{-}C_5Me_5)IrCl_2]_2$ in the presence of *N,N,N′,N′*-tetramethylnaphthalene-1,8-diamine, which results in formation of *nido*-$9\text{-}Cl\text{-}8\text{-}(\eta^5\text{-}C_5Me_5)Ir\text{-}7\text{-}HNB_9H_{10}$ (**46**).[34]

A *closo* azarhodaborane has also been reported.[35] Deprotonation of *nido*-7-azaundecaborane, $7\text{-}HNB_{10}H_{12}$ (**14**), with $Li[B(Et)_3H]$ in the presence of tetramethylethylenediamine (TMEDA), followed by reac-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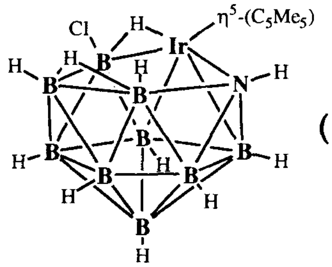

(46)

tion with $(Ph_3P)_3RhCl$, results in the formation of *closo*-1-$[(Ph_3P)_2HRh]$-2-$HNB_{10}H_{10}$ (**47**). The structure of **47** was crystallographically determined to be that of a distorted icosahedron.

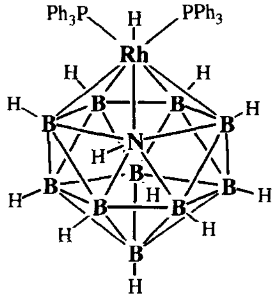
Paetzold has shown that the metallation of the $HNB_{10}H_{10}^{2-}$ fragment is quite general. This was illustrated by its reaction with $[Ni(PPh_3)_2]^{2-}$ to form *closo*-1-$[Ni(PPh_3)_2]$-2-$NB_{10}H_{11}$, and with $CoCl_2$ to produce the sandwich-type product $[1\text{-}Co(2\text{-}HNB_{10}H_{10})_2]^-$. In addition, reaction of $HNB_{10}H_{10}^{2-}$ with $[\eta^6\text{-}(C_6Me_6)RuCl_2]_2$ dimer produces the arene–azaborane sandwich compound 1-$[\eta^6\text{-}(C_6Me_6)Ru]$-2-$NB_{10}H_{11}$.[36]

OTHER NITROGEN-CONTAINING BORON HYDRIDE CLUSTERS

The first fully characterized nitrogen-containing boron hydride cluster appeared in 1963 in a report by Lipscomb and co-workers.[37] The reaction of the sulfide adduct $B_9H_{13}SEt_2$ with ethylamine produces an anionic species formulated as $[EtNH_2B_8H_{11}NHEt]^-$ (**48**). The crystallographically determined structure of **48** shows that an (NHEt) moiety bridges between two boron atoms in the cluster framework.

A bridging nitrogen atom between two boron atoms is also seen in the azacarborane 8,9-μ-H_2N-5,6-$C_2H_2B_8H_{10}$. (**49**).[27] Compound **49** is a product in the reaction of the carborane anion 7,8-$[C_2B_9H_{12}]^-$ with nitrous acid in water.

Another species exhibiting a bridging nitrogen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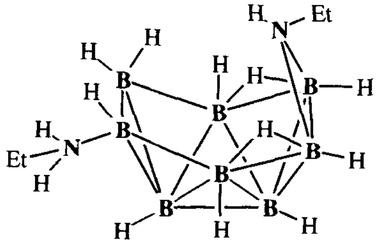
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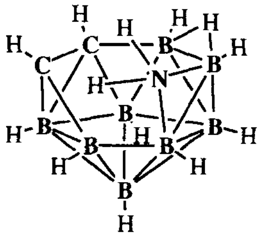
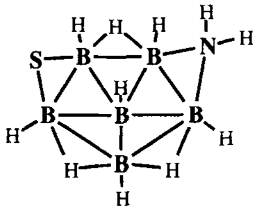

(49)

is *hypho*-7-S-8-HNB_6H_{10} (**50**), formed in the reaction of *arachno*-4-SB_8H_{12} with excess n-butyl nitrite in diethyl ether.[30]

Two bridging nitrogen atoms are seen in the structure of the bis(dimethylamino)borane cluster μ-$(Me_2N)_2B_4H_8$ (**51**).[38] Compound **51** is formed in the reaction of $(Me_2N)_2BBr$ with $Me_4NB_4H_8$. NMR and IR data indicate a structure based on the structure of tetraborane (10), with two bridge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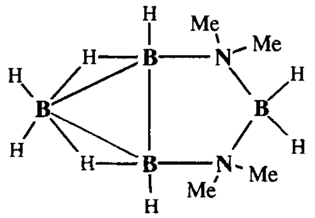
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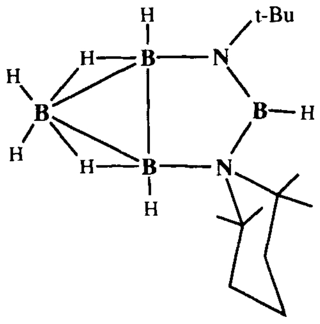

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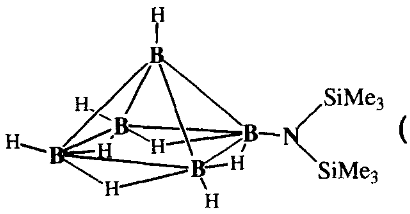

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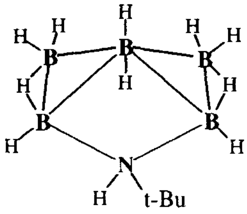

(54)

hydrogen atoms replaced by bridging dimethylamino groups.

A structurally similar compound has been prepared by triborane(7) · THF hydroboration of (t-butylimino)(tetramethylpiperidino)borane to form μ-(t-butylimino)-μ-(tetramethylpiperidino)-tetraborane(8) (**52**).[39] Terminal substitution of a nitrogen-containing moiety on a borane cage is seen in 2-bis(trimethylsilyl)aminopentaborane(9), $[(Me_3Si)_2N]B_5H_8$ (**53**).[40] Compound **53** is formed in the reaction of 2-bromopentaborane(9), $2\text{-}BrB_5H_8$ and hexamethyldisilazane, $(Me_3Si)_2NH$.

Reaction of $2\text{-}BrB_5H_8$ with t-butylaminotrimethylsilane produces a 2-aminopentaborane similar to **53** and a *hypho* aminopentaborane cluster, *hypho*-2,3-μ-(t-butylamino)pentaborane(11), $2,3\text{-}\mu\text{-}(tBuNH)B_5H_{10}$ (**54**).

CONCLUSIONS

The insertion and attachment of nitrogen to borane clusters has provided some interesting synthetic challenges. Nitrogen insertions are for the most part mechanistically devious and often involve redox processes and/or deboronation reactions that are still not well understood. Nevertheless, some synthetic, structural and reaction patterns are beginning to emerge, as indicated below.

Virtually all of the known azaboranes are isostructural with the corresponding isoelectronic boranes (and carboranes). The nitrogen atoms prefer to occupy the lower coordination sites in the cluster framework in *nido*, *arachno* and other fragment species. In fact, N is found adjacent to five other cluster atoms only in *closo*-$HNB_{11}H_{11}$ (**21**).[13] While mechanistic details of the syntheses of many azaboranes are not well established, some general trends can be identified.

First, multiple-bonded nitrogen compounds such as $Me_2N{=}N{-}S$[3] and hydrazoic acid,[10] HN_3, have led to nitrogen incorporation, as illustrated by compounds **1–4** and **11–18**, though the mechanisms are quite obscure at this point. Neither route is understood on the basis of rational mechanistic considerations.

Second, the use of ionic nitrites[3,7,9] and molecular organonitriles,[19] illustrated by the syntheses of **3**, **5** and **7**, have figured prominently in the formation of the large azaboranes. Nitrites have also been used to introduce a second nitrogen into an azaborane,[26] as in **37**, and to introduce nitrogen heteroatoms into mono- and dicarbaboranes, as in **41**[29] and **38**[27] respectively.

Third, the pyrolysis of compounds and adducts having B–N bonds of various types has led to nitrogen incorporation into clusters, though no synthetic patterns have yet emerged. Perhaps the most straightforward example is the pyrolysis of the *arachno*-$B_9H_{13}(NH_3)$ which produces **7**, though in quite a modest yield. By contrast, the pyrolysis of **11**, which contains two quite different kinds of BN bonds, produces **7** quantitatively.

Fourth, a number of the above-mentined reaction examples result in boron loss at some point before or during nitrogen insertion. There are also boron growth reactions similar to those used in borane and carborane chemistry. These are relatively straightforward, as illustrated by the reaction of the *nido*-eleven atom **14** with Et_3NBH_3 to form the *closo* 12-atom **20**,[13] and similar reactions to produce **28**.

While thermal reactions often lead from *arachno* to *nido* or from *nido* to *closo* species, for example from *nido*-**7** to *closo*-**8**, there is precedence for conversion in the opposite direction, from *closo* to *nido*, in the methanolysis of *closo*-

22 to *nido*-**24**.[14]

Fifth, the syntheses of small azaboranes has been dominated by assembly from small B–N ring systems via addition of BH_3 as illustrated by the many examples of derivatives of the *nido*-NB_3 cluster, **33**.[20–22]

Diazaborane clusters have only recently been prepared, usually by metal reductions of diborylamines containing B–halogen bonds to form a variety of *nido*-N_2B_4 derivatives, **34**.[23–25] Reaction of azadiboriridenes with trialkylboranes to form other derivatives of **34**, or with $B_3H_7 \cdot L$ to form the unique *arachno*-N_2B_6 **35**. *arachno*-N_2B_3 derivatives, **36**, have been prepared from azadiboriridines by reactions with aminoboranes. These constitute the only established routes to small azaborane clusters, though there are several potential precursors to such clusters, as illustrated in Section 4.

Metal–azaborane clusters have structures similar to those of metal–borane and other metal–heteroborane clusters. Their syntheses involve ligated metal insertions into preformed azaboranes that are for the most part straightforward compared with the complexity of the syntheses of the azaboranes.

The potential applications of azaboranes range from boron neutron capture therapy (BNCT), to the boron nitride type of solid-state materials, to new compound syntheses in a variety of areas. The future determination of rational nitrogen insertion mechanisms will make these applications feasible.

REFERENCES

1. K. Wade, *Adv. Inorg. Chem. Radiochem.* **18**, 1 (1976).
2. W. N. Lipscomb, *Boron Hydrides*, Benjamin, New York, 1963.
3. W. R. Hertler, F. Klanberg and E. L. Muetterties, *Inorg. Chem.* **6**, 1696 (1967).
4. K. Base, J. Plesek, S. Hermanek, J. Huffman, P. Ragatz and R. Schaeffer, *J. Chem. Soc., Chem. Commun.* 934 (1975).
5. K. Base, F. Hanousek, J. Plesek and B. Stibr, *J. Chem. Soc., Chem. Commun.* 1162 (1981).
6. K. Base, *Coll. Czech. Chem. Commun.* **48**, 2593 (1983).
7. A. Arafat, J. Baer, J. C. Huffman and L. J. Todd, *Inorg. Chem.* **25**, 3757 (1986).
8. L. Schneider, U. Englert and P. Paetzold, *Z. Anorg. Allg. Chem.* **620**, 1191 (1994).
9. G. J. Kester, J. C. Huffman and L. J. Todd, *Inorg. Chem.* **27**, 4528 (1988).
10. J. Müller, P. Paetzold and R. Boese, *Heteroatom. Chem.* **1**, 461 (1990).
11. J. Müller, P. Paetzold, U. Englert and J. Runsink, *Chem. Ber.* **125**, 97 (1992).
12. F. Meyer, P. Paetzold and U. Englert, *Chem. Ber.* **125**, 2025 (1992).
13. J. Müller, J. Runsink and P. Paetzold, *Angew. Chem., Int. Ed. Engl.* **30**, 175 (1991).
14. F. Meyer, J. Müller, P. Paetzold and R. Boese, *Angew. Chem., Int. Ed. Engl.* **31**, 1227 (1992).
15. F. Meyer, J. Müller, M. U. Schmidt and P. Paetzold, *Inorg. Chem.* **32**, 5053 (1993).
16. L. D. Brown and W. N. Lipscomb, *Inorg. Chem.* **16**, 2989 (1977).
17. D. Hnyk, M. Bühl, P. V. Schleyer, H. V. Volden, S. Gunderson, J. Müller and P. Paetzold, *Inorg. Chem.* **32**, 2442 (1993).
18. L. Schneider, U. Englert and P. Paetzold, *Chem. Ber.* **127**, 87 (1994).
19. T. Jelinek, J. D. Kennedy and B. Stibr, *J. Chem. Soc. Chem. Commun.* 677 (1994).
20. P. Paetzold, B. Redenz-Stormanns, R. Boese, M. Bühl and P. V. Schleyer, *Angew. Chem., Int. Ed. Engl.* **29**, 1059 (1990).
21. S. Küpper, P. Paetzold and R. Boese, *Chem. Ber.* **126**, 1787 (1993).
22. M. Müller, T. Wagner, U. Englert and P. Paetzold, *Chem. Ber.* **128**, 1 (1995).
23. R. Boese, B. Kröckert and P. Paetzold, *Chem. Ber.* **120**, 1913 (1987).
24. P. Paetzold, B. Redenz-Stormans and R. Boese, *Chem. Ber.* **124**, 2435 (1991).
25. P. Paetzold and B. Redenz-Stormanns, *Inorg. Synth.* **29**, 54 (1992).
26. B. Stibr, J. D. Kennedy and T. Jelinek, *J. Chem. Soc., Chem. Commun.* 1309 (1990).
27. J. Plesek, B. Stibr and S. Hermanek, *Chem. Ind. (London)* 662 (1974).
28. J. Plesek, S. Hermanek, J. Huffman, P. Ragatz and R. Schaeffer, *J. Chem. Soc., Chem. Commun.* 935 (1975).
29. J. Holub, T. Zelinek, J. Plesek, B. Stibr, S. Hermanek and J. D. Kennedy, *J. Chem. Soc., Chem. Commun.* 1389 (1991).
30. T. Jelinek, J. D. Kennedy and B. Stibr, *J. Chem. Soc., Chem. Commun.* 1628 (1993).
31. K. Base, A. Petrina, B. Stibr, V. Petricek, K. Maly, A. Linek and I. A. Zakharova, *Chem. Ind. (London)* 212 (1979).
32. K. Base, B. Stibr and I. Zakharova, *Synth. React. Inorg. Metal. Org. Chem.* **10**, 509 (1980).
33. K. Base, M. Brown, B. Stibr, X. L. R. Fontaine, N. N. Greenwood, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.* 1240 (1988).
34. K. Nestor, X. L. R. Fontaine, J. D. Kennedy, M. Thornton-Pett, K. Base and B. Stibr, *Collect. Czech. Chem. Commun.* **56**, 1607 (1991).
35. H.-P. Hansen, J. Müller, U. Englert and P. Paetzold, *Angew. Chem., Int. Ed. Engl.* **30**, 1377 (1991).
36. P. Paetzold, J. Muller, F. Meyer, H. P. Hanson and L. Schneider, *Pure Appl. Chem.* **66**, 255 (1994).

37. R. Lewin, P. G. Simpson and W. N. Lipscomb, *J. Chem. Phys.* **39**, 1352 (1963).
38. D. F. Gaines and J. C. Kunz, *Inorg. Chem.* **27**, 1839 (1987).
39. G. Geisberger, G. Linte and H. Nöth, *Chem. Ber.* **125**, 2691 (1992).
40. D. F. Gaines and R. W. McGaff, *Inorg. Chem.* **32**, 2612 (1993).