APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 199–208 (1996)

REVIEW

The Synthesis and Thermal Decomposition Reactions of Compounds Containing the Silicon–Nitrogen–Boron Bond Linkage

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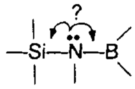
INTRODUCTION

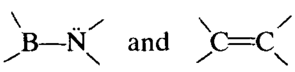
The chemistry of compounds containing Si–N–B bonds (silylaminoboranes) has been of interest for over four decades, and appears to be undergoing something of a revival. As is frequently the case, the emphasis has shifted from academic curiosity to practical application. More specifically, these compounds are undergoing active re-examination as potential precursors to macromolecules of importance to materials science (boron nitride and related ceramics, polymers, etc.). In this article we hope to provide some historical perspective, review the applicable literature, and describe some new directions relevant to this area of research.

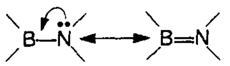
Structure and bonding

Much of the initial interest in silylaminoboranes concerned the nature of the covalent bonding — specifically, the fate of the nitrogen lone pair in compounds containing Si–N and/or B–N bonds:



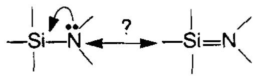
As early as 1948, Wiberg suggested correlation between the isoelectronic moieties.[1] The two systems do in fact exhibit marked similarities in bond angles, bond lengths and the planarity of their skeletal frameworks. A simple example is Me_2BNMe_2, which shows a strong structural relationship to 2,3-dimethylbutene, including planarity about the nitrogen.[2] This is consistent with delocalization of the lone pair into the 'empty' p-orbital of boron, and suggests an effective hybridization of sp^2 about *both* the boron and nitrogen atoms.





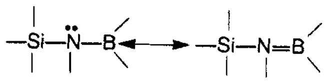
More complex examples include the borazines (see below); hexagonal boron nitride, with a crystalline arrangement reminiscent of graphite;[3] and the calculated structures of B–N-substituted fullerenes.[4, 5]

The notion that similar interactions occur within silicon–nitrogen compounds has been more controversial, since in that case the involvement of the 3d-orbitals of silicon would be required.[6]



The planarity, 120° bond angles and short Si–N bond distances in trisilylamine, $(H_3Si)_3N$, have frequently been cited as evidence for the delocalization of nitrogen's 'non-bonded' electron pair onto silicon.[7]

From these perspectives, then, the question of electron distribution in Si–N–B compounds is intriguing, and spurred early interest in such species. The evidence accumulated so far suggests that silicon cannot effectively compete with boron for the nitrogen lone pair. That is, although a silicon-containing group may exert a steric effect within an aminoborne, it appears to have little influence on the electronic distribution; dative $(p\rightarrow p)\pi$ bonding between nitrogen and boron is observed.



CCC 0268–2605/96/030199–10

Received 10 May 1995
Accepted 14 July 1995

This conclusion has arisen from several types of studies, including dynamic NMR analysis.[8]

SYNTHETIC PATHWAYS TO SILYLAMINOBORANES

The formation of the Si–N–B bond linkage has most often been accomplished by either of two general methods: so-called *cleavage* reactions, in which a silicon–nitrogen bond is ruptured by a covalent halide leading to the formation of some halosilane as a side product; and *dehydrohalogenation*, in which the elements of a hydrogen halide are eliminated. We include under dehydrohalogenation both one-step syntheses (typically utilizing an agent such as Et_3N) and related, multiple-step processes such as metallation (see below). Less commonly, *transamination* (the replacement of one amino group by another, with elimination of a neutral amine) and *addition* to low-coordinate boron–nitrogen species have been employed.

Cleavage reactions

The synthesis of the first acyclic silylaminoboranes were reported by Burg and Kulijian in 1950.[9] This was accomplished via the reaction

$$(H_3Si)_2NR + BCl_3 \rightarrow H_3SiN(R)BCl_2 + H_3SiCl \quad R = Me, SiH_3 \qquad [1]$$

It was subsequently realized that Si–N bonds are reactive toward a variety of polar covalent moieties including H—Cl,[10] P—Cl,[11] As—Cl,[12] Sn—Cl,[13] S(O)Cl[14] and even C(O)Cl.[15] For reactions of silylamines with haloboranes, the nature of the products can frequently be controlled by the choice of limiting reagent (Eqns 2–4).[16]

$$(Me_3Si)_2NMe + PhBBr_2 \rightarrow Me_3SiN(Me)B(Ph)Br + Me_3SiBr \qquad [2]$$

$$2(Me_3Si)_2NMe + PhBBr_2 \rightarrow [Me_3SiN(Me)]_2BPh + 2Me_3SiBr \qquad [3]$$

$$(Me_3Si)_2NMe + 2PhBBr_2 \rightarrow MeN[B(Ph)Br]_2 + 2Me_3SiBr \qquad [4]$$

Trimethylsilazide has proven to be a useful reagent for the formation of B–N bonds via cleavage pathways (Eqn [5]).[17,18]

$$iPr_2NB(Cl)P(SiMe_3)_2 + Me_3SiN_3 \rightarrow iPr_2NB(N_3)P(SiMe_3)_2 + Me_3SiCl \qquad [5]$$

Paine and co-workers have applied this approach to the polymerization of borazine derivatives (see below).[19]

Steric effects

Cleavage reactions may be inhibited by steric bulk. For example, reaction [6] is rapid well

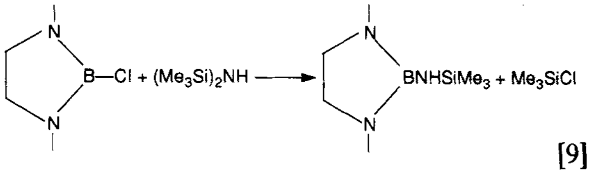
$$Me_3SiNHR + BCl_3 \rightarrow RNHBCl_2 + Me_3SiCl \qquad [6]$$

below room temperature when R = Me or Et; it is slower when R = t-Bu or $SiMe_3$, and requires heating for R = $tBuMe_2Si$ (in several of these cases the 'product' $RNHBCl_2$ is thermally unstable, undergoing an elimination reaction to produce a borazine).[20] Kinetic factors also play a role in reactions of boron trichloride with the hindered tris(trimethylsilyl)amine: in that case the products depend upon the reaction temperature (Eqns [7], [8]).[10]

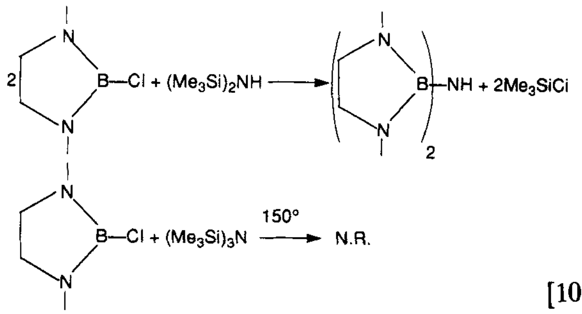
$$(Me_3Si)_3N + BCl_3 \xrightarrow{25\,^{\circ}C} (Me_3Si)_2N\text{—}BCl_2 + Me_3SiCl \qquad [7]$$

$$(Me_3Si)_3N + BCl_3 \xrightarrow{150\,^{\circ}C} (Me_3Si)_2NSiMe_2Cl + MeBCl_2 \qquad [8]$$

Similarly, the cyclic chloroborane $[CH_2N(Me)]_2BCl$ undergoes cleavage with $(Me_3Si)_2NH$ (Eqns [9], [10]), but not with the more hindered $(Me_3Si)_3N$.[21,22]



[9]

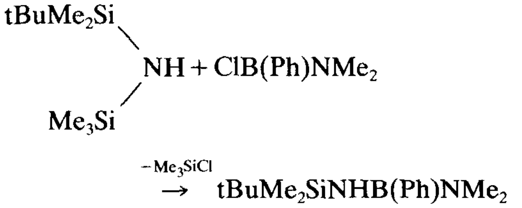


[10]

An interesting application of cleavage reactions involves the coupling of borazine rings. Niedenzu and co-workers report that both bicyclic compounds and polymers can be isolated from such reactions.[23]

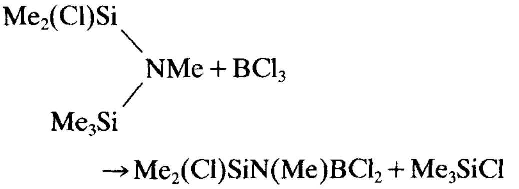
Selective cleavage as a synthetic tool

Selective cleavage reactions (for our purposes, the rupture of an Si–N linkage in preference over another labile bond to nitrogen) are sometimes possible. For unsymmetrical disilylamines, the observed reaction typically occurs at the less sterically hindered site. An example is given by Eqn [11].[24]



$$\mathrm{(tBuMe_2Si)(Me_3Si)NH + ClB(Ph)NMe_2 \xrightarrow{-Me_3SiCl} tBuMe_2SiNHB(Ph)NMe_2} \qquad [11]$$

Le Chatelier's Principle probably plays a role in such situations. Me_3SiCl is the most volatile compound in the system described by Eqn [11], and heating the reaction mixture causes its evolution as a gas. This idea also provides rationalization for a selective cleavage reaction (Eqn [12]) reported by Barlos and Nöth.[25]



$$\mathrm{(Me_2(Cl)Si)(Me_3Si)NMe + BCl_3 \rightarrow Me_2(Cl)SiN(Me)BCl_2 + Me_3SiCl} \qquad [12]$$

The greater volatility of Me_3SiCl (b.p. 57 °C) presumably causes that species to be produced rather than Me_2SiCl_2 (b.p. 71 °C).

However, the situation is not always straightforward (see Eqn [8]). Neilson has observed H–Cl exchange instead of Si–N cleavage (Eqn [13]).[26]

$$\mathrm{(Me_3Si)_2NSi(H)Me_2 + BCl_3 \rightarrow (Me_3Si)_2NSi(Cl)Me_2 + HBCl_2} \qquad [13]$$

In certain mixed systems (e.g. those containing both silicon–nitrogen and tin–nitrogen bonds), the weaker bond may be cleaved preferentially (Eqn [14]).[13]

$$\mathrm{Me_3SiN(SnMe_3)_2 + BCl_3 \rightarrow Me_3SiN(SnMe_3)BCl_2 + Me_3SnCl} \qquad [14]$$

In this regard, silicon–nitrogen bonds are more labile than boron–nitrogen (Eqns [15], [16]). This facilitates the conversion of Si–N–B to B–N–B compounds (diborylamines).[27,28]

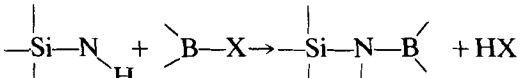
$$\mathrm{Me_3SiNHBR_2 + R_2BCl \rightarrow (R_2B)_2NH + Me_3SiCl}$$

$$\mathrm{R = nPr, nBu}$$

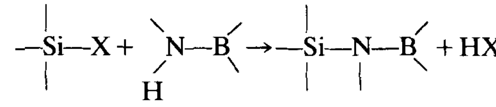
$$\mathrm{(Me_3Si)_2NH + 2Me_2NB(R)Cl \rightarrow [Me_2NB(R)]_2NH + 2Me_3SiCl} \qquad [16]$$

Dehydrohalogenation

Dehydrohalogenation reactions involve the chemically or thermally induced elimination of a hydrogen halide. When applied to the formation of Si–N–B connections, a typical reaction follows the general pattern of Eqn [17] or less, commonly, of Eqn [18].



$$\mathrm{{-}Si{-}N(H){-} + {>}B{-}X \rightarrow {-}Si{-}N{-}B{<} + HX} \qquad [17]$$



$$\mathrm{{-}Si{-}X + HN{-}B{<} \rightarrow {-}Si{-}N{-}B{<} + HX} \qquad [18]$$

Tertiary amines are useful agents for promoting dehydrohalogenation. Triethylamine has frequently been used for this purpose, as exemplified in Eqns [19] and [20].[10,29,30]

$$\mathrm{(Me_3Si)_2NH + Et_3N{\cdot}BCl_3 \rightarrow (Me_3Si)_2NBCl_2 + Et_3NH^+Cl^-} \qquad [19]$$

$$\mathrm{(HNBCl)_3 + 3(Me_3Si)_2NH + 3Et_3N \rightarrow [HNBN(SiMe_3)_2]_3 + 3Et_3NH^+Cl^-} \qquad [20]$$

Paciorek and co-workers used this approach to prepare some long-chain, acyclic Si–N–B frameworks (Eqn [21]).[30]

$$\mathrm{(Me_3Si)_2NB(NHSiMe_3)Cl + (Me_3Si)_2NH + Et_3N \rightarrow [(Me_3Si)_2N]_2BNHSiMe_3 + Et_3NH^+Cl^-} \qquad [21]$$

Aminolysis reactions

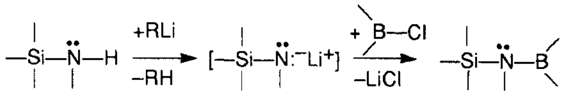
A variation involves the use of excess reactant amine. The stoichiometry of 2 molar equivalents of amine per mole of chloroborane converts the hydrogen halide side product to an ammonium salt, often as a precipitate from non-polar solution. This approach is most successful with NH_3 and small primary amines. It has been exploited for the synthesis of a number of silylaminoboranes containing an —NH_2 group.[20, 31, 32]

$$\underset{R = Ph,\ NMe_2}{tBuMe_2SiN(H)B(R)Cl + 2NH_3} \xrightarrow{-78\,^{\circ}C} tBuMe_2SiN(H)B(R)NH_2 + NH_4Cl \quad [22]$$

$$\underset{R = Ph,\ NHSiMe_3}{(Me_3Si)_2NB(R)Cl + 2NH_3} \rightarrow (Me_3Si)_2NB(R)NH_2 + NH_4Cl \quad [23]$$

Metallation

Aminolysis reactions may fail when the amine is a poor nucleophile (such as a silylamine or an aniline derivative). In such cases *metallation* reactions (typically employing Grignard or alkyllithium reagents) (Eqn [24]) often succeed.



[24]

These are convenient, 'one-pot' syntheses. When n-butyl-lithium is used, the lithium amide is formed upon the addition of the organometallic reagent to a stirred solution of silylamine in some non-polar solvent, such as hexane or diethyl ether. This is followed by the controlled addition of the chloroborane. The progress of the reaction can often be monitored by the precipitation of LiCl from the solution.

Several highly-hindered bis- and tris-(silylamino)boranes were obtained in this manner (Eqns [25], [26]), as well as a series of novel diborylamines (Eqn [27]).[20, 31]

$$2tBuMe_2SiNHLi + PhBCl_2 \rightarrow (tBuMe_2SiNH)_2BPh + 2LiCl \quad [25]$$

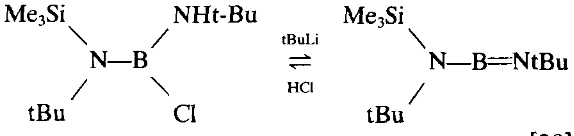
$$3tBuMe_2SiNHLi + BCl_3 \rightarrow (tBuMe_2SiNH)_3B + 3LiCl \quad [26]$$

$$(Me_3Si)_2NB(tBu)NH_2 \xrightarrow[2.\ ClBXY]{1.\ nBuLi} (Me_3Si)_2NB(tBu)NHBXY \quad [27]$$

$X, Y = NMe_2, Ph$, etc.

Niedenzu and co-workers used metallation for the silylation of borazine rings.[33]

Metallation reactions are generally not reversible. An interesting exception involves the interconversion of an aminoborane and an amino iminoborane (Eqn [28]).[34, 35]



[28]

Paine has discussed some limits of, and alternatives to, metallation reactions.[36]

Transamination reactions

In a transamination reaction one amino group replaces another, with the reaction proceeding to form the more volatile free amine. It has long been recognized that steric factors play an important role in this kind of reaction.[37] The first application of this method to silylaminoboranes was by Alsobrook *et al* (Eqn [29]).[38]

$$(Me_2N)_2B{-}B(NMe_2)_2 + 4Et_3SiNH_2 \rightarrow (Et_3SiNH)_2B{-}B(NHSiEt_3)_2 + 4Me_2NH \quad [29]$$

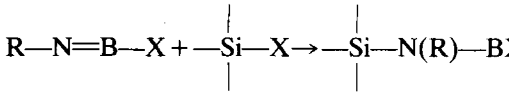
Reactions of this genre are probably the reason why compounds having the general formula $RB(NH_2)_2$ are rare. For example, Paciorek's group reported the synthesis and purification of $(Me_3Si)_2NB(NH_2)_2$.[30a] However, the product mixture also contained $[(Me_3Si)_2NB(NH_2)]_2NH$, presumably formed by the transamination process

$$2(Me_3Si)_2NB(NH_2)_2 \rightarrow [(Me_3Si)_2NB(NH_2)]_2NH + NH_3 \quad [30]$$

More recently, efforts to prepare pre-ceramic polymers by transamination were described.[39]

Addition reactions

A very different method for generating the Si–N–B linkage involves the addition of some silicon-containing moiety to a low-coordinate boron–nitrogen compound, as for example according to the general equation [31].



$$R{-}N{=}B{-}X + {-}Si{-}X \rightarrow {-}Si{-}N(R){-}BX_2 \qquad [31]$$

Iminoboranes

A relatively new area of boron–nitrogen chemistry involves low-coordinate iminoboranes, RNBX, and aminoiminoboranes, RNBNR'$_2$. The research groups headed by Paetzold and Nöth have led this effort.[35, 40, 41] Iminoboranes may be represented by the resonance structures

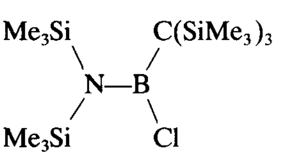
$$R{-}\ddot{N}{=}B{-}X \leftrightarrow R{-}N{\equiv}B{-}X$$

These species are readily identified by IR-spectroscopy. The B—N stretching absorption is located at or above 1785 cm^{-1} (1900–2000 cm^{-1} is typical), much higher than for an aminoborane.[35] As would be expected, the B–N bond distances are quite short.[42, 43]

Iminoboranes exhibit a strong tendency to oligomerize to cyclic products, especially borazines (see below). ΔH for reaction [32] is calculated to be –194 kcal mol^{-1} (–812 kJ mol^{-1}).[44] As a result, only those iminoboranes having sterically large groups tend to be isolable at room temperature.

$$3HNBH \rightarrow (HNBH)_3 \qquad [32]$$

Most of the known iminoboranes have been prepared in vacuum pyrolysis experiments. An example is $Me_3SiN{=}B{-}C(SiMe_3)_3$, which was obtained by the elimination of Me_3SiCl from $(Me_3Si)_2NB(Cl)C(SiMe_3)_3$ above 400 °C (Eqn [33]).[45]



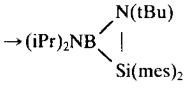
$$\rightarrow Me_3SiN{=}B{-}C(SiMe_3)_3 + Me_3SiCl \qquad [33]$$

Not surprisingly, compounds of this type readily undergo addition reactions (Eqn [34]) with a wide variety of polar covalent compounds.[35, 40]

$$R{-}N{=}B{-}X + EY \rightarrow E(R)N{-}BXY \qquad [34]$$

Some of the silylaminoboranes prepared in this manner include: $(Me_3Si)_2N{-}B(iPr)NHiPr$, from the addition of $(Me_3Si)_2NH$ to $iPrN{=}B(iPr)$;[34] $Me_3Si(tBu)N{-}B(tBu)N_3$, from an azidosilane;[45] $Me_3Si(tBu)N{-}B(NHiPr)tmp$ (tmp = tetramethylpiperidine), from a silylamine;[35] several compounds formulated $Me_xCl_{3-x}Si(tBu)N{-}B(H)tmp$, by hydrosilylation;[35] the salt $Me_3Si(tBu)N{-}B(tmp)^+I^-$, from Me_3SiI;[35] and a number of diborylamines having the general formula $Me_3Si(tBu)N{-}B(Cl)N(tBu)BR_2$, from dialkylchloroboranes.[34] Another novel approach is the addition of silylenes (SiR_2) to iminoboranes to produce three, four, or six-membered rings.[46] This is exemplified by reaction [35].

$$(iPr)_2NB{=}NtBu + {:}Si(mes)_2$$



[35]

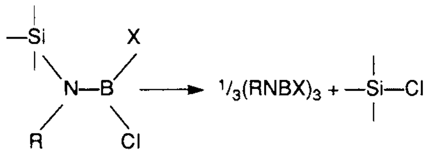
mes = 2,4,6—$Me_3C_6H_2$

THERMAL DECOMPOSITION REACTIONS

As was noted earlier, the thermochemistry of Si–N–B-bonded compounds has been studied extensively. The earliest work, frequently utilizing sealed tube reactors, has been reviewed.[47]

Chlorosilane elimination leading to cyclization

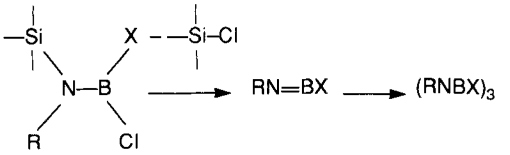
For halogen-containing silylaminoboranes, the best-known thermal degradation pathway involves the elimination of some small molecule such as Me_3SiCl. In the absence of prohibitive steric effects the boron-containing product is usually a borazine, as for example in Eqn [36].



[36]

A wide variety of substituted borazines have been produced in this manner.[48]

Several plausible mechanisms can be suggested for reactions of this type. One possibility begins with intramolecular elimination of the chlorosilane to give an iminoborane, which may or may not be isolable (Eqn [37]).

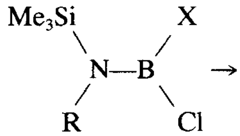


[37]

Alternatively, the initial step of the reaction might be intermolecular, forming longer-chain species which subsequently undergo cyclization. Paetzold has summarized data in support of these two pathways, and suggests that certain related reactions may occur through a concerted cycloaddition process.[40] Yet another possibility involves the formation of a borinium cation.[49]

Steric effects

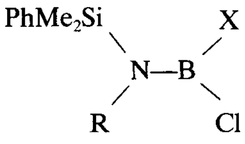
In general, the elimination of chlorosilane from a chloro(silylamino)borane tends to become less facile as the steric demands of the substituents increase. Such steric effects have been observed at the nitrogen, silicon and boron atoms. Examples are provided by reactions conforming to the general equation [38].



$$\rightarrow 1/3(\mathrm{RNBX})_3+\mathrm{Me_3SiCl} \qquad [38]$$

This transformation occurs well below room temperature when X = Cl and R = H or Me, but compounds having larger groups (iPr, tBu) are stable at room temperature.[50] The same applies when X = Ph. However, analogues having X = $\mathrm{NMe_2}$ appear to have generally higher thermal stability.[50] Parallel results have been obtained for aminoboranes containing other silyl groups, including the $\mathrm{tBuMe_2Si}$— series.[20]

Compounds formulated as



(X = Cl, Ph; R = Me, Et, iPr, Bz and $\mathrm{PhMe_2Si}$) have recently been studied in our laboratories.[51] We find that the phenyl-sbustituted compounds behave in the expected manner. They are converted to the borazines $(\mathrm{RNBPh})_3$ in high yield upon heating to about 100 °C; the process can either be carried out in a sealed tube, or monitored instrumentally by thermogravimetric analysis (TGA). However, the thermal behavior seems to be less predictable for the X = Cl series. This may be due to the evaporation of small amounts of reagent during the TGA experiments.[51]

Very large substituents on the nitrogen may lead to tetramers (i.e. the eight-membered borazocine ring system). For example, the compound $(\mathrm{tBuNBCl})_4$ has been obtained via both dehydrohalogenation and pyrolysis (Eqns [39], [40]).[52, 53]

$$\mathrm{tBuNH_2{\cdot}BCl_3}+2\mathrm{Et_3N} \rightarrow 1/4(\mathrm{tBuNBCl})_4+2\mathrm{Et_3NH^+Cl^-} \qquad [39]$$

$$\mathrm{Me_3Si(tBu)NBCl_2} \xrightarrow{150\,^\circ\mathrm{C}} 1/4(\mathrm{tBuNBCl})_4+\mathrm{Me_3SiCl} \qquad [40]$$

More recently, other borazocines have been obtained from thermal elimination reactions of bulky silicon-containing compounds (Eqn [41]).[34, 35]

$$2\mathrm{Me_3Si(tBu)N{-}B(R)N(tBu)B(R)X} \xrightarrow{-2\mathrm{Me_3SiX}} (\mathrm{tBuNBR})_4 \qquad [41]$$

$$\mathrm{R=Me,\ X=Cl;\ R=X=OMe}$$

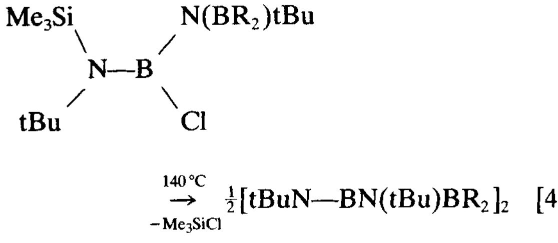
Which ring system is obtained depends in part on the atom positioned α to the nitrogen. For example, there appears to be a significant steric difference between t-butyl (with a relatively short N–C bond) and silicon-containing groups (with a longer N–Si connection); contrast Eqn [38] (trimer formation) with Eqns [39]–[41] (tetramers). Differences in thermal behavior between C- and Si-substituted amines have been observed for other systems; see for example Ref. 54. Also, the decomposition pathways for several t-butyldimethysilyl-substituted aminoboranes lead to borazines (either according to Eqn [42], or less directly via Eqn [43]), rather than borazocines.[20]

$$\mathrm{tBuMe_2SiN(H)BXCl} \xrightarrow[\substack{\mathrm{X=Cl},\ 25\,^\circ\mathrm{C}\\ \mathrm{X=Ph},\ 85\,^\circ\mathrm{C}}]{} (\mathrm{HNBX})_3+\mathrm{tBuMe_2SiCl} \qquad [42]$$

$$2\mathrm{tBuMe_2SiN(H)B(Cl)NMe_2} \rightarrow (\mathrm{HNBCl})_3+\mathrm{tBuMe_2SiCl}+\mathrm{tBuMe_2SiN(H)B(NMe_2)_2} \qquad [43]$$

It is believed that Eqn [43] actually represents a two-stage process — a redistribution reaction of $tBuMe_2SiN(H)B(Cl)NMe_2$ to form $tBuMe_2SiN(H)B(NMe_2)_2 + tBuMe_2SiN(H)BCl_2$, followed by thermal decomposition of the dichloro compound according to Eqn [42].[20]

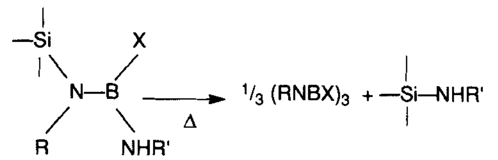
For cases involving steric hindrance at *both* boron and nitrogen, four-membered rings (diazadiboretanes) may be observed (Eqn [44]).[34]



$$(Me_3Si)(tBu)N{-}B(Cl)N(BR_2)tBu \xrightarrow[-Me_3SiCl]{140\,°C} \tfrac{1}{2}[tBuN{-}BN(tBu)BR_2]_2$$ [44]

It is sometimes possible to convert one ring system into another. For example, Paetzold has discussed a number of dimer–trimer and dimer-tetramer interconversions.[40]

Elimination/cyclization processes of this general type do not absolutely require a halogen; other good leaving groups may serve as well. Borazines have been obtained from the thermal loss of silylamines (Eqn [45]).

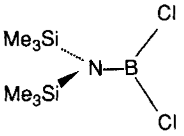


[45]

Thus heating the compound $tBuMe_2SiN(Me)B(Ph)NH_2$ to 190 °C for 10 h produced *B*-triphenylborazine in nearly quantitative yield.[20]

Another option is to vary the substituents on silicon. Here again, increasing steric bulk generally leads to increased thermal stability. For example, the decomposition of $(R_3Si)_2N{-}BCl_2$ ($R = H$) occurs at lower temperature than when $R = Me$; the latter is stable above 100 °C. [Although the compound $(Me_3Si)_2N{-}BCl_2$ was originally believed to decompose in refluxing xylene, it was more recently reported that a temperature of 150 °C is required.[55,56]] The more hindered $tBuMe_2Si(Me_3Si)NBCl_2$ is stable to at least 210 °C.[20]

It has been suggested that the comparatively high thermal stabilities of disilylaminoboranes derive from their molecular conformations.[32] Unlike most aminoboranes, $(Me_3Si)_2NBCl_2$ (**1**) is non-planar: the trimethylsilyl groups are rotated by 90° from the molecular plane, providing steric protection from intermolecular attack.



There is evidence that this structural feature is common to other disilyl-substituted aminoboranes.[32]

Thermal degradation leading to macromolecular species

Much study has recently been devoted to the thermal conversion of silylaminoboranes to polymers and/or to boron nitride and related ceramics, and some excellent summaries have appeared.[19,36,56–61]

Boron nitride exists in several crystalline forms. The thermodynamically stable state is hexagonal BN (h-BN or α-BN), a structural analog of graphite. It is a low-density ceramic material, transparent when pure, with good resistance to oxidation. Like graphite, its layered structure causes h-BN to have anisotropic mechanical and electrical properties. It has most often been used as a solid lubricant.

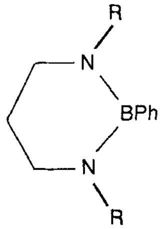
A cubic form (c-BN or β-BN), structurally related to the diamond lattice, is also known. It has traditionally been manufactured by high-temperature/high-pressure processes, and has applications as an abrasive. The industrial literature also refers to pyrolytic BN, made by chemical vapor deposition techniques. Its most common use is for high-temperature crucibles.[62]

Hexagonal BN can be synthesized by a variety of routes. On an industrial scale it has traditionally been made by 'hot-pressing' ammonia/boric oxide or urea/boric acid mixtures at 900–1000 °C. However, such preparations yield materials of insufficient purity for certain purposes. Moreover, they produce powders, while certain applications require fibers or coatings.[56–58] Partly because of this, a number of chemical systems including silylaminoboranes are being examined as thermal precursors to BN.

In principle, appropriately constructed silylaminoboranes might be converted to BN either through acyclic or cyclic intermediaries. For example, the overall conversion of Eqn [46] might conceivably involve long-chain acyclic compounds, iminoboranes, borazines or other species (see above).

$$(Me_3Si)_2NBCl_2 \rightarrow BN + 2Me_3SiCl \qquad [46]$$

Logical acyclic precursors include silicon-containing bisaminoboranes (Si–N–B–N) and diborylamines (–Si–N–B–N–B). For example, the products of Eqns [21] and [27] can be viewed as potential precursors either to BN, or to polymers having boron–nitrogen frameworks.[30,31] Another promising series of compounds contains the 1,3,2-diazaboracyclohexane ring system (**2**). It was suggested that these species might lead to linear polymers having boron–nitrogen backbones; such species are analogues of polyacetylenes.[59,63]



(R,R' = H, SiMe$_3$, BXY, etc.)

Working from borazines, a number of approaches have been reported. Here again, though, a 'simple' conversion such as that represented by Eqn [47] is not necessarily simple either mechanistically or in practice, although it has been accomplished for the parent borazine (R = X = H).[64,65]

$$1/3(RNBX)_3 \xrightarrow{-RX} BN \qquad [47]$$

Success has been achieved using borazine derivatives as well. For example, it has long been known that *B*-triaminoborazines eliminate RNH_2 upon heating.[66] This reaction was recently re-examined. It was found that two different aminoborazines eliminate amines upon heating, producing residues of hexagonal BN (Eqn [48]).[19,39,67] However, Paciorek *et al.* report a tendency for certain reactions of this type to be incomplete, leading to impure products. For example, $(H_2NBNPh)_3$ undergoes degradation below 200 °C, but the residue contains carbon even when the decomposition is carried out at 1000 °C.[56]

$$\underset{R = H,\, Me}{(HNBNHR)_3 \rightarrow 3BN + 3RNH_2} \qquad [48]$$

The research groups headed by Paine and Paciorek have made extensive studies of the condensation reactions of borazine rings, promoted either thermally or by reagents such as silylamines. Special attention has been given to the B-trichloroborazine/hexamethyldisilazane combination:[19,56,57,68–70]

$$(HNBCl)_3 + (Me_3Si)_2NH \xrightarrow{-2Me_3SiCl} \text{polymers} \qquad [49]$$

When $(HNBCl)_3$ is used, the potential exists for what Paine has described as 'three-point' polymers — that is, each of the three borons in a given ring becomes connected to borons of adjacent rings through bridging nitrogens. This is somewhat akin to cross-linking in traditional organic polymers. For unsymmetrical borazines in which one chlorine is replaced with an alkyl group ($H_3N_3B_3RCl_2$), this is not possible; the result is a 'two-point' (essentially linear) polymer, with increased solubility.[19]

Those interested in the processing of materials of this type are referred to recent reviews by Paine.[19,57,58,61]

CONCLUSIONS

In this report we have summarized both the early and more recent efforts towards understanding the thermal decomposition pathways characteristic of species containing the silicon–nitrogen–boron bond linkage. A number of areas can be suggested for future research, as follows.

Synthesis of composite materials

As was pointed out by Paine and Narula,[58] the choice of ceramic material for a given application has frequently been based on one dominant property (mechanical strength, electrical conductivity, etc.). However, there is growing need for multipurpose materials having some desired combination of attributes. This often requires a chemical mixture, e.g. boron nitride intimately mixed with or coated onto the surface of a second compound. The pursuit of synthetic methodologies to produce such mixtures has already begun.[71]

Alternative forms of boron nitride

A number of new uses for high-purity h-BN have recently been developed.[72] Some of these require physical states other than powders. Thus, thermal degradation reactions leading to BN as a fiber, foam, etc., are under study. The groups headed by Paine, Paciorek and Sneddon have already reported significant progress in this area.[19,60,61,64,70,73]

Thermal precursors to linear polymers

Another area of interest concerns linear polymers having frameworks composed of alternating boron and nitrogen atoms. These polyacetylene analogs have proven to be elusive, probably because of the high stabilities of cyclic alternatives, especially borazines. Among others, Neilson and co-workers have reported acyclic compounds which are potential precursors to linear polymers.[59,63] It should also be possible to design iminoboranes or amino imino boranes for which cyclization is impeded; such species might well undergo thermal decomposition to produce polymers.

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