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BORON–NITROGEN COMPOUNDS, ORGANIC

The first attempt to systematize the field of BN-containing organic compounds was made in 1948 (1, 2) upon recognition of the isoelectronic relationship between B–N and C–C moieties. There are four classes of organic B–N compounds. (*1*) Amine boranes, $R_3B–NR'_3$, have the nitrogen atom which supplies both electrons in the B–N bond; these are isoelectronic with alkanes, $R_3C–CR'_3$. (*2*) Aminoboranes, $R_2B{=}NR'_2$, have a covalent bond between B and N. Here, the hybridization of both boron and nitrogen is sp^2 resulting in a planar $R_2BNR'_2$ unit capable of a π-interaction between nitrogen's free-electron pair and the empty *p* orbital on boron; these are isoelectronic with alkenes, $R_2C{=}CR'_2$. (*3*) Iminoboranes, $RB{\equiv}NR'$, have a two-coordinate boron interacting with the nitrogen via a triple bond; these are isoelectronic with alkynes, $RC{\equiv}CR$. (*4*) Borazines, $(–RB–NR'–)_x$, are cyclic compounds containing alternating tricoordinate boron and nitrogen atoms. These compounds are nearly planar and have B–N bond lengths that are substantially shorter than those for single bonds, indicating partial double-bond character. Borazines are isoelectronic with benzene, C_6H_6. There are also B–N ring systems of other sizes. Although these compounds are isoelectronic and nearly isostructural with conventional organic species, properties and reactivity patterns are considerably different. The primary reason for this dissimilarity is the polar nature of the B–N bond.

Reviews covering the literature through 1970 for all areas except iminoboranes (3) and through 1984 (4) are available.

1. Amine Boranes

Amine–borane adducts have the general formula $R_3N{\cdot}BX_3$ where R = H, alkyl, etc, and X = alkyl, H, halogen, etc. These compounds, characterized by a coordinate covalent bond between boron and nitrogen, form a class of reducing agents having a broad spectrum of reduction potentials (5).

1.1. Synthesis

An efficient, convenient synthesis for the preparation of ammonia borane [13774-81-7], the inorganic analogue of ethane, is shown in equation 1 where THF is tetrahydrofuran (6).

$$(NH_4)_2\,CO_3 + 2\;NaBH_4 \xrightarrow{\text{anhydrous THF}} 2\;H_3N{\cdot}BH_3 + 2\;H_2 + Na_2CO_3 \qquad (1)$$

A synthesis using liquid ammonia and $NaBH_4$ has also been described (7). Both methylamine borane [1722-33-4], $(CH_3)H_2N{\cdot}BH_3$, and ethylamine borane [15860-41-0], $(C_2H_5)H_2N{\cdot}BH_3$, can also be prepared in this manner.

Dimethylamine borane [74-94-2], important as a reducing agent in electroless plating (qv) (8), can be synthesized as shown in equation 2 (9).

$$(CH_3)_2\,NH_2Cl + NaBH_4 \xrightarrow[RT]{ether} (CH_3)_2\,HN{\cdot}BH_3 + H_2 + NaCl \qquad (2)$$

Pyridine borane [110-51-0] can be prepared using benchtop techniques via

$$C_5H_5N + THF{\cdot}BH_3 \xrightarrow[0^\circ C]{THF} C_5H_5{\cdot}BH_3 \qquad (3)$$

excess

The synthesis of a number of other amine–borane complexes from $THF{\cdot}BH_3$ [14044-65-6] have also been described (10).

Using a procedure similar to the synthesis of amine boranes, a series of amine cyanoboranes where the amine = $(CH_3)_3N$, $(CH_3)_2NH$, $(CH_3)NH_2$, C_5H_5N, or $(C_6H_5)NH_2$ have been prepared as shown in equation 4 (11).

$$NaBH_3CN + amine - HCl \xrightarrow[65^\circ C]{THF} amine - BH_2CN + H_2 + NaCl \qquad (4)$$

Trimethylamine carboxyborane can be synthesized from the cyanoborane precursor [30353-61-8] according to equations 5 and 6 (12).

$$(CH_3)_3\,N{\cdot}BH_2CN + (C_2H_5)_3\,O^+BF_4 \xrightarrow[\Delta]{CH_2Cl_2} (CH_3)_3\,N{\cdot}BH_2CN\,(C_2H_5)^+\,BF^-{}_4 + (C_2H_5)_2\,O \qquad (5)$$

$$(CH_3)_3\,N{\cdot}BH_2CN\,(C_2H_5)^+\,BF^-{}_4 + 2\,H_2O \longrightarrow (CH_3)_3\,N{\cdot}BH_2COOH + (C_2H_5)\,NH_3^+BF^-{}_4 \qquad (6)$$

This carboxyborane can undergo an amine exchange reaction with liquid ammonia (eq. 7) to yield the boron analogue of glycine, the simplest alpha-amino acid (13). There has been a great deal of work on the pharmacological activity of these amino acid analogues (14).

$$(CH_3)_3\,N{\cdot}BH_2COOH + NH_3 \longrightarrow H_3N{\cdot}BH_2COOH + N\,(CH_3)_3 \qquad (7)$$

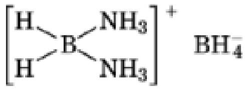
Compounds of the type $L{\cdot}BH_2X$ can be prepared by the reaction of the appropriate amine borane and hydrogen halides or halogens. The synthesis of the trimethylamine iodoborane [25741-81-5] adduct (eq. 8) yields a precursor for the preparation of the trimethylamine isocyanoborane [60045-36-5] adduct as shown in equation 9 (15).

$$2\,(CH_3)_3\,N{\cdot}BH_3 + I_2 \longrightarrow 2\,(CH_3)_3\,N{\cdot}BH_2I + H_2 \qquad (8)$$

$$(CH_3)_3\,N{\cdot}BH_2I \xrightarrow{AgCN,\ H_2S} (CH_3)_3\,N{\cdot}BH_2\,(NC) + AgI \qquad (9)$$

1.2. Amine–Boronium Cations

The most extensively studied boronium cation is the diammoniate of diborane [23777-63-1] (16–18).



In this compound, synthesized in the low temperature reaction between diborane and excess ammonia, the cationic boron is coordinatively saturated in a tetrahedral environment. More recently, cations having boron in tricoordinate or dicoordinate environments have been observed. These cationic species, called borenium and borinum ions, respectively, have been reviewed (19, 20).

1.3. Properties and Reactions

Amine boranes are usually colorless, crystalline compounds, which exhibit sharp melting points and thermal stability when pure. Primary and secondary amine boranes are generally solids at ambient temperatures. With the exception of trimethylamine borane, the aliphatic *t*-amine boranes are liquids. The nature of the bonding in amine boranes has been the subject of theoretical investigations (21–23). Representations of the bonding have used symbols such as $R^3N \longrightarrow BX_3$ or $R_3N^{+}\text{—}BX_3-$ to indicate the direction of charge-transfer and origin of the bonding electrons. These symbols refer to the relative change in electron density with respect to the individual precoordination donor and acceptor molecules, not to charges on N and B in the adduct. Molecular orbital calculations indicate that the change in electron density upon coordination reduces, but is insufficient to reverse, the initial positive charge on boron that is a consequence of the differences in electronegativity between B and N. Experimental results are consistent with this representation: nucleophilic reagents always attack B in amine–borane complexes, electrophilic reagents preferentially attack N.

Amine boranes have been examined by a variety of spectroscopic methods (24–29). The boron-substituted alpha-amino acids have been utilized in animal model studies. These compounds along with their precursors and selected derivatives have been shown to possess antineoplastic, antiarthritic, and hypolipidemic activity (30–32). The boron amino acid analogues are also being evaluated for possible utility in boron neutron capture therapy (BNCT) (33).

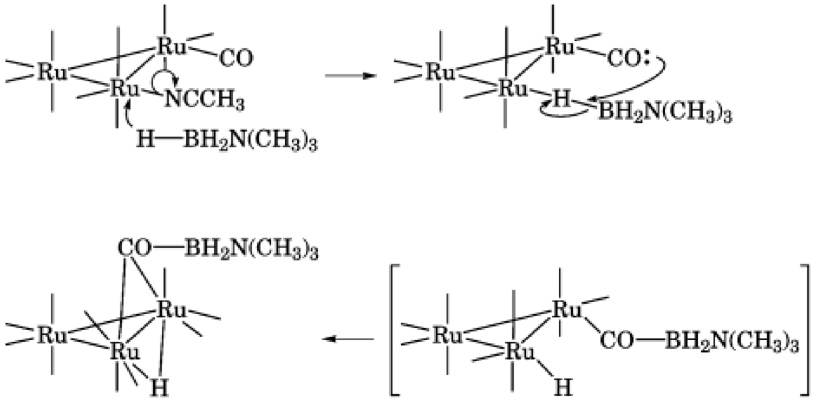
Amine–borane complexes are widely used as reducing agents in organic and inorganic chemistry; examples of reactions are available (8, 34, 35). Compared to sodium borohydride they offer good solubility in organic solvents and are less sensitive to acids but are generally weaker reducing agents. The reduction of cyclohexanone using a variety of amine–BH_3 complexes has been investigated (10) and a mechanism involving prior dissociation of the amine borane was proposed. A similar reaction pathway has been proposed for the hydroboration of alkenes using amine–BH_3 complexes (36).

The influence of boron-bonded ligands on the kinetics and mechanistic pathways of hydrolysis of amine boranes has been examined (37, 38). The stoichiometry of trimethylamine azidoborane [61652-29-7] hydrolysis in acidic solution is given in equation 10. It is suggested that protonation occurs at the azide ligand enabling its departure as the relatively labile HN_3 species.

$$(CH_3)_3\,N\cdot BH_2N_3 + H^+ + 3\,H_2O \longrightarrow (CH_3)_3\,NH^+ + B\,(OH)_3 + 2\,H_2 + HN_3 \qquad (10)$$

A series of metal complexes containing trimethylamine boranecarboxylato ion ligand [103904-11-6], $(CH_3)_3N\cdot BH_2COO^-$, have been prepared with Co(III), Co(II), Zn(II), Ca(II), Cr(III), and Fe(III) (39, 40). This ligand, derived from the boron analogue of the amino acid glycine, behaves similarly to organic carboxylato ligands.

The reaction between a trinuclear metal carbonyl cluster and trimethylamine borane has been investigated (41) and here the cluster anion functions as a Lewis base toward the boron atom, forming a B–O covalent bond (see Carbonyls). Molecular orbital calculations, supported by structural characterization, show that coordination of the amine borane causes small changes in the trinuclear framework.



2. Aminoboranes

The aminoboranes are characterized by a normal covalent bond between boron and nitrogen in which an electron from each atom is shared. In this case the hybridization of both boron and nitrogen is sp^2, resulting in a planar moiety capable of π-interaction by utilizing the nitrogen's free-electron pair and boron's vacant p orbital. There exists a wide variety of aminoborane compounds; among those that have been thoroughly investigated are the monoaminoboranes X_2BNR_2, bisaminoboranes $XB(NR_2)_2$, and trisaminoboranes $B(NR_2)_3$. The substituents X and R may vary widely, but generally R is an alkyl or aryl group, or hydrogen, whereas X can represent a rather wide variety of atoms or groups. There also exist aminoborane compounds, which have multiple boron substituents bonded to a single nitrogen; such as the diborylamines $X_2B\text{–}NR\text{–}BX_2$ and the triborylamines $(X_2B)_3N$. Coordinative saturation in aminoboranes can be achieved not only through partial double-bond formation (π-interaction) but also by association (usually dimerization) of the monomeric units. The presence of bulky groups on either B or N hinders dimer formation. In general, the monomeric compounds are more reactive than the associated species.

2.1. Synthesis

One of the more common routes for the synthesis of aminoboranes involves the aminolysis of the appropriate boron halide. Trisaminoboranes are most conveniently prepared by adding BCl_3 to an excess of amine in an inert solvent at low temperatures (42). For example for tris(dimethylamino)borane [4375-83-1]:

$$BCl_3 + 6\ HN(CH_3)_2 \xrightarrow[80^\circ C]{\text{pentane}} \left[(CH_3)_2N\right]_3B + 3\ (CH_3)_2NH_2Cl \qquad (11)$$

A widely used reaction for preparing unsymmetrical aminoboranes is the treatment of an aminoborane $B(NR_2)_3$ with another boron compound BX_3 to induce an exchange of the substituents; an example is given in equation 12 (43).

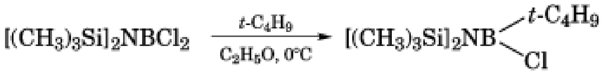
$$2\ B(C_2H_5)_3 + B\left[N(C_2H_5)_2\right]_3 \xrightarrow[120^\circ C]{\text{catalyzed } H_3B/THF} 3\ (C_2H_5)_2BN(C_2H_5)_2 \qquad (12)$$

Here diethylaminodiethylborane [4023-39-6] is obtained in nearly quantitative fashion (97%). The novel trifluoromethylaminoboranes $CF_3(X)BN(C_2H_5)_3$, where $X =$ Cl [126810-68-2], Br [126827-53-0], have been prepared (44).

$$\left[(C_2H_5)_2\,N\right]_3 P + CF_3Br + X_2BN\,(C_2H_5)_2 \longrightarrow CF_3\,(X)\,BN\,(C_2H_5)_2 + \left[(C_2H_5)_2\,N\right]_3 PX^{+}Br^{-} \qquad (13)$$

The stability toward additional disproportionation is dependent on the increase in B–N bond strength as well as steric effects resulting from the R group.

The chemistry and stereochemistry of aminoboranes containing the silicon–nitrogen–boron linkage have been the subject of numerous studies. Many of these compounds are useful precursors to other B–N systems including diboryl-amines (45) and B–H substituted aminoboranes (46). A series of alkyl[bis(trimethylsily)amino]boranes have been prepared by alkylating $((CH_3)_3Si)_2NBCl_2$ [6591-26-0] using the appropriate organometallic reagent (47). For example:



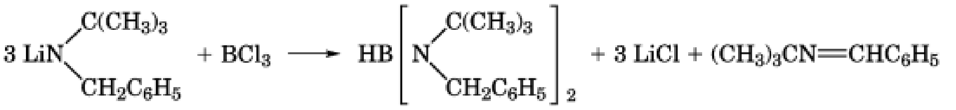
$$[(CH_3)_3Si]_2NBCl_2 \xrightarrow[C_2H_5O,\ 0°C]{t\text{-}C_4H_9} [(CH_3)_3Si]_2NB\begin{matrix} t\text{-}C_4H_9 \\ Cl \end{matrix} \qquad (14)$$

The *t*-butyl derivative [87487-06-9] reacts with ammonia as shown in equation **15** to yield a stable primary aminoborane [99748-68-2] (48). The stability of primary aminoboranes has been attributed to the presence of a bulky substituent on boron (49).

$$[(CH_3)_3Si]_2NB\begin{matrix} t\text{-}C_4H_9 \\ Cl \end{matrix} + 2\,NH_3 \xrightarrow{\text{hexane}} [(CH_3)_3Si]_2NB\begin{matrix} t\text{-}C_4H_9 \\ NH_2 \end{matrix} + NH_4Cl \qquad (15)$$

This primary aminoborane is a useful reagent for attaching B–N moieties to other elements, eg, (borylamino)phosphines, or for extending short B–N chains, eg, diborylamines.

A series of lithium complexes have been utilized as synthons in the preparation of aminoborane complexes. (*N*-Lithiomethylamino)dimethylborane is used as a reagent for the preparation of borylamino(amino)boranes and diborylamines (50). Lithium benzyl-*tert*-butylamide reacts with BCl_3 to yield the bisaminoborane [91573-50-1] shown in equation **16** (51).



$$3\,LiN\begin{matrix} C(CH_3)_3 \\ CH_2C_6H_5 \end{matrix} + BCl_3 \longrightarrow HB\left[N\begin{matrix} C(CH_3)_3 \\ CH_2C_6H_5 \end{matrix}\right]_2 + 3\,LiCl + (CH_3)_3CN{=}CHC_6H_5 \qquad (16)$$

Both symmetrically and unsymmetrically substituted diborylamines can be prepared using sterically demanding *N*-lithioaminoboranes (52).

2.2. Properties and Reactions

Monoaminoboranes readily undergo association, the extent of which primarily depends on the steric requirements of the groups attached to boron and nitrogen. The monomers are generally liquids or low melting solids whereas the dimers and trimers are crystalline solids. The bis- and trisaminoboranes do not show a tendency to dimerize, and are also less sensitive to hydrolysis than the monomeric monoaminoboranes; they are generally high boiling liquids or crystalline solids.

The bonding in aminoboranes has been represented as $X_2N^{+}\overset{---}{\text{—}}{}^{-}BR_2$ or $X_2N\overset{--\rightarrow}{\text{—}}BR_2$ to show the contribution of some π-orbital interaction between the lone pair on N and the vacant orbital on trigonal boron. As with the amine–borane adducts this does not necessarily indicate net charges on N and B. The greater electronegativity of N should cause the sigma bond to be polarized in the opposite sense. Calculations carried out on the pure inorganic aminoborane, H_2NBH_2, however, indicate a covalent π-bond, producing positive charge on N, negative on B (53–55). The sp^2 hydridization of both boron and nitrogen lead to planar X_2BNR_2 fragments with the contribution of a π-interaction being supported by B–N separations of ca 0.14 nm as compared to a B–N bond distance of ca 0.16 nm in amine boranes.

In aminoboranes there is a barrier to rotation about the boron–nitrogen bond resulting from the high B–N bond order. There have been numerous studies carried out using variable-temperature nmr to obtain activation parameters for restricted rotation about the B–N bond (56–59). The steric effects of the substituents was shown to be the principal factor affecting the barrier. In general, monoaminoboranes all have rather high rotational barriers 71–100 kJ/mol (17–24 kcal/mol). Multinuclear nmr has been used to determine the coupling constants in aminoboranes (60, 61). The vibrational spectra of bis(dimethylamino)boranes have been examined (62).

Monoaminoboranes containing hydrogen attached to nitrogen, and hydrogens or halogens bonded to boron undergo an internal elimination reaction on heating, yielding borazines (63). Bisaminoboranes in general are thermally stable; when pyrolysis does occur a principal reaction product is a borazine as illustrated in equation 17 (64).

$$3\ (C_2H_5NH)_2\,BH \longrightarrow (\text{—}BH\text{—}NC_2H_5\text{—})_3 + 3\ C_2H_5NH_2 \qquad (17)$$

The emphasis in the approaches to boron nitride [10043-11-5], BN, precursors has been concentrated on cyclic compounds. There have been recent reports of trimethylsilyl-substituted aminoboranes being evaluated as B–N precursors. These are linear borylamines containing up to four boron atoms. Compounds were also synthesized with free $-NH_2$ groups amenable to condensation with either dihaloboranes or dihaloborazines (65) and offering suitable monomers for linear B–N polymer synthesis and borazine-ring-linking applications.

Aminoboranes have been used as ligands in complexes with transition metals (66); in one instance giving a rare example of two-coordinate, non-d^{10} transition-metal complexes. The molecular structure of the iron complex $Fe[N(Mes)B(Mes)_2]_2$ where $\text{Mes} =$ 2,4,6-$(CH_3)_3C_6H_2$ is shown in Figure 1. The less sterically demanding lithium borylamide, $LiN(CH_3)B(CH_3)_2$, used to prepare mercury and tin complexes, has also been prepared (67).

The reduction of (alkylamino)haloboranes using hydride reagents can provide a convenient route to (alkylamino)boranes: for example, $LiAlH_4$ has been utilized to prepare bis(dimethylamino)borane [23884-11-9] from chlorobis(dimethylamino)borane [6562-41-0] (68). When this same strategy is applied to (bis(trimethylsilyl)amino)chloro((trimethylsilyl)amino)borane [10078-93-0], the expected compound is obtained along with the formation of two borazine derivatives (69).

$$\left[(CH_3)_3\,Si\right]_2 NB\,(Cl)\,N\,(H)\,Si\,(CH_3)_3 \xrightarrow{LiBH_4}$$

$$\left[(CH_3)_3\,Si\right]_2 NBH_2 + \left[(CH_3)_3\,SiN\,(H)\,BH_2\right]_3 + \left[(CH_3)_3\,SiNBH\right]_3 \qquad (18)$$

3. Iminoboranes

A new class of boron–nitrogen compounds was reported in 1975 when the first iminoborane having two-coordinate boron, $(C_6F_5)B{\equiv}N(t\text{-}C_4H_6)$ [72886-65-8], was isolated (70). Since then more than 50 iminoboranes have been synthesized and characterized. Iminoboranes, XBNR, are isoelectronic with alkynes, XCCR. Whereas

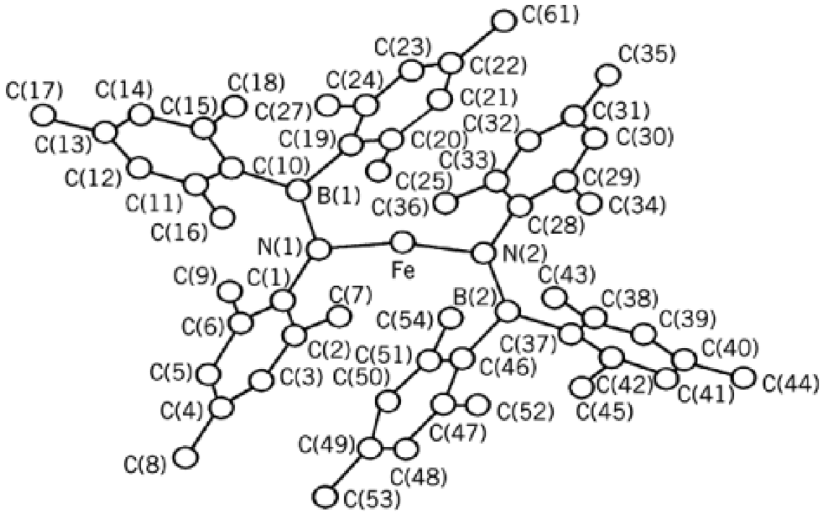
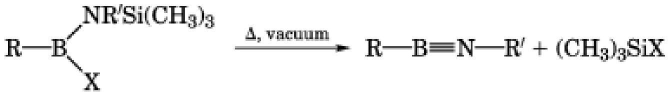


Fig. 1. Structure of $Fe[N(Mes)B(Mes)_2]_2$ where Mes is 2,4,6-$(CH_3)_3C_6H_2$.

the structural and physical properties of these species are rather parallel, this similarity does not hold for reactivity. The polarity of the B–N bond makes iminoboranes much more reactive than the analogous XCCR species. Comprehensive reviews of iminoboranes may be found in the literature (71, 72). A class of B–N compounds with a *sp*-hybridized nitrogen attached to a three-coordinated boron, $R_2C{=}N{-}BX_2$, have also been classified as iminoboranes (73–75).

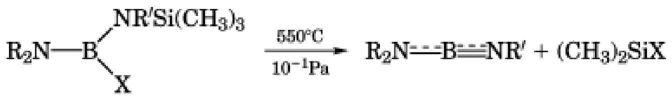
3.1. Synthesis

Iminoboranes, thermodynamically unstable with respect to oligomerization can be isolated under laboratory conditions by making the oligomerization kinetically unfavorable. This is facilitated by bulky substituents, high dilution, and low temperatures. The vacuum gas-phase pyrolysis of (trimethylsilylamino)(alkyl)haloboranes has been utilized as an effective method of generating iminoboranes $RB{\equiv}NR'$ as shown in equation **19** for X = F, Cl, Br, and OCH_3 (72).



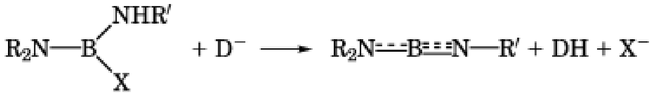
$$R{-}B\begin{matrix} NR'Si(CH_3)_3 \\ X \end{matrix} \xrightarrow{\Delta,\ \text{vacuum}} R{-}B{\equiv}N{-}R' + (CH_3)_3SiX \qquad (19)$$

The products are trapped at liquid nitrogen temperature. This strategy can also be employed in the synthesis of amino iminoboranes (76), where X = F, Cl.



$$R_2N{-}B\begin{matrix} NR'Si(CH_3)_3 \\ X \end{matrix} \xrightarrow[10^{-1}\text{Pa}]{550°\text{C}} R_2N\overset{--}{-}B\overset{--}{=}NR' + (CH_3)_2SiX \qquad (20)$$

Iminoboranes have been suggested as intermediates in the formation of compounds derived from the pyrolysis of azidoboranes (77). The intermediate is presumed to be a boryl-substituted nitrene, RR′BN, which then rearranges to the amino iminoborane, neither of which has been isolated (78). Another approach to the synthesis of amino iminoboranes involves the dehydrohalogenation of mono- and bis(amino)haloboranes as shown in equation **21**. Bulky alkali-metal amides, MNR_2, have been utilized successfully as the strong base, D^-, in such a reaction scheme. Use of lithium-*tert*-butyl(trimethylsilyl)amide yields an amine, DH, which is relatively volatile (76, 79).


(21)

3.2. Properties and Reactions

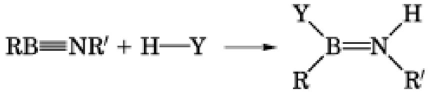
The structure of (alkyl)iminoboranes $RB{\equiv}NR'$ is characterized by a linear C–B–N–C geometry and a B–N bond order approaching three. Amino iminoboranes can be described using three resonance structures:

$$R_2N{-}B{\equiv}NR' \leftrightarrow R_2N{=}B{=}NR' \leftrightarrow R_2N{-}B{=}NR'$$

A B C

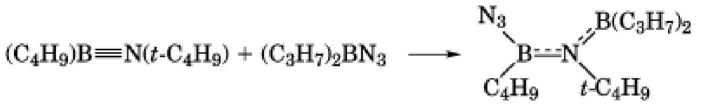
The boron atoms in resonance structures A and B possess a formal negative charge. The simplest representation for these compounds is $R_2N{\cdots}B{\cdots}NR'$. The relative stability of iminoboranes and amino iminoboranes shows strong dependence on the steric bulk offered by R and R′. This is illustrated by the stability of t-$C_4H_9B{\equiv}Nt$-C_4H_9 at 0°C whereas the permethyl analogue, $(CH_3)B{\equiv}N(CH_3)$, decomposes above $-110°C$ (72). The high B–N bond order in iminoboranes has been verified by the results of single-crystal x-ray structure determinations: there is a B–N separation of 0.122 nm in $[(CH_3)_3Si]_3Si{-}B{\equiv}N$-$t$-$C_4H_9$ (80). Spectroscopic characterization of these compounds has been carried out at low temperature using ^{11}B nmr and ir spectroscopy (81).

The chemistry of these compounds reflects the unsaturated nature of the B–N triple bond. Polar compounds add to iminoboranes, provided the addition proceeds more rapidly than oligomerization of $RB{\equiv}NR'$ (82). For example, for $R = R' = CH(CH_3)_2$ or t-C_4H_9.


(22)

where $HY =$ HCl, t-C_4H_9OH, $(C_2H_5)_2NH$, $(i$-$C_3H_7)_2NH$, t-$C_4H_9NH_2$, $((CH_3)_3Si)_2NH$.

In an analogous fashion to the hydroboration reaction, a variety of boron-containing substrates react with iminoboranes. Addition of $X_2B{-}Cl$, $X_2B{-}N_3$, $X_2B{-}SR$, $X_2B{-}NR_2$, and $X_2B{-}R$ to the unsaturated B–N system is called chloro-, azido-, thio-, amino-, and alkyloboration, respectively. The azidoboration and chloroboration of two iminoboranes are shown in equations **23** and **24** (72).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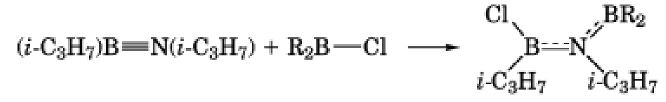
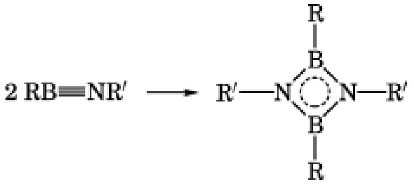

(24)

A general type of stabilization for iminoboranes is a cyclodimerization, which yields diazadiboretidines $(RBNR')_2$ that are isoelectronic with cyclobutadienes.



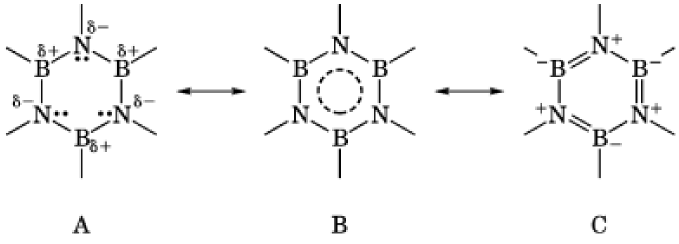
(25)

Transformations to the cyclotrimeric borazines and cyclotetrameric tetraza-2,4,6,8,1,3,5,7-tetraboracanes also occur. The rate of dimerization for amino iminoboranes has been shown to be stabilized by bulky substituents (76, 79, 83). This stabilization through dimerization is essentially a [2 + 2] cycloaddition. There are a number of examples of these compounds forming cycloadducts with other unsaturated polar molecules (78). Iminoboranes can add to electron-deficient carbene complexes of titanium such as $(C_5H_5)_2Ti(CH_2)$ [84601-70-7] by [2 + 2] cycloaddition, yielding the metallacycle shown in equation **26** (84).

(26)

4. Borazines

The largest and most extensively studied family of boron–nitrogen compounds is that of the borazines, characterized by a six-membered ring system containing alternating boron and nitrogen atoms. Borazines are tricoordinated, nearly planar, and have B–N bond lengths considerably shorter than single bonds, indicating partial double-bond character. Because borazine is isoelectronic and isostructural with benzene, it has been called inorganic benzene. The physical properties of borazines tend to confirm π-electron delocalization as in benzenes; however, chemical evidence indicates that the reactions of borazines are dominated by polarization of the B–N bonds.



Formal electron counting would suggest that donation of π-electrons from nitrogen to boron would result in a positive charge on nitrogen and a negative charge on boron as in resonance structure C. However a number of studies have shown the opposite is true with partial negative character on nitrogen and partial positive character on boron resulting from electron-withdrawal by nitrogen through the σ-system (85–88).

Several review articles detailing various aspects of borazine chemistry are available (4, 89–93), as well as two comprehensive treatises on preparations, reactions, and properties of borazines (94, 95).

4.1. Synthesis

The parent compound, borazine [6569-51-3], is best prepared by a two-step process involving formation of *B*-trichloroborazine followed by reduction with sodium borohydride. These reactions have been studied in some detail (96).

$$3\ \mathrm{BCl_3} + 3\ \mathrm{NH_4Cl} \longrightarrow (\!-\!\!-\mathrm{BCl}\!-\!\!-\mathrm{NH}\!-\!\!-)_3 + 9\ \mathrm{HCl} \qquad (27)$$

$$(\!-\!\!-\mathrm{BCl}\!-\!\!-\mathrm{NH}\!-\!\!-)_3 + 3\ \mathrm{NaBH_4} \longrightarrow (\!-\!\!-\mathrm{BH}\!-\!\!-\mathrm{BH}\!-\!\!-)_3 + 3\ \mathrm{NaCl} + {}^3\!/_2\ \mathrm{B_2H_6} \qquad (28)$$

The heating of sodium borohydride with ammonium chloride in high boiling glycol ether gives borazine in 35% yield (97). A commercially feasible method of producing borazine involves decomposing ammonia borane by heating in a high boiling glycol ether solvent (98).

Symmetrically substituted borazines are generally prepared by reaction of amines and boranes (94).

$$3\ \mathrm{BX_3} + 3\ \mathrm{NH_2R} \longrightarrow (\!-\!\!-\mathrm{BX}\!-\!\!-\mathrm{NR})_3 + 6\ \mathrm{HX} \qquad (29)$$

where $\mathrm{X = H}$, halogen, or alkyl; $\mathrm{R = H}$, alkyl, or aryl. *B*-Trihaloborazines are formed, which are useful in preparing *B*-trialkyl or triarylborazines by reaction with Grignard reagents (97). A process for preparing *B*-trichloroborazine [41265-87-6], $\mathrm{B_3Cl_3H_3N_3}$, from boron trichloride and excess ammonia has been patented (99). *B*-Trichloro-*N*-trisubstituted borazines can be reduced using sodium borohydride (eq. 30) to *N*-trisubstituted borazines (96).

$$(\!-\!\!-\mathrm{BCl}\!-\!\!-\mathrm{NR}\!-\!\!-)_3 + 3\ \mathrm{NaBH_4} \longrightarrow (\!-\!\!-\mathrm{BH}\!-\!\!-\mathrm{BR}\!-\!\!-)_3 + {}^3\!/_2\ \mathrm{B_2H_6} + 3\ \mathrm{NaCl} \qquad (33)$$

Substitution reactions of *B*-trichloro-*N*-trialkyl(or triaryl)borazines and alchohols, phenols, or excess amine yield the corresponding borazines (100, 94).

N-Trimethoxyborazines are available from reaction of dichloroboranes and *O*-methyl-*N,N*-bis(trimethylsilyl)hydroxylamine (eq. 31). The *B*-trichloro-borazines undergo substitution reactions at the B atoms to give *B*-tri(*tert*-butoxy)- or *B*-tri(*tert*-butyl)-*N*-trimethoxyborazines (101)

$$3\ \mathrm{CH_3ON}\left[\mathrm{Si(CH_3)_3}\right]_2 + 3\ \mathrm{Cl_2BX} \longrightarrow (\!-\!\!-\mathrm{BX}\!-\!\!-\mathrm{NOCH_3}\!-\!\!-)_3 + 6\ \mathrm{(CH_3)_3\,SiCl} \qquad (31)$$

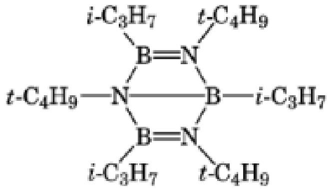
where $\mathrm{X =}$ Cl, $\mathrm{OCH_3}$. *N*-Borylated borazines are formed by heating stannylamines with dibromoboranes according to equation 32 (102). *N*-Tri(*tert*-butyl)borazines have been prepared via

$$3\ \mathrm{R_2B}\!-\!\!-\mathrm{N(SnR_3)_2} + 3\ \mathrm{RBBr_2} \xrightarrow{\Delta} (\!-\!\!-\mathrm{RB}\!-\!\!-\mathrm{NBR_2}\!-\!\!-)_3 + 6\ \mathrm{BrSnR_3} \qquad (32)$$

trimerization of unstable iminoboranes (103). The sterically crowded *B*-tri(isopropyl)-*N*-tri(*tert*-butyl)borazine, synthesized via equation 33, is the first reported example of a Dewar borazine, which by x-ray crystallography was found to have two short peripheral B–N double bonds (0.136–0.138 nm) and an extra long bridge B–N single bond (0.175 nm).

$$3\ \mathrm{RClB - N}(t\mathrm{-C_4H_9})\left[\mathrm{Si(CH_3)_3}\right] \xrightarrow[-3\ \mathrm{ClSi(CH_3)_3}]{\Delta} 3\ \left[\mathrm{R}\!-\!\!-\mathrm{B}\!=\!\!=\mathrm{N}-t-\mathrm{C_4H_9}\right] \longrightarrow (\!-\!\!-\mathrm{BR}\!-\!\!-\mathrm{N}t-\mathrm{C_4H_9}\!-\!\!-)_3 \qquad (33)$$

As with Dewar benzene, the increased stability of this structure over the planar borazine is thought to result from the extreme interactions of the alkyl groups (104).



Unsymmetrically B-substituted borazines can be prepared by the reaction of N-substituted borazines or B-trihalogeno-N-substituted borazines and the appropriate amount of Grignard reagent (94). Borazines unsymmetrically substituted on nitrogen have been prepared by the reaction of lithium borohydride and ammonium chloride and alkylammonium chlorides (105, 106), and by lithiation of B-trimethylborazine followed by reaction with alkyl halides (107).

4.2. Properties and Reactions

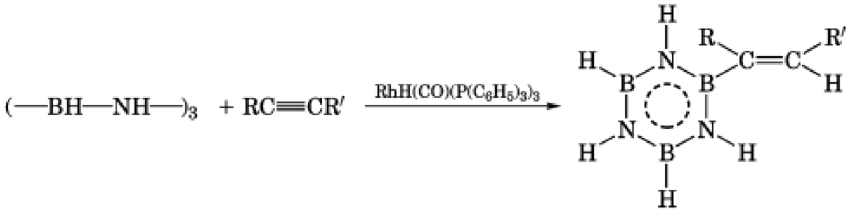
Borazines are liquids or crystalline solids depending on the substitution pattern. Most are sensitive to moisture and must be handled in an inert atmosphere. Borazines are essentially planar except in hexasubstituted cases where there may be some puckering of the borazine ring. A great deal of effort has gone into trying to understand the nature of aromaticity in the borazine ring vis-a-vis benzene. Borazines undergo addition reactions rather than electrophilic substitution reactions typical of benzene compounds. The direction of addition suggests the importance of the polar resonance structure A, ie, Lewis acids add to the ring nitrogen atoms and Lewis bases add to boron atoms. Structural determinations all indicate a planar structure with D_{3h} symmetry (91), and spectroscopic data are consistent with delocalized π-electrons and a bond order greater than 1 (91, 108–111). A detailed comparison of spectral data concluded that borazine has a delocalized π-electron system like that of benzene (112); other workers, however, have concluded from spin-coupled calculations that borazine has little aromatic stabilization as compared to benzene (113).

It has been shown that aromatic rings of B-triaryl-N-triaryl substituted rings are orientated perpendicular to the plane of the borazine ring (114, 115). If the aryl rings are substituted it is possible to obtain mixtures of cis and trans isomers (atropisomerism) in which the aryl substituents are on the same or opposite sides of the plane of the borazine ring, respectively (115).

4.3. Thermal Stability

Borazine itself shows negligible decomposition at 0–5°C. At ambient temperature 1–2% decomposition has been observed during the first month followed by an increase in rate thereafter, and at higher temperatures appreciable decomposition occurs (89). There has been much interest in utilizing borazine or derivatives as precursors to boron nitride which has the same stoichiometric boron–nitrogen ratio and a hexagonal structure. Yields of boron nitride by ordinary thermolysis of borazine are very low because borazine is a volatile compound. Thermolysis of borazine at 250–700°C under 100 MPa (145,000 psi) pressure produced amorphous boron nitride in good yield (116). The latter compound was converted to cubic boron nitride by much higher temperature and pressure treatment in the presence of cubic B–N seed (117). Cross-linking of borazines through amino groups has produced preceramic polymers, which form hexagonal boron nitride on heating (118). The polymeric compositions can be shaped to form coatings and fibers that yield the corresponding boron nitride-shaped articles on pyrolysis (119).

Heating borazine *in vacuo* at 70°C yields poly(borazylene) polymers, which are soluble in solvents such as tetrahydrofuran or glyme and could be thermolyzed to boron nitride in good yields (120). Other soluble preceramic polymers were produced by transition-metal catalyzed formation of B-alkenylborazines (eq. **34**) which were thermally polymerized under mild conditions to poly(alkenylborazines). The latter yielded boron nitride having low carbon contents when thermolyzed in an ammonia atmosphere (121).



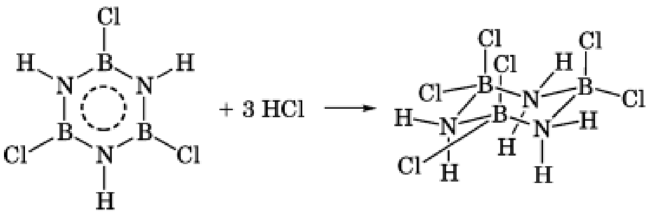
(34)

4.4. Hydrolysis

Borazine is slowly hydrolyzed by water at ambient or higher temperatures to boric acid. Substituted borazines react with water to give ring-cleavage products, eg, boronic acids and amines (122). *B*-Trichloroborazine reacts with water to give boric acid and chloramine (123).

4.5. Addition Reactions

In general, polar molecules such as hydrogen halides add across the B–N bonds, the more electronegative group bonding to boron (91). The adducts are cyclotriborazanes such as the product formed by reaction of *B*-trichloroborazine and hydrogen chloride (eq. **35**). X-ray crystal analysis shows the structure exists in a chair conformation (124).



(35)

4.6. Substitution Reactions

Substitution reactions on borazines are confined mainly to substitution by nucleophilic groups on boron; substituents on nitrogen are inert to most reagents. Treatment of *B*-halo or *B*-hydridoborazines with organolithium or Grignard reagents results in substitution at boron with the organic moiety (91, 125). Indirect substitution of nitrogen on *B*-trimethylborazine has been effected by formation of the intermediate *N*-trilithioborazine followed by alkylation (107).

4.7. Miscellaneous Reactions

4.7.1. Photolysis

Borazine absorbs strongly in the ultraviolet region between 170–200 nm. Irradiation of borazine in the gas phase with ammonia, water, alcohols, and D_2 produces *B*-monosubstituted derivatives (126–128). From quantum yield studies of the deuterium exchange reaction it was concluded that the exchange proceeds via formation of an excited borazine molecule (128). Photolysis of gaseous borazine itself produced borazanaphthalene and other condensed products (129). Photosensitization of alkylborazines in the presence of hydrogen resulted in dimers formed by joining at the alkyl groups (130).

4.7.2. Complex Formation

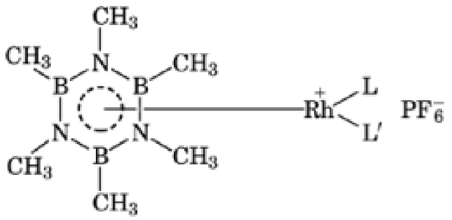
B-Trichloroborazine was reported to readily form crystalline adducts of uncertain structure with pyridine (131). The Lewis acids aluminum tribromide or gallium trichloride form 1:1 adducts with hexamethylborazine (eq. 36) in which the metal atom coordinates with a nitrogen with loss of planarity of the ring (132, 133).

$$(\text{—BCH}_3\text{—NCH}_3\text{—})_3 + \text{MX}_3 \longrightarrow (\text{—BCH}_3\text{—NCH}_3)_3 \cdot \text{MX}_3 \qquad (36)$$

where $\text{M} = $ Al, $\text{X} = $ Br or $\text{M} = $ Ga, $\text{X} = $ Cl. π-Complexes are formed from hexaalkylborazines and transition metals as in equation **37** (134, 135).

$$(\text{—BR—BR—})_3 + (\text{CH}_3\text{CN})_3\,\text{Cr}\,(\text{CO})_3 \longrightarrow (\text{—BR—BN—})_3\,\text{Cr}\,(\text{CO})_3 + 3\,\text{CH}_3\text{CN} \qquad (37)$$

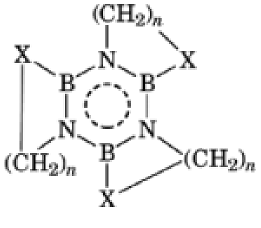
Although isostructural with hexaalkylbenzene metal π-complexes, the borazine complexes are less stable than the benzene analogues, and spectroscopic evidence suggests that the borazine rings are poorer π-acceptor ligands (135). Cationic-mixed ligand rhodium complexes have been formed with hexamethylborazine. The borazine is easily displaced by σ- or π-donor ligands such as acetonitrile or benzene (136).



where LL′ = diolefin or L = L′ = ethylene or CO

4.8. Fused Rings and Polymers

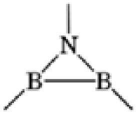
Borazine analogues of naphthalene and substituted phenalenes are known; the latter compound is formed by reaction of distannylamine and a large excess of tris(methylthio)borane (137). A general method for the preparation of the polycyclic borazines using fused carbon–heteroatom rings, where $\text{X} = \text{O}$, NR and $n = 2$, 3, has been given (137).



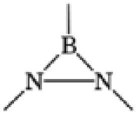
The preparation of a variety of other fused-ring borazine derivatives has been reviewed (95). Oligomers and polymers have been formed in which the borazine rings are linked directly by B–N bonds and where the rings are bridged by *O, N,* or organo groups (91). Borazines linked by urea groups have been prepared as possible preceramic oligomers (138).

4.9. Other B–N Ring Systems

A number of unusual ring systems containing only B–N linkages have been reported (139). Derivatives of both possible three-membered ring systems, azadiboradine **(1)** and diazaboridine **(2)** have been prepared and the geometries and stabilization energies of these systems calculated (140–142).

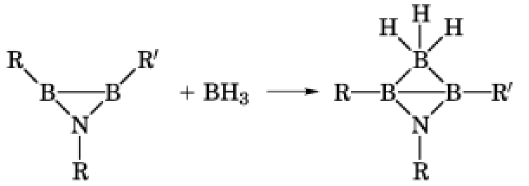


(1)



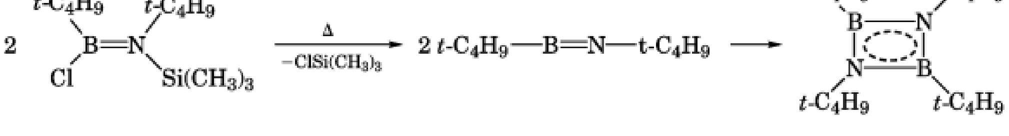
(2)

Unexpectedly the Lewis acid BH_3 was found to add across the B–B bond of azadiboridines rather than to the *N*-atom to give the *nido*-1-azatetraboranes as in equation **38** (143) where $R = R' = t\text{-}C_4H_9$, and $R = t\text{-}C^4H^9$, $R' = i\text{-}C_3H_7$.



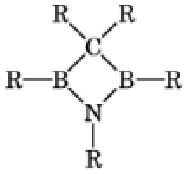
(38)

The four-membered diazadiboretidine ring system has been formed by several routes including replacement of Sn with B in diazadistannetidines (144), thermolysis of diarylazidoboranes (145), reductive elimination of S from six-membered 1,4-dithia-2,6-diaza-3,5-diborinane rings (146), and generally by dimerization of iminoboranes, which are intermediates formed by thermal elimination of chlorotrimethylsilane from aminoboranes as in equation **39** (147, 148). Diazadiboretidines act as 4-electron donors forming chromium and tungsten tetracarbonyl complexes (149).

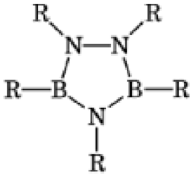


(39)

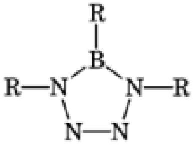
The four-membered azadiboretidine **(3)** ring-system has been reported (150, 151). Examples of larger B–N ring systems are triazadiborolidines **(4)** (150), tetraazaborolines **(5)** (151, 152), tetraazadiborines **(6)** (153), and tetraazatetraborocanes **(7)** (139, 154). The incorporation of B–N linkages into carbocyclic systems has been reviewed (4, 154).



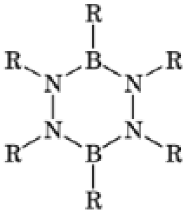
(**3**)



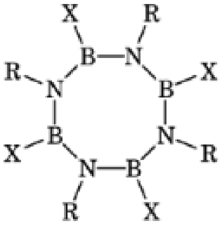
(**4**)



(**5**)

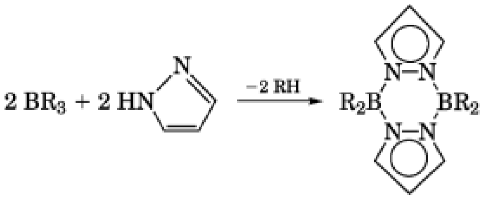


(**6**)



(**7**)

Of commercial interest are benzo- and other fused aromatic 1,2,3-diazaborine derivatives which have exhibited good antibacterial activity against a variety of microorganisms (155–157). The reaction of pyrazole or *C*-substituted pyrazoles with boranes yields the pyrazabole system, a class of exceptionally stable compounds. More than 70 species in this system have been reported and the subject comprehensively reviewed (158). These compounds have been used as ligands in transition-metal complexes (159).



(40)

5. Manufacture and Uses

Organic boron–nitrogen compounds have not found extensive usage, and therefore, very few are manufactured on a large scale. Callery Chemical Co. appears to be the largest manufacturer of amine boranes and borazines. Research quantities of some compounds are available from Callery, Aldrich Chemical Co., Alfa, Strem Chemicals, Atomergic, K & K, and Eagle-Picher.

Amine boranes are principally used as reducing agents in inorganic and organic synthesis and in the metal plating industry (see Electroless plating). Boron analogues of amino acids and peptides have antitumor and hypolipidemic activities and are offered for development by Boron Biologicals, Inc. (see Chemotherapeutics, anticancer).

Borazines, particularly polymeric compounds, have been extensively investigated as preceramic materials from which coatings and fibers of boron nitride can be produced upon thermolysis. *B*-aryl and halogeno-amino borazines are reported to have use as fire retardantsin cotton and nylon textiles. Other reported uses for borazines are as epoxy resin catalysts, polymerization inhibitors of unsaturated alcohols and esters, and catalysts for polymerization of alkenes (95).

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